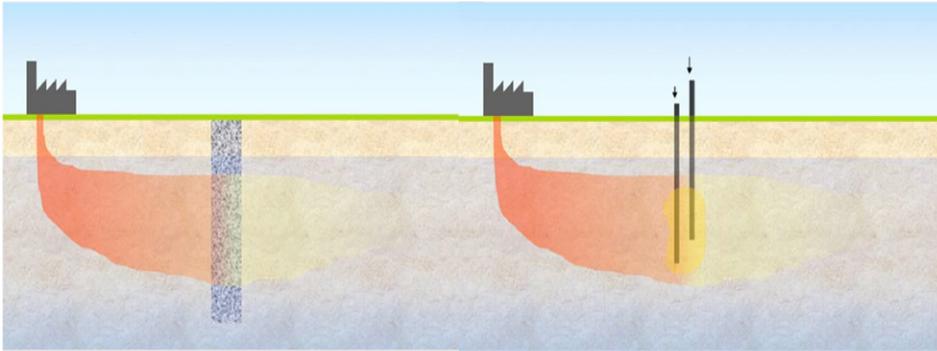


2010

Permeable Reactive Barriers & Reactive Zones

Proceedings of the 4th International symposium, July 6-8, 2010



Final conference of the EU-LIFE project MULTIBARDEM

MULTIBARRIER

Permeable Reactive Barriers & Reactive Zones PRB/RZ 2010

Proceedings of the 4th International Symposium,
Antwerp, July 6-8, 2010



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Table of contents

Introduction	6
Session 1 - Developments in CAH-control	8
Biodegradation of CHC in an aerobic aquifer: Characterisation of the contaminated site as a basis for implementation of passive funnel & gate treatment - <i>Alge G., Schramm C., Ausserleitner M., Hüther T., Pümpel T., Pümpel E., Jussel, B., Kolesar, C.</i>	9
Biodegradation of CHC in an aerobic aquifer: Active nutrient dosing versus passive funnel & gate treatment - <i>Pümpel, T., Pümpel, E., Jussel, B., Ausserleitner, M., Schramm, C., Hüther, T., Alge, G., Kolesar, C.</i>	10
Chemical Reduction of PCE by Zero Valent Iron Colloids Comparison of Batch and Column Experiments - <i>C.V. de Boer, N. Klaas, and J. Braun</i>	15
In situ remediation of a chlorinated ethene contaminated source zone by injection of zero-valent iron: from lab to field scale - <i>Uyttebroeck M., Baillieul H., Vermeiren N., Scholiers R., Devleeschauwer P., Gemoets J. and L. Bastiaens</i>	20
Effect of guar gum on CAHs removal by micro scale zero-valent iron particles - <i>Velimirovic, M., Simons, Q., Seuntjens P., and L. Bastiaens</i>	24
Session 2 - The challenge of combining pollutant removal process - mixed pollution	29
ISMP of a Zn-contamination in combination with enhanced attenuation of VOCs by injection - <i>Havermans W.J.M., Peppel Ruurd and Przepiora Andrzej</i>	30
Design of a multibarrier for the treatment of landfill leachate contamination: laboratory column evaluation - <i>Van Nooten T., Diels L. and L. Bastiaens</i>	34
Enhancing biotic and abiotic reductive dechlorination in ZVI-PRB combined with a slow releasing carbon source (PHB) - <i>Petrangeli Papini M., Baric M., Aulenta F., Majone M., Beccari M., Alifano L. and Steardo M.</i>	35
Demonstration of the multibarrier technology for leachate containing water at the landfill Hooze Maey: 2 Pilot systems - <i>T. Van Nooten, H. Sterckx, Q. Simons, T. Van Mechelen, P. Verkaeren, L. Horckmans, D. Dirickx and L. Bastiaens</i>	36
Session 3 - Poster session	37
Wetlands with <i>Phragmites australis</i> degradation material as reactive zones applied to remediation of groundwater contaminated by nitrates - <i>A. Guzmán, V. Martí, O. Gibert, J. Giménez, J. De Pablo, M. Calderer, I. Jubany, P.J. Jiménez</i>	38
Verification of Transport of Zero-Valent Iron Colloids in Porous Media - <i>C.V. de Boer, N. Klaas, J. Braun</i>	40
Development of rehabilitation technologies and approaches for multipressured degraded waters and the integration of their impact on river basin management. - <i>Bastiaens L. & AQUAERHAB consortium</i>	41
Effect of carbon sources on CAH degradation kinetics in the aquifer of the Zenne site - <i>Atashgahi S., Cai Z., Calderer M., Hendrickx D., Hamonts K., Simons Q., Ryngaert A., Springael D., Brouyère S., Wilson R. and Dejonghe W.</i>	42
Full scale horizontal ZVI PRB in combination with enhanced anaerobic bioremediation - <i>Havermans W.J.M. and Przepiora Andrzej</i>	43
Use of different zero-valent iron particles for CAHs degradation - <i>Velimirovic, M., Simons, Q., Seuntjens P., and L. Bastiaens</i>	44
Abstract Submission for the PRB-RZ Symposium: Application of In-Situ Precipitation to Remediate Heavy Metals Contamination in Groundwater - <i>Muguet, S., Verkaeren, P., de Bournonville, G., Vanbroekhoven, K., Gemoets, J., Zeuwts, L. and Gommers, K.</i>	45
Four Years Performance of the first continuous iron PRB in KATWIJK, The Netherlands - <i>Havermans W.J.M., Zanden Tanja and Przepiora Andrzej</i>	46
Clinoptilolite as Microbial Mediated Regenerable Reactive Material for Remove Ammonium from Landfill Leachate in a Multibarrier - <i>Van Nooten T., L. Bastiaens</i>	47
NanoZox™, an innovative application of ozone in water treatment - <i>Van Nooten T., Scheffer, B., Van Bree, M. and T. Leenen</i>	48
Design of a multifunctional permeable reactive barriers (Multibarrier) for treatment of a VOCl, BTEX & MTBE contamination plume - <i>Q.Simons, L. Bastiaens</i>	49
Impact of microbiology on performance of Zero Valent Iron based Permeable Reactive Barriers and Reactive Zones: A comparative study - <i>Naresh Kumar, Fabienne Battaglia-Brunet, Romain Millot, Vanbroekhoven Karolien,</i>	

<i>Ludo Diels, Leen Bastiaens</i>	50
Emulsified metallic nano- and micro-iron particles for in-situ Remediation of Chlorinated Ethenes in Groundwater - <i>J. Gemoets, Q. Simons, R. van Roten, P. Vanderauwera, L. Bastiaens</i>	51
Multibarrier Comprising Abiotic and Biotic Removal Processes to Remediate Chlorinated Ethenes in Groundwater - <i>Q.Simons, H.Sapion, G. Schoups, L. Bastiaens</i>	52
Session 4 - Progress in basic research	53
Transport of highly concentrated slurries of iron colloids for groundwater remediation: experimental and modeling - <i>Tosco T and Sethi R.</i>	54
The Effect of Chemical Oxidation on Heavy Metal Release and Microbial Community Diversity in Sediments - <i>Eylem DOĞAN, Frederik ACCOE, Nico BOON, Leen BASTIAENS, Winnie DEJONGHE</i>	59
Effect of ZVI Particle size on biostimulation of sulfate reducing bacteria for metal removal from groundwater: A batch study - <i>Naresh Kumar, Leen Bastiaens, Karolien Vanbroekhoven, Romain Millot, Ludo Diels</i>	60
Micro-scale modelling of iron particles transport in saturated porous media - <i>Lince F., Tosco T., Marchisio D.L. and Sethi R.</i>	61
Geochemical modelling of Fe0 permeable reactive barriers - <i>Carniato L., Schoups G., Seuntjens P. and Bastiaens L.</i>	67
Industrial Scale Bimetallic Nano-alloys With High Potential For In Situ POP Abatement - <i>Dick J., Weyn E., De Windt W. and Lakaye F.</i>	68
Session 5 - Lessons learned from the field & Economics	72
Stretching limits of Reactive Zones: 3 examples - <i>Hoekstra N.K., and J. de Weert</i>	73
Permeable Reactive Barriers for Ground Water Remediation at Contaminated Former Manufactured Gasworks Plants and Related Sites: Design Features, Performances Achieved, and Outlook - <i>Volker Birke, Christine Schuett, Harald Burmeier, Christian Weingran, Birgit Schmitt-Biegel, Jörn Müller, Roland Feig, Andreas Tiehm, Axel Müller, Sebastian Maenz, Eric Naumann, Wolf-Ulrich Palm, Wolfgang K.L. Ruck</i>	74
Economical Potential of Multibarriers as a Sustainable Method for In-Situ Groundwater Pollution Treatment - <i>Horckmans, L., Verkaeren, P., Vannooten T., Bastiaens, L.</i>	75
Multidisciplinary approaches for in-situ remediation of complex groundwater pollution: Experiences from the field - <i>Van Nooten T., Van de Ven E. and A. Lobs</i>	80
Retrofitting an existing pump and treat system into a sustainable DNAPL remediation with a combined bioremediation and pumping system - <i>Hans Baillieul, Rik Scholiers, Gerlinde De Moor, Karen Van Geert and Wouter Gevaerts, Daan Touw, Catherine Van Wouwe and Sofie Claus</i>	85
Session 6 - Field trip to the landfill Hooze Maey (Antwerp)	86
MULTIBARDEM: a LIFE demonstration project of multibarriers as a sustainable approach for groundwater remediation - <i>Leen Bastiaens & MULTIBARDEM consortium</i>	87

Introduction

The quality of natural water resources is a major concern for the coming decades. According to the EU Water framework Directive, also the quality of groundwater needs to be improved besides the quality of surface water.

Permeable reactive barriers (PRBs) and reactive zones (RZs) are recognized technologies for the in situ improvement of the groundwater quality. Both technologies aim to realize a local stimulation of pollutant removal processes to prevent further migration of pollutions. Over the past 20 years a variety of PRBs and RZs based on biotic as well as abiotic removal processes have been studied and implemented to cope with different pollutants and pollutant mixtures. An ongoing search for new materials, additives and concepts widens the application areas for PRBs and RZs. More recent aspects are sustainability and the impact of the technologies on the water quality in the wider environment and in time.

The PRB/RZ-symposium is relevant for scientists, policy makers, consultants, site owners and remediation companies who are working on or involved with permeable barriers or reactive zones. The purpose was to bring together pioneers and experts from all over the world to exchange information and new experience.

The following topics are addressed during the symposium:

- Developments in CAH-control (Sessions 1)
- The challenge of combining pollutant removal processes-mixed pollution (Session 2)
- Poster session (Session 3)
- Progress in basic research (Session 4)
- Lessons learned from the field & economics (Session 5)
- Field visit (Session 6)
- Key notes:
 - How Innovative groundwater remediation technologies can contribute realizing the European Water Framework Directive & Groundwater Directive - Panagiotis Balabanis – European commission (DG Research Europe)
 - Implementation and stimulation of innovative groundwater remediation technologies in Flanders. - Nick Bruneel (OVAM)

MULTIBARDEM is a LIFE project (LIFE06 EBV/B/000359) aiming at demonstrating multibarriers at pilot scale for different applications and geological situations. Multibarrier.vito.be. The final conference of the project is integrated in the PRB/RZ-2010 symposium.



The International Scientific Committee and the Local Organizing Committee would like to thank all the attendees of the symposium, and especially the oral and poster presenters for their appreciated contribution.

First International Symposium on Permeable Reactive Barriers

Belfast, March 14-16, 2004

Organized by PRB-NET (UK)

Second International Symposium on Permeable Reactive Barriers and Reactive Zones

Antwerp, November, 14-16, 2005

Organized by VITO (Belgium)

Third International Symposium on Permeable Reactive Barriers and Reactive Zones

Rimini, November 8-9, 2007

Organized by CERI, University of Rome, (Italy)

Fourth International Symposium on Permeable Reactive Barriers and Reactive Zones

Antwerp, July 6-8, 2010

Organized by VITO (Belgium)

Session 1

Developments in CAH-control

Biodegradation of CHC in an aerobic aquifer: Characterisation of the contaminated site as a basis for implementation of passive funnel & gate treatment

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At the selected site agricultural machines are produced since the 60-ies in the 20th century. Due to the handling and application of chemical solvents this site represents a typical CHC contaminated industrial site, even though the concentration of CHC are moderate but stable for many years. Soil and groundwater is polluted with different CHC compounds. Main contaminants are TeCE, TCE, TCA and also cDCE as a dechlorination product. Based on former remediation activities it exists a funnel&gate at the site, it was filled in the past with activated carbon and it should be reused in this demonstration project as a PRB with stimulating biological degradation of CHC.

Existing information from former investigation und remediation activities have been collected, further investigations of geology and hydrogeology are necessary for developing a ground water model. Before filling the gate specific chemical measures are needed to describe the initial hydrochemical situation of the groundwater.

Velocity of groundwater is high, the groundwater contains about 0.5 to 6 mO₂/L and so all wells show oxidative conditions.

Results of lab scale tests and experiments with aquifer material from new drillings are the basis for investigating different filling materials concerning permeability and stimulating microbial activity. Selected filter materials have to meet defined physical, chemical and biological requirements.

The design of the filling material and the monitoring program based on the ground water model and the results of lab scale tests will be presented as the system boundary for biodegradation of CHC at the selected site.

ACKNOWLEDGEMENTS

The project MULTIBARDEM (LIFE06 ENV/B/000359) is financed by the EU program "LIFE environment demonstration" and the Austrian "Bundesministerium für Land- und Forstwirtschaft, Umwelt- und Wasserwirtschaft". Accounts receivable management by "Kommunalkredit public consulting GmbH".

Biodegradation of CHC in an aerobic aquifer: Active nutrient dosing versus passive funnel & gate treatment

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ABSTRACT

At the historically contaminated industrial site "Altlast O24", a metal works in Upper Austria, an aerobic, fast flow shallow aquifer is primarily contaminated with tri- and tetrachlorinated hydrocarbons TeCE (=PCE), TCE and TCA. Additionally, substantial concentrations of dichlorinated degradation products cDCE and DCA were detected, although all sampling wells revealed oxidative conditions in the bulk water phase by positive redox potentials up to 400 mV and dissolved oxygen concentrations ranging from 0.5 to 6 mg/L. Batch and column experiments with aquifer material revealed that added electron donors (organic acids, sugars, alcohols, wood) immediately stimulated oxygen consumption and dechlorination. Under anaerobic conditions only cDCE accumulated which was further metabolised aerobically. Our concept aimed at the stimulation of both, aerobic and anaerobic processes, and was tested on the site by two different approaches: 1) infiltration of molasses-pulses in order to create oscillating redox conditions, and 2) use of a funnel & gate system with five parallel compartments alternately filled with pure gravel and a mixture of gravel and wood particles serving as slow-release nutrient, thereby creating alternating spatial zones of different redox conditions downstream.

INTRODUCTION

The majority of remediation projects for sites contaminated with chlorinated hydrocarbons (CHC) has been realised for more or less reducing aquifers with slowly moving ground water. Various techniques and materials are well proven now and partly commercially available for such cases, ranging from more or less abiotic reducing iron applications and adsorption barriers or gates, to mostly biotic nutrient infiltration zones or biobarriers. Under strictly reducing conditions higher chlorinated hydrocarbons like tetrachloroethene (TeCE = PCE), trichloroethene (TCE) or trichloroethane (TCA) are rapidly dechlorinated bioreductively to di- and mono-chlorinated species which often accumulate. The latter are more favourable degraded cometabolically under aerobic conditions. In order to stimulate their mineralisation special measures, either creation of extremely low redox potential or subsequent aerobic zones are needed.

The aquifer at site "Altlast O24" (for details see Alge et al. in this publication) is primarily contaminated by TCE, TeCE and 1,1,1-TCA which were used mainly for degreasing of metallic construction parts from 1960 into the 1980ies. The use of CHCs was terminated more than 20 years ago and their concentrations in the aquifer fell accordingly, from milligrams per litre to a few dozens of micrograms per litre today. However, after a rather steep decline of concentrations in the 1990ies the residual concentrations are now rather stable for years. Without sanitation measures the CHC-levels are expected to stay above Austrian regulatory thresholds for several decades.

The low-level contamination by CHC in highly mobile, aerobic groundwater and the availability of an already installed pilot funnel & gate system were the key-points for designing a sustainable, in particular economically viable treatment option.

The bulk water phase in this shallow, highly conductive aquifer is aerobic with dissolved oxygen concentrations ranging from 0.5 to 6 mg/L. Nevertheless, also cis-1,2-DCE and 1,1-DCA are present, which are products from biotic, reductive dechlorination of TCE and TCA, respectively. Hidden anaerobic areas obviously provide the conditions needed for the first steps of dechlorination. Such niches for dechlorinating bacteria could be located on a micro-scale in pores or fissures of the aquifer rocks, within aggregates of fine particulate matter and on a macro scale at the interface between aquifer and underlying aquiclude. Monochlorinated species were always below detection limits (<5 µg/L), most probably due to immediate aerobic metabolisation and losses by evaporation. Downstream gradients of the contaminants pointed to natural attenuation processes which could be stimulated in laboratory experiments by addition of various carbon-substrates as reported previously (Pümpel et al., 2007).

The MULTIBARDEM project aimed at the demonstration of plume treatment options for groundwater contaminated

by a mixture of chlorinated ethenes and ethanes, considering the above mentioned boundary conditions on the site. Neither source zone treatment nor complete site restoration were foreseen.

OPTIONS FOR CHC PLUME TREATMENT AT “ALTLAST O24”

Basically, CHC-plumes may be tackled physically (e.g. physisorption to activated carbon), chemically (e.g. reductive dechlorination by zero-valent iron) and biologically by various pathways of dechlorination and mineralisation. “In the field” it will probably never be possible to provoke only one specific process; especially biological activity will inevitably affect (support or hinder) physical and chemical processes by microorganisms settled down on carbon or iron placed in permeable barriers or reactive zones.

Activated carbon

Sorption to activated carbon seems to be the first choice given the conditions on the site, in particular the high flow rate leading to very short hydraulic residence times of around an hour in the gate. Within this timeframe physisorption already reaches more than 80% of equilibrium (Kowalzik and Pilchowski, 1999), and the process is not intrinsically affected by the presence of oxygen. The option was tested at “Altlast O24” with a pilot funnel & gate system by company Porr Umwelttechnik in the 1990ies and worked well for a limited period of time. After reaching the equilibrium saturation given by adsorption isotherms for the compound of interest, the contaminants will break through and the carbon has to be replaced.

With the actual concentration of TCA (ca. 0.15 µmol/L), Freundlich adsorption parameters (Kowalzik and Pilchowski, 1999), dimension of the gate (5x1 m; 12 tons of carbon) and flow rate through the gate (ca. 22,000 m³/a) it can be calculated that only around 1 kg of TCA may be adsorbed to 12 tons of carbon, which have to be replaced every 10–20 months. The system works but operational costs are rather high when related to the retained mass of contaminant.

Zero-valent Iron

Chlorinated hydrocarbons and ZVI is probably the best known and best investigated couple of contaminant and permeable barrier material, addressed by numerous projects and papers for many years. An actual trend in this area is the investigation of chemical behaviour and transport, and modelling of micro- and nano-scaled iron particles introduced in reactive zones. ZVI has proven to work well for dechlorination of some but not all CHCs in reduced, slowly moving groundwaters for many years, but not all reactions are fully understood yet (e.g. role and interactions of mineral surface precipitates and settled bacteria in the overall process).

Blends and composites of ZVI with slow release carbon sources to additionally support anaerobic microbial activity found their way to application and already commercialisation. Such products can enable or speed up reductive processes, where pure ZVI fails. Pure and blended ZVI work best under already reducing conditions; residual oxygen in the water phase may be acceptable, but reduces lifetime of the materials.

In contrast, the high concentration of dissolved oxygen in combination with the high flow rate at “Altlast O24” rules out the application of pure and blended ZVI. Inserted iron would oxidise completely within months.

Biocatalysts

Chlorinated ethenes and ethanes are degradable by various microorganisms. Under strictly anaerobic conditions the CHCs are sequentially dehalogenated to ethene or ethane. The process either generates energy in a growth-coupled pathway called dehalorespiration, where CHCs serve as terminal electron acceptors, or runs co-metabolically, uncoupled from growth. All of the known dehalorespiring microorganisms are bacteria and up to now only one species, *Dehalococcoides ethenogenes*, was identified capable of complete dechlorination from TeCE to ethene (only the last step from vinyl chloride to ethene is co-metabolical and does not yield energy; Futagami et al., 2008). Usually, tetra- and trichlorinated hydrocarbons are rapidly dechlorinated in aquifers provided that negative redox potential and sufficient amount of electron donor are available. Due to slower kinetics of the further degradation steps often di- and monochlorinated species accumulate in the water and pose increased risk by their higher toxicity. However, these compounds are much better degraded aerobically. They may serve as a carbon source or again as a “useless” co-substrate, e.g. in ammonium oxidation by nitrifying bacteria.

Our site of investigation offers a broad range of microbial activity. Despite the highly oxidising bulk water phase we detected definitely anaerobically born dichlorinated degradation products of the primary contaminants TeCE, TCE and TCA, but no monochlorinated species. Amendment of aquifer samples with adequate nutrients in the lab stimulated anaerobic, sequential dechlorination as well as aerobic co-degradation by autotrophic nitrifying and heterotrophic bacteria.

Concept selected for pilot testing

The main objective of our concept was to stimulate aerobic **and** anaerobic biological processes, as both were shown to already contribute to natural degradation of chlorinated hydrocarbons on the site. This was tested by two different

approaches:

1. infiltration of molasses-pulses in order to create oscillating redox conditions, and
2. use of the already available funnel & gate system with five parallel compartments. Alternate filling of the compartments with pure gravel and a mixture of gravel and wood particles serving as slow-release nutrient, should create alternating spatial zones of different redox conditions downstream.

MATERIALS AND METHODS

Investigation area

The area is characterised and shown in detail by Alge et al. in this publication. Figure 1 shows the target zone with monitoring wells and funnel & gate system. The main flow direction of the groundwater is from north–west to south–east along the line of circled wells. Distance from H41 to downstream–well H22: 98 m.

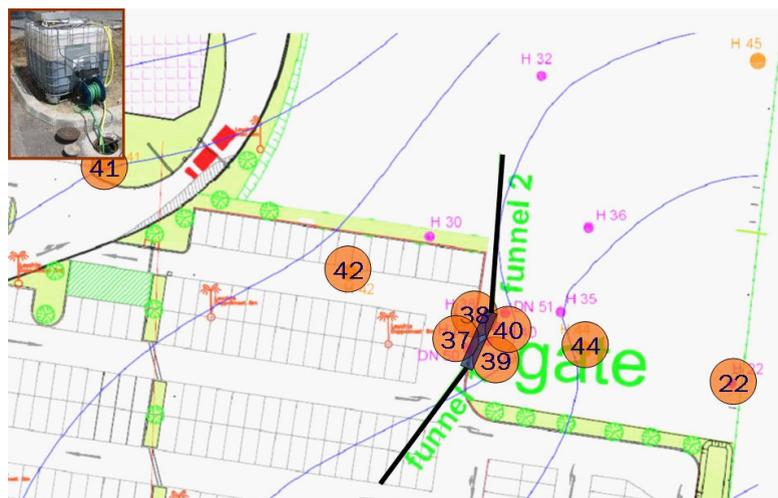


Figure 1: Detail of the investigation area highlighting the locations of molasses dosing station (H41), selected monitoring wells and funnel & gate (gate was empty during molasses-dosing period).

Dosing of Molasses

Sugar cane molasses was dosed into well H41 for a period of 50 days. An immersion pump was placed in the well, the extracted water amended with molasses by a peristaltic pump and returned to the same well. About 300 kg of molasses were dosed to target a concentration of 100 mg/L molasses and 20 mg/L carbon, resp., on average in the area of influence. (From hydraulic data an average flow rate of 60 m³/d through the gate was calculated.) Electrical breakdown of the immersion pump caused the delivery of substantial mass of molasses without mixing, creating an unplanned dense molasses zone around the well.

Operation of Funnel & Gate

According to microbial and hydraulic laboratory tests a blend of fine gravel and grape marc as slow–release carbon source was filled into 50% of the gate compartments. The other 50% were filled with pure gravel to allow some of the ground water to pass without oxygen depletion. The hydraulic conductivity of the gate filling was adjusted below that of the aquifer in order to avoid bypassing of the F&G. The effective flow velocity in the gate is ca. 20 m/d, which relates to a hydraulic residence time of only 1.2 hours.

RESULTS AND DISCUSSION

Dosing of Molasses

The original plan of applying a series of molasses pulses had to be withdrawn due to the unintended dense molasses zone created in and around well H41 which fed the aquifer for months. The scheduled test of the funnel & gate system for a feasible period of time within the project time frame did not allow to continue investigations with molasses, and so the effects of only one molasses pulse could be analysed. In dosing–well H41 the redox potential dropped by over 600 mV to –300 mV immediately after dosing start and remained lowered for 250 days after stopping the active molasses supply. More downstream the potential regained original values after 150–200 days (H42, H37/38), and after 98 m in H22 the potential was only slightly affected (Fig. 2). Dissolved oxygen concentrations reacted similarly, but regained their starting levels faster. Even in H22 the oxygen dropped from 3–4 to below 0.5 mg/L for a couple of weeks.

In coincidence with laboratory results the addition of carbon source immediately boosted microbial activity in the aquifer, even dechlorinating activity. Figure 2 shows time patterns of 1,1,1–TCA and its first dechlorination product

1,1-DCA. For easier interpretation all XCA data were normalised on a molar basis to TCA in well H41, thereby eliminating seasonal fluctuations. Samples from the dosing well show decreased TCA and increased DCA concentrations for more than 200 days. The DCA peak can be followed down to well H44, but does not show up in H22. TCA reacts more slowly and obviously degradation and mobilisation of TCA, as seen in H42, interfere. Chlorinated ethenes responded in a similar way.

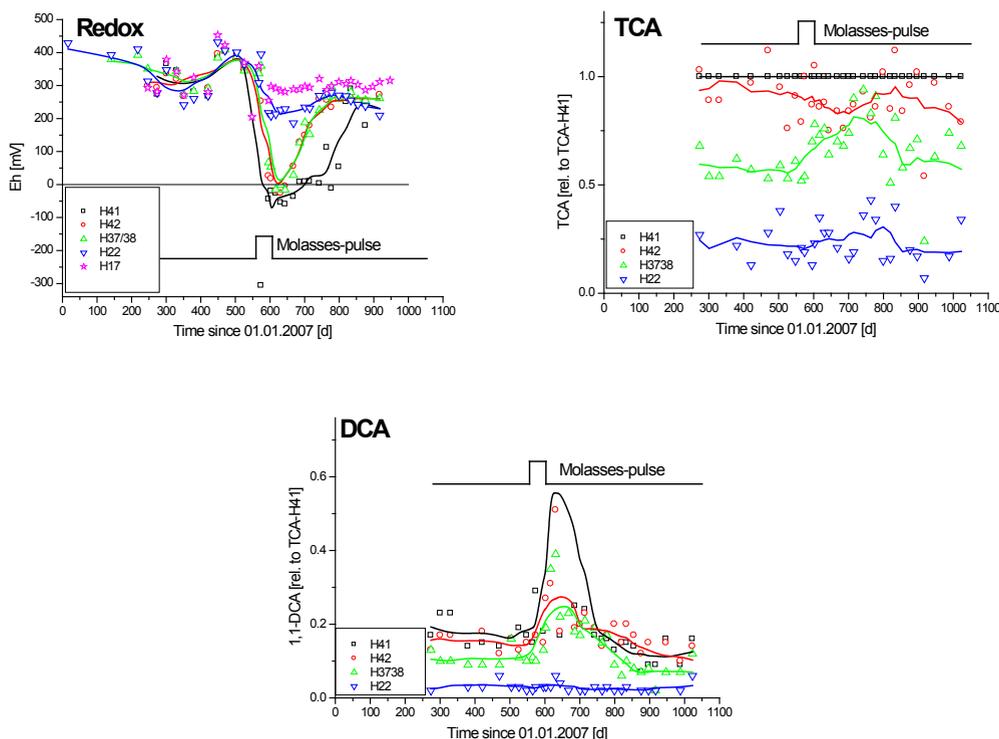


Figure 2: Time pattern of redox potential, 1,1,1-TCA and 1,1-DCA in downstream wells in response to a molasses pulse, dosed into well H41 (for locations of wells see Fig. 1; H17: reference-well outside the investigation area). Lines are moving averages over 9 data points, consult text for y-axis scaling.

Operation of Funnel & Gate

Microbial activity in the gate emerged within a few weeks after filling despite the extremely low hydraulic residence time of only one hour. A drop of redox potential by 100 mV and an increase of DCA (Fig. 3) and cis-1,2-DCE (not shown) across the gate were the most pronounced effects observed, indicating biological activity. Interestingly, this obvious formation of intermediates is not reflected by stoichiometric losses of their parent compounds. As with molasses dosing, mobilisation of adsorbed species may also here partially mask degradation. Further observation is necessary for clarification of these data. At present, a sound quantitative evaluation of the function of the gate is impossible, mainly due to the unexpectedly extended, interfering effects of molasses dosing before. Especially TCE and some cDCE are still being formed from TeCE in the area upstream the gate, whereas DCA and TCA nearly gained their original levels.

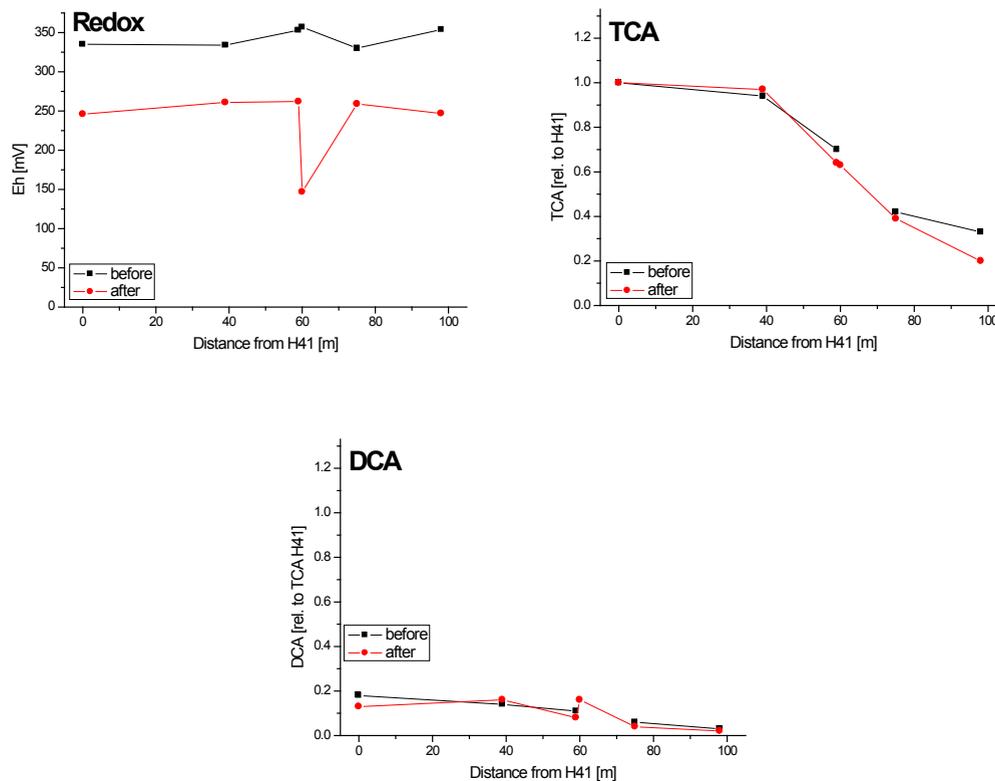


Figure 3: Longitudinal profiles of redox potential and chlorinated ethanes before and after installation of the gate, from well H41 (0 m) to H22 (98 m downstream), gate located from 59-60 m. Data averaged over months and normalised to TCA in H41 (molar ratio).

CONCLUSIONS

Anaerobic dehalogenating bacteria found adequate niches even in the investigated oxidising, highly conductive aquifer. Nutrient (molasses) dosing immediately stimulated mobilisation and biodegradation of CHCs.

The aquifer reoxygenates from the surface and from side streams within short distances downstream anaerobic areas created by nutrient dosing. Special measures like pulse dosing or segmented gates to provide oxygen for complete contaminant degradation as proposed here were therefore not necessary.

Well balanced, well distributed nutrient dosing is probably the best way to a well controlled and also economically feasible CHC plume treatment under the given conditions.

The biogate started to operate, but one hour of hydraulic residence time is clearly insufficient for satisfactory plume treatment. However, a continuous permeable wall filled with the tested material could work successful due to longer residence time.

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REFERENCES

- Pümpel, E.; Jussel, B.; Schwind, S.; Bunge, M. and Pümpel, T. (2007). Biodegradation of Chlorinated Hydrocarbons in Aerobic Groundwater. In: Papini, M.P. (Ed.), Proceedings of the 3rd International Symposium on Permeable Reactive Barriers & Reactive Zones, Rimini (I), November 8-9, 2007. Casa Editrice Università La Sapienza, 159–162.
- Kowalzik, A. and Pilchowski, K. (1999). Investigations of the adsorptive separation of volatile chlorinated hydrocarbons (VCHC) from water with humic substance by novel polymeric adsorbents and activated carbons. Part I: Isotherms and kinetics of adsorption. Acta Hydrochimica et Hydrobiologica 27: 79-86.
- Futagami, T., Goto, M., Furukawa, K. (2008). Biochemical and Genetic Bases of Dehalorespiration. The Chemical Record 8: 1–12.

Chemical Reduction of PCE by Zero Valent Iron Colloids Comparison of Batch and Column Experiments

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ABSTRACT

In order to remove contaminants from the groundwater, a relatively new and promising method is the injection of an aqueous suspension of zero valent iron colloids into the subsurface using injection wells. The iron attaches to the sand grains and fills up favourite deposition sites in the porous medium to form a reactive zone.

One of the advantages of this technology is the possibility to inject the reactants directly into the source zone. The reactant is then very close to the contaminant phase and chemically reduces the dissolved chlorinated solvent before the contaminants are being diluted, as it would be the case further downstream. The reaction close to the pure phase strongly reduces the contaminant concentration in water. This in turn increases the rate of dissolution and hence the remediation time.

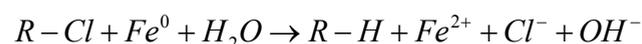
In order to determine degradation rates, and hence, longevity of the iron particles, batch experiments are conducted. However, the results are not directly transferable to the field scale since in batch experiments the contact between iron colloids and the chlorinated solvent is optimized by shaking or rotating the vial. In porous media flow, the distribution of the chlorinated solvent is diffusion controlled resulting in a decrease in the availability of contaminants for the chemical reduction. In addition, the corrosion is self inhibiting due to the rising pH which does not occur in the field, where the continuous flow of fresh ground water keeps the pH neutral. In the field the corrosion is thus much stronger, which shortens the longevity and, moreover, hydrogen as a by-product of the corrosion process will be produced. If this happens in larger amounts, the hydrogen becomes a separate gas phase and can clog the porous medium. The continuous delivery of fresh water thus is necessary to be able to transfer the lab results to the field situation. Preliminary column experiments have therefore been performed. These experiments showed that the production of hydrogen gas could be reduced by adding burned chalk ($\text{Ca}(\text{OH})_2$) in granular form to the suspension during injection.

INTRODUCTION

Zero valent iron (Fe^0) is known to be a possible remediation reagent for chlorinated hydrocarbons and other contaminants in groundwater. Up to now, Fe^0 has been emplaced into the subsurface in granular form to create permeable reactive barriers or funnel and gate systems [O'Hannesin and Gillham, 1998; Molfetta and Sethi, 2006], restricting the application to the plume area.

In order to remove contaminants from the groundwater, a relatively new and promising method is the injection of a zero valent iron colloid suspension into the subsurface using injection wells. The colloids attach to the sand grains and fill up favourite deposition sites in the porous medium to form a reactive zone. Recent and current studies at VEGAS focus on the transport distances that can be achieved with nano- and micro sized iron colloids. So far the results showed that it is possible to distribute the colloids in the subsurface to an economically reasonable distance and that the colloids will remain in location after the injection stops. The latter is due to the significant reduction of the flow rate that occurs when the injection pump is switched off and the porous media flow returns to the original groundwater flow regime. This behaviour of the colloids can make it possible to maintain a reactive zone for an economically sufficient time. Having a reactive zone physically stable in position is not enough, also the reactive zone needs to be chemically reactive for the same period. Directly related to this is the longevity of the reactive colloids themselves.

The general reaction between zero valent iron and a chlorinated solvent is given by:



Focus of the presented work lies at the solvent Tetrachloroethylene (PCE). Stoichiometrically it means that for a full dechlorination at least 1.37 grams of iron are needed for each grams of PCE present, the reaction then produces 0.85 grams Chloride. This is a minimum amount of iron because beside the above mentioned reaction also other reactions occur. One of the main side reactions that occur in the ground water is anaerobic corrosion:



The anaerobic corrosion is strongly dependent on the pH as becomes clear from the reaction equation. At a high pH the corrosion almost ceases, whereas at a very low pH the corrosion is very rapid.

Batch experiments are commonly used for chemical studies on the behaviour of iron particles, especially when the performance of a remediation reactant is to be tested for a specific contaminant. In a batch experiment the external influences on the chemical system are minimized and the natural system is strongly idealized for the experiment. In general the batch experiments are set up to observe the pure reaction between the reactant and the contaminant. However, due to this strong simplification of the system, the chemical behaviour in batch experiments differs significantly from the outdoor reality.

In the following several advantages and disadvantages of batch experiments as well as alternatives to batch experiments for more nature realistic reaction conditions are presented by providing several examples from a Diploma Thesis performed at VEGAS by Steiert [2008].

BATCH EXPERIMENTS

Methods

Batch- and column experiments were performed to make an estimation of the transferability of the results from batch experiments to the field scale. Batch experiments were set up in a single bottle for a whole testing period, but also with separate vials for each sampling time.

An experiment was prepared in a single bottle of one litre. The experiment contained a droplet of one gram pure PCE in one litre of water. The reaction was expected to be fast in the beginning of the experiment since at that time the iron is fresh. Therefore the sampling interval was short in the beginning and longer after a few weeks. The sampling was done at 0, 15 and 30 minutes, then at 1, 2, 4 and 6 hours and for the following two weeks once a day, after that the sampling was done once every two weeks. A result of the frequent sampling from one bottle was that after two weeks less than half of the initial volume was left over. The bottle had thus to be filled up to one litre again to be able to continue the experiment and make further sampling possible.

The next batch experiment was then set up with single headspace vials for each sampling time. For this experiment a PCE concentration of 50 mg/l with 1.25 g/l nano sized zero valent iron (nZVI, RNIP 10E Toda Kogyo, Japan) was prepared in separate vials. For each sample time a duplicate and a blank sample with 50 mg/l PCE and no iron were prepared. The total experiment ran over 30 weeks with 11 sampling times, again with most samples taken at the beginning of the experiment.

Results

Since the bottle needed to be opened for each sampling moment, the gas phase (nitrogen with some PCE, corresponding to the equilibrium concentration in the gas phase above an aqueous solution) in the bottle was exchanged completely by nitrogen gas to avoid oxygen in the system. This resulted in an increased removal of PCE, not due to a chemical reaction with iron, but due to evaporation. The only suitable method to determine the amount of PCE removed by iron was then through Chloride measurement and a back calculation of the removed mass of PCE (Table 1).

Table 1: Chloride production and conversion rate of PCE by nZVI

H ₂ O [ml]	PCE [mg]	$\frac{m_{Fe^0}}{m_{PCE}}$	Total mass of produced Cl ⁻ [mg]	Maximum possible Cl ⁻ based on PCE reduction [mg]	Relative Cl ⁻ concentration [-]
998	1000	< 1	< 16	< 400	< 0.004
991	1000	1	34	812	0.04
978	1000	3	294	850	0.35
957	1000	6	551	850	0.65

The setup with separate vials containing dissolved PCE turned out to be a very good method for measuring the removal by directly measuring the PCE concentration (Fig. 1). A verification of the completeness of the dechlorination could be achieved by measuring the chloride concentration. Ideally the relative Chloride concentration would be 1. Since there

has been no removal through evaporation, it could be stated that all removed PCE that did not produce Chloride must still have been present as a side product or intermediate product (TCE, VC, cis-DCE, etc.). For the data presented in figure 1 also TCE was measured, which showed to be present soon after the experiment started and reduced towards the end, which was in accordance with the relative Chloride concentration which rose towards 1 at the end.

Since an exponential behaviour for the PCE removal was expected, the effect of evaporation was underestimated. Due to an almost exponential decrease in sampling moments the PCE removal also shows an exponential decrease in concentration, which at first was thought of to be caused by the iron. From the results of the separate vials it became clear that the removal due to chemical reduction by iron was much slower and the faster removal in the single bottle must have been caused by evaporation. The water phase in the bottle was then analysed for its Chloride concentration to determine the total mass of PCE that had been dechlorinated due to the reaction with iron (Table 1). What can be seen as a result from this experiment is that the reaction kinetic was improved by the increased iron to PCE ratio, furthermore it could be proven that the nZVI colloids were able to stay reactive and keep removing PCE over a long period, even if the PCE concentration within the solution is kept high due to the presence of a pure phase of the contaminant.

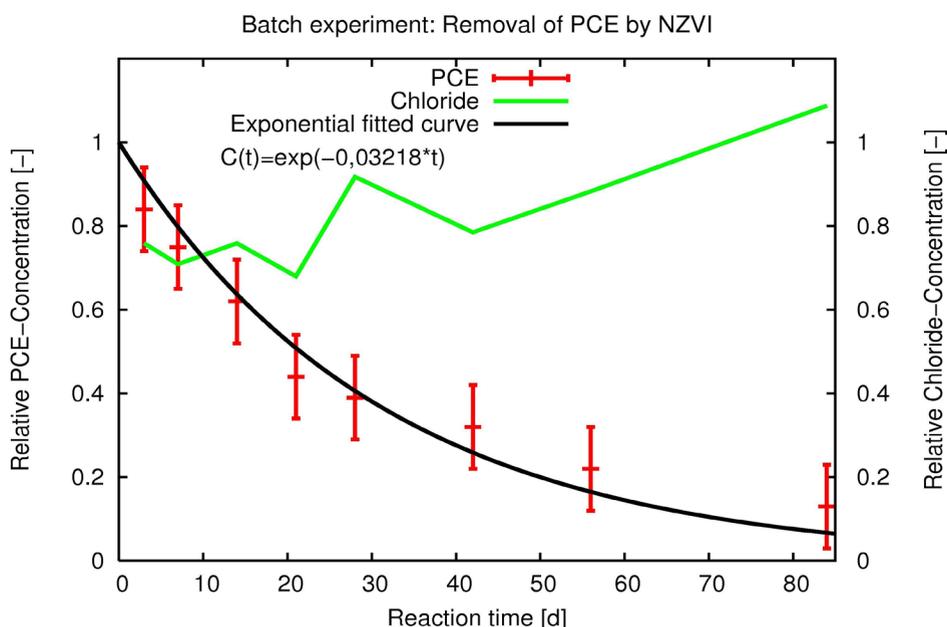


Figure 1: Removal of PCE by nZVI and the production of Chloride

COLUMN EXPERIMENTS

The results of batch experiments are not directly transferable to the field scale since in batch experiments the contact between iron colloids and the chlorinated solvent is optimized by the absence of a porous medium matrix and due to shaking or rotating the vial. In porous media flow, the distribution of the chlorinated solvent is diffusion controlled resulting in a decrease in the availability of contaminants for the chemical reduction.

In batch experiments the pH quickly increases due to the anaerobic corrosion, which in its turn results in a stagnation of the anaerobic corrosion. This increased pH is one of the main reasons why the reaction kinetics determined from a batch experiment with zero valent iron can not be transferred to a natural system. In general, in a natural situation the reactive zone built from zero valent iron is placed in an aquifer with pH neutral (or close to neutral) water. The buffer capacity of the ground water is usually sufficient that there will be no significant increase in pH within the reactive zone and the iron is continuously being removed by anaerobic corrosion.

Setup of Column Experiments

A better method to determine the longevity of zero valent iron to be used in a reactive zone is the application of a sand filled, water saturated column experiment. For this purpose a setup was used in which it was possible to maintain a porous media flow that had a seepage velocity representative for a natural system ($v \approx 0.5$ m/d). In the setup eight columns could be placed, of these columns six could continuously be provided with degassed water with dissolved PCE and two columns with uncontaminated degassed water (Fig. 2). Iron was injected into six of the columns, two of them were placed in the uncontaminated positions, two at the high concentration places and two at the saturated positions.

The two blank columns were placed at a high and low concentration place to determine the removal of PCE due to possible non-tightnesses in the system, sorption at the sand grains or other causes of losses.

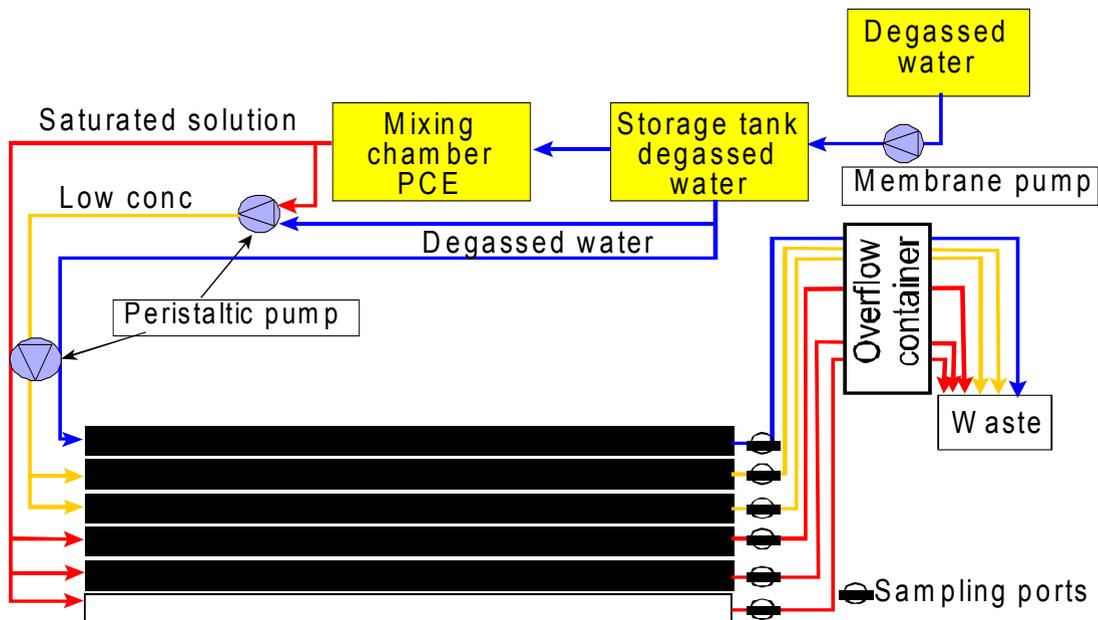


Figure 2: Schematic overview of the column experiment setup.

RESULTS

The first results of these column experiments showed that H₂-gas production was a serious problem to keep the system running. Water in the columns was pushed out of the column due to the internally built up gas pressure and the porous medium was clogged due to the presence of H₂ gas. After the reactivity of the iron ceased due to the consumption by the reaction with PCE and corrosion with water, the produced H₂ gas occupied a large volume of the column and could only be partly dissolved in the degassed water passing through the column. This was caused by trapping effects of the gas phase in the porous medium making the gas inaccessible for the passing water.

In a preliminary experiment following the first column experiment the production of H₂ gas was proven to be significantly reduced due to the addition of solid calcium hydroxide (Ca(OH)₂) to the iron suspension (increasing the pH in the column to 11). The amount of solid Ca(OH)₂ needs to be such that it will be sufficient for the total period of which the iron is expected to be reactive under the new conditions. Further column experiments to get a quantitative estimation of the longevity of zero valent iron colloids in a natural environment have been planned to start soon at VEGAS, this should give the possibility to make a good estimation of the necessary amount of zero valent iron and calcium hydroxide.

CONCLUSIONS

A short overview of two different types of batch experiments was presented. The self inhibition in batch experiments with zero valent iron makes the batch setup less suitable for the production of field transferable dechlorination rates. A much more adequate method is the application of column experiments. These can represent a natural system closely due to the continuous delivery of pH neutral water to the reactive zone. The first results of the column experiments are very promising and are a sound basis for further investigations on zero-valent iron based remediation of contaminated groundwater.

OUTLOOK

Several long term experiments have been planned for the column scale. Among these are investigations on the longevity of zero valent iron particles in porous media, either with pure phase present or in contact with dissolved contaminants. Alongside, the effect of calcium hydroxide on the longevity and reactivity will be studied in more detail.

ACKNOWLEDGEMENTS

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REFERENCES

- de Boer, C.V., N. Klaas, J. Braun, 2007, Machbarkeitsstudie zum Einsatz von Eisenkolloiden zur Sanierung von CKW-Kontaminationen (Fahnensanierung), Wissenschaftlicher Bericht Nr. 2007/3, (VEG 21) Abschlussbericht zum BW-Plus Projekt BWR25001, Institut für Wasserbau, Universität Stuttgart
- de Boer, C.V., N. Klaas, J. Braun, 2009, Anwendung nanoskaliger Eisenkolloide zur In-Situ-Sanierung anthropogener CKW-Kontaminationen im Untergrund . Wissenschaftlicher Bericht Nr. VEG 36, 2009/05. Institut für Wasserbau, Universität Stuttgart
- O'Hannesin, S. F. and R.W. Gillham, 1998, 'Long-term performance of an in situ "iron wall" for remediation of VOCs', Ground Water 36(1), 164--170.
- Molfetta, A. and R. Sethi, 2006, 'Clamshell excavation of a permeable reactive barrier', Environmental Geology 50(3), 361--369.
- Steiert, S., 2008, Reaktivität und Langzeitstabilität von nullwertigem Nano-Eisen bei der Sanierung von CKW-Schadensfällen in Grundwasserleitern. Diplomarbeit an der Universität Stuttgart, Institut für Wasserbau, VEGAS 7/2008.

***In situ* remediation of a chlorinated ethene contaminated source zone by injection of zero-valent iron: from lab to field scale**

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ABSTRACT

Zero-valent iron (ZVI) is a solid-phase reducing agent that can be used in the subsurface to create a chemical *in situ* reactive barrier or zone for remediation of contaminated groundwater. ZVI is often used in a permeable reactive barrier (PRB). An alternative method is direct injection of the ZVI into the aquifer to create a reactive zone. The major challenge of the injection of an insoluble compound like ZVI is to create a homogeneous distribution of the ZVI in the aquifer for good contact of the ZVI with the contamination.

In lab tests, several types of ZVI were screened for reactivity with chlorinated ethenes. One nanoscale ZVI and one microscale ZVI were selected for dose-response tests in the lab. These tests confirmed a higher reactivity of the nanoscale ZVI, compared to the microscale ZVI and can be explained by the high surface area to volume ratio of the nanoscale ZVI. For both types of ZVI, minimal doses for effective reduction of chlorinated ethenes were obtained. Trichloroethene (TCE) had a significantly higher degradation rate compared to tetrachloroethene (PCE), while cis-1,2-dichloroethene (cis-1,2-DCE) was degraded very slowly.

To study the distribution of ZVI in an aquifer under controlled conditions, the nano- and microscale ZVIs were injected by two different injection techniques in two containers filled with aquifer. The injection was compared between an injection filter with wire wound screen (WWS) and injection using a permeable lance over short-screened intervals. For both types of ZVI and both injection techniques, preferential pathways with heterogeneous distribution of the ZVI were observed.

Microscale ZVI has a lower cost compared to nanoscale ZVI. Furthermore, lab tests showed significant aggregation of the nanoscale ZVI to microscale size, reducing the advantage of the nanoscale ZVI over the microscale ZVI. Therefore, the microscale ZVI was injected during a pilot test in the field. At a depth of 6 to 8 m below ground level (bgl), no contamination was present and the microscale ZVI was injected using the injection lance and the WWS filter to compare the ZVI distribution between both injection techniques under field conditions. At a depth of 17 to 18 m bgl, a contamination with chlorinated ethenes (especially TCE and cis-1,2-DCE) is present. The microscale ZVI was injected with two WWS filters to test the reactivity and distribution of the microscale ZVI in the field. The injection of the microscale ZVI was difficult due to clogging of the injection filters with ZVI. The ZVI was spread along preferential pathways, resulting in a heterogeneous distribution of the ZVI in the field. Since only a very small amount of ZVI could be injected, no significant effect on the chlorinated ethene concentration in the groundwater of the monitoring filters was observed.

INTRODUCTION

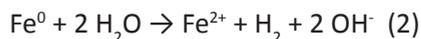
Zero-valent iron (ZVI), Fe⁰, is a solid-phase reducing agent to create a chemical *in situ* reactive barrier or zone for remediation of contaminated groundwater. Several factors determine the reactivity of the metal, including surface area per volume, processing and handling protocols and alloys and impurities (Suthersan and Payne, 2005).

ZVI is often used in a permeable reactive barrier (PRB), i.e., a kind of trench, perpendicular to the groundwater flow, which is backfilled with a mixture of granular ZVI (millimeter size) and a porous medium like sand. However, the installation of a PRB at a depth larger than 7 m below ground level (bgl) is often not economically feasible. An alternative method is direct injection of the ZVI into the aquifer to create a reactive zone. Microscale (1-100 µm) and nanoscale (<1 µm) particles are used for direct injection. The smaller the particle, the higher the specific surface area (SSA) per volume, and therefore a much smaller mass of metal is required. Smaller particles are more reactive: they show a higher degradation rate and are reactive with a wider range of pollutants. Furthermore, smaller particles are more mobile in the aquifer. On the other hand, smaller particles have a shorter life time (months) and a limited stability and they are more difficult to handle safely in the field.

The reaction of ZVI with a chlorinated compound is shown in equation (1):



The competing reaction of ZVI with water is shown in equation (2):



These reactions with ZVI lead to a significant pH increase through consumption of protons (1) and production of hydroxyl anions (2).

ZVI can treat several organic (e.g. chlorinated ethenes, tetrachloromethane, pesticides,...) and inorganic (e.g. chromium,...) contaminants. The chlorinated ethenes are not equally reactive with ZVI. Tetrachloroethene (PCE) and trichloroethene (TCE) react more quickly than cis-1,2-dichloroethene (cis-1,2-DCE), 1,1-dichloroethene (1,1-DCE) and vinyl chloride (VC). Potential dechlorination reaction mechanisms are β -elimination and catalytic hydrogenation (Suthersan and Payne, 2005).

The major challenge of the injection of an insoluble compound like ZVI is to create a homogeneous distribution of the ZVI in the aquifer for good contact of the ZVI with the contamination. Therefore, two types of ZVI and two different injection techniques were compared in lab, container and field tests.

LAB TESTS

In lab tests, two types of nanoscale ZVI and two types of microscale ZVI were screened for reactivity with chlorinated ethenes (results not shown). One nanoscale ZVI (SSA 5 m²/g) and one microscale ZVI (SSA 1 m²/g) were selected for dose-response tests in the lab. These tests confirmed a higher reactivity of the nanoscale ZVI, compared to the microscale ZVI and can be explained by the high surface area to volume ratio of the nanoscale ZVI. The minimal dose for source zone treatment of chlorinated ethenes was 5 to 25 g ZVI per kg slurry for nanoscale ZVI and 15 to >100 g/kg for microscale ZVI. TCE had a significantly higher degradation rate compared to PCE, while cis-1,2-DCE was degraded very slowly.

Furthermore, lab tests showed significant aggregation of the nanoscale ZVI to microscale size, reducing the advantage of the nanoscale ZVI over the microscale ZVI in terms of SSA, reactivity and mobility (results not shown).

CONTAINER TESTS

To study the distribution of ZVI and the formation of preferential pathways in an artificial aquifer under controlled conditions, the selected nano- and microscale ZVIs were injected by two different injection techniques in two containers filled with glauconite rich sand and water. The nanoscale ZVI was injected at a concentration of 8 kg/m³, the microscale ZVI at 80 kg/m³.

The injection was compared between an injection filter with wire wound screen (WWS) and injection using a permeable lance over short-screened intervals (Fig. 1) with two inflatable packers. The latter system can be used to create hydraulic fractures in the horizontal plane. Hydraulic fracturing increases the injectability of reagents and concentrates groundwater flow in the newly formed fractures (Payne *et al.*, 2008).

In different directions from the injection point, filters ('flow filters') were installed to collect water that was displaced during the injection. The volume and pH of the collected water were monitored. An unequal amount of water was obtained from the different flow filters, indicating an heterogeneous water flow in preferential pathways in the artificial aquifer of the container.

After injection, water from flow filters was analyzed for dissolved Fe. Soil samples were taken in different directions and different distances from the injection point. Fe in the soil was analyzed by X-ray diffraction and HCl was added to the soil samples to analyze released H₂ gas.

Based on the Fe and H₂ analysis in the soil (results not shown), the radius of influence was at least 0.5 m. In addition, for both types of ZVI and both injection techniques, preferential pathways up to the borders of the containers at 2 m from the injection point were observed, resulting in a very heterogeneous distribution of the ZVI. The injection lance showed a somewhat better injection compared to the WWS filter, probably due to specific injection over a short interval.



Figure 1: Injection filter with wire wound screen (top left) and injection using a permeable lance (right) over short-screened intervals (bottom left).

FIELD TESTS

Microscale ZVI has a lower cost compared to nanoscale ZVI. As previously noted, significant aggregation of the nanoscale ZVI to microscale size was observed. Therefore, the microscale ZVI was chosen for injection during pilot tests in the field. Two injections at different depth were performed: a shallow injection at 6 to 8 m bgl and a deep injection at 17 to 18 m bgl.

Site description

The site is located in Antwerp, Belgium. The geology can be described as fine sand with glauconite. The groundwater is contaminated with chlorinated ethenes, especially TCE and cis-1,2-DCE.

Shallow injection

At a depth of 6 to 8 m bgl, no contamination was present and the microscale ZVI was injected using the injection lance and the WWS filter to compare the ZVI distribution between both injection techniques under field conditions. The WWS filter was installed between 6 and 8 m bgl. The permeable lance was used over seven short-screened intervals of 0.1 m from 5.5 to 8 m bgl. During injection, injection volume and pressure were monitored. After injection, soil was sampled between 4 and 8 m bgl with a Geoprobe in different directions and different distances from the injection point. HCl was added to the soil samples and released H_2 gas was analyzed. Groundwater was sampled from temporary monitoring wells (filter 6.4 to 7.5 m bgl) with a Geoprobe and dissolved Fe and H_2 were analyzed. Some H_2 was found in the groundwater and soil samples (results not shown), but a clear radius of influence could not be determined.

In the WWS filter, 2.4 m³ of the ZVI slurry (45 kg/m³) was injected. With the injection lance, 2.9 m³ of slurry (90 kg/m³) was injected over seven screens: 53 % was injected in the deepest screen at 8 m bgl, while 47 % was injected over the six other screens. This unequal distribution of injected ZVI over the seven screens shows that the injected ZVI was not spreading uniformly around the filter screen in the soil. Furthermore, a breakthrough of ZVI at ground level was observed at 3.6 m from the injection point, indicating the formation of a preferential pathway.

In general, the main problem of the shallow injection was clogging of the injection system, i.e., injection filters, tubing, mixing tank, with the non-dissolved microscale ZVI.

Deep injection

At a depth of 17 to 18 m bgl, a DNAPL contamination with chlorinated ethenes is present: 0 to 877 mg/L TCE and 3 to 82 mg/L cis-1,2-DCE. The broad range of the pollutant concentrations shows a very heterogeneous distribution of the contamination in the aquifer. At this depth, the groundwater flow is very slow (1 m per year).

The microscale ZVI was injected with two WWS injection filters (IF3043 and IF3044, filter screen 17 to 18 m bgl) to test the reactivity and distribution of the microscale ZVI in the field. Two monitoring filters (MF3048 and MF3049, filter screen 17 to 18 m bgl) at 2 m distance from the injection filters in the direction of the groundwater flow were used.

In injection filter IF3043, only 0.3 m³ of ZVI slurry (90 kg/m³) could be injected. In injection filter IF3044, 0.5 m³ of water, followed by 0.8 m³ of ZVI slurry (45 kg/m³), was injected. The pressure-flow diagram of IF3044 is shown in Fig. 2. During the first hour, water was injected, followed by the injection of the ZVI slurry. The sharp decrease of flow, combined with the large increase of pressure, after about two hours, indicates clogging of the injection filter with ZVI.

In the groundwater of the monitoring filters, no increased pH and no H₂ were found indicating that the injected ZVI could not reach the monitoring filters. This was expected due to the very small amount of injected ZVI slurry. As a result, no significant effect on the chlorinated ethene concentrations was observed in the groundwater of the monitoring filters (results not shown).

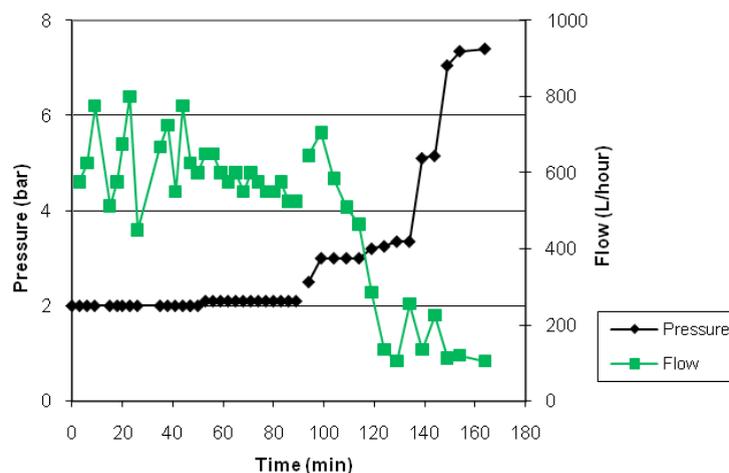


Figure 2: Pressure-flow diagram for injection filter IF3044.

CONCLUSIONS AND RECOMMENDATIONS

Injection of ZVI to create an *in situ* reactive zone for chemical reduction of chlorinated ethenes is an innovative soil remediation technology. The main problem is the distribution of ZVI in the aquifer since:

- ZVI does not dissolve in water, resulting in a difficult injection of a ZVI slurry in an aquifer;
- ZVI is heavy, resulting in clogging, i.e., precipitation of ZVI in the injection system (filters, tubing, mixing tank,...).

Based on these container and field tests in an aquifer with a relatively fine texture (fine sand with glauconite), preferential pathways were formed, resulting in a very heterogeneous distribution of ZVI in the aquifer. A homogeneous distribution of ZVI should not be expected. To obtain an acceptable distribution of ZVI in the aquifer, some recommendations are given:

- Injection of other types of ZVI (e.g. nanoscale ZVI);
- Injection of lower ZVI concentrations and smaller volumes of ZVI slurry per injection point;
- Direct push injection with close spacing of injection points;
- Stabilizing agent to keep ZVI in solution, especially for microscale ZVI.

These aspects are further studied in the FP7 SQUAREHAB project.

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REFERENCES

- Payne, F.C., Quinnan, J.A., Potter, S.T. 2008. Remediation hydraulics. CRC Press, Boca Raton, Florida, USA.
- Suthersan, S.S., Payne, F.C. 2005. *In situ* remediation engineering. CRC Press, Boca Raton, Florida, USA.

Effect of guar gum on CAHs removal by micro scale zero-valent iron particles

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ABSTRACT

Chlorinated aliphatic hydrocarbons (CAHs) represent frequently detected groundwater contaminants in industrialized countries. The use of zero-valent irons (ZVI) for removal of CAHs via abiotic reductive dehalogenation is a promising in situ remediation technique. During the last year, the focus shifted from granular particles (mm-size) to finer particles (micro and nano scale), which can be injected in the subsurface as a slurry. To prevent sedimentation of micro zero-valent iron (MZVI) particles during injections, the use of a stabilizing agent is necessary. Polymers like guar gum, xanthan gum, carboxymethyl cellulose, starch etc. have already been studied to improve technological and environmental performance of ZVI, mostly considering mobility and stability of ZVI particles. In this study, the focus is rather on the impact of the polymer on the reactivity of the ZVI particles towards CAHs. Considering relatively low cost, high resistance and its stabilizing and biodegradable properties, guar gum was identified as a promising stabilizer in lab experiments. The impact of the green polymer guar gum on MZVI reactivity has been studied via lab-scale batch degradation experiments. The results of a first set of batch experiments indicated that the presence of the guar gum had a significant negative influence on CAH-removal from simulated groundwater by MZVI particles. Additional batch reactivity experiments were set-up with MZVI to evaluate the impact of the guar gum concentration, and the impact of removing the guar gum by cleaving the polymer with enzymes, and removing subsequently the sugars by flushing the sugar containing water. Up to now, obtained results indicate that from a reactivity point of view, guar gum may not be the best choice as stabilizer.

INTRODUCTION

Chlorinated aliphatic hydrocarbons such as perchlorethylene (PCE), trichloroethylene (TCE), cis-dichloroethylene (cDCE) and 1,1,1 trichloroethane (111-TCA) were mainly used in dry cleaning and metal degreasing processes and represent the most frequently detected groundwater contaminants in industrialized countries (Prommer et al., 2008). Remediation of such a site is a difficult and time consuming process (Haest et al., 2010). The use of zero-valent iron as a nontoxic material has been shown as one of the most promising remediation techniques for in situ removal of CAHs via abiotic reductive dehalogenation based on pseudo-first order kinetics (Gillham and O'Hannesin, 1992, 1994; Mathenson and Traynek, 1994).

Initially granular ZVI particles were used to construct reactive barriers in the subsurface by digging and refilling a trench. During several years now, finer ZVI particles (micro and nano scale) are gaining more interest because of their higher reactivity and the fact that they can be injected in the subsurface as a slurry. They can be applied either to react directly with the contaminants sorbed on the soil particles or to build reactive barriers for dissolved contaminants degradation. This technology is promising, but injectability and transport of the particles in the subsurface are aspects that need further investigation to optimise the technology. When using micro scale zero-valent iron (MZVI) particles, sedimentation of the particles in the slurry reservoir, tubings and injection wells prior and during injection causes difficulties. To enhance the mobility and prevent sedimentation of MZVIs the use of stabilizing agents in natural aquifers is necessary. Stabilisers used by different research groups include different polymers like guar gum (Tiraferri et al., 2008), xanthan gum (Comba and Sethi, 2009; Vecchia et al., 2009), carboxymethyl cellulose (He et al., 2007), starch (He and Zhao, 2005). Some of the studied stabilizers are expensive and are not economical for large-scale applications. Guar gum is already used as a dispersing and stabilizing agent in different technological processes (pharmaceutical sector, oil, textile and food industry) (Kawamura, 2008). It has also been used in groundwater remediation to stabilize trenches during the installation of reactive barriers. In the field guar gum was used for installation of full-scale permeable reactive barrier (PRB) systems for TCE removal (EPA, 1999). Interestingly, EPA research showed that low temperature and high pH negatively affect guar gum degradation. Guar gum breakdown occurred and TCE reduction was observed after pH buffer and additional enzymes were injected in PRB.

Stabilizers have mainly been studied to improve technological and environmental performance of ZVI, mostly considering mobility and stability of ZVI particles. In this study guar gum was chosen as a green stabilising polymer and the impact of guar gum on the CAHs removal by micro scale zero-valent iron particles was evaluated via lab-scale batch

degradation experiments.

MATERIALS AND METHODS

Batch dechlorination tests

Simulated groundwater for batch tests consisted of MiliQ water containing 0,5 mM $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0,5 mM $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. After deoxygenating by flushing with nitrogen gas 0,5 mM NaHCO_3 and 0,5 mM KHCO_3 were added. In anaerobic conditions the pH was set at 7.0 and simulated groundwater was spiked with approximately 5 mg/l of PCE, 5 mg/l of TCE, 5 mg/l of cDCE and 5 mg/l of 111-TCA.

Batch tests were prepared in a 160 ml glass vials with butyl/PFTE grey septum containing 5 g of micro scale iron (Höganäs, Sweden), 0.2, 0.4 or 0.6 g guar gum (Apex Resources) and 100ml of anaerobic simulated groundwater, leaving a 60 ml headspace. Control conditions were set up following the same procedure but in the absence of ZVI particles and guar gum.

The experiments were set up under anaerobic conditions and in quadruplicate, and were incubated (shaking) at groundwater temperature (12 °C). Remaining concentrations of CAHs, ethane, ethane, acetylene were measured at the start (only blanc) and after 7, 14, 21, 35 and 42 days. Also formation of hydrogen was analysed.

After 42 days two batches from quadruplicate were sacrificed for adding enzymes (LEB-H, Rantec Corporation). Commercial enzyme LEB-H had been added and sampling was continued. After 70 days from the beginning of experiment dissolved sugars were flushed from bottles where enzymes were added simulating groundwater flow.

A summary of batch experiments is given in Table 1.

At each time point mass balances were made on molar basis (PCE + TCE + cDCE + VC + 111-TCA + 1,1 DCA + acetylene + ethane + ethane) to determine whether sorption occurred.

Table 1: Batch experiments set up

Treatment	Components		
	MZVI (g)	Guar gum (g)	Enzymes after 42 days (ml)
Blanc	-	-	-
Control	5.0	0.0	0.0
Condition 1	5.0	0.2	0.4
Condition 2	5.0	0.4	0.4
Condition 3	5.0	0.6	0.4

Chemical analyses

Concentrations of CAHs, ethane, ethane and acetylene were determined via headspace measurements using a Varian GC-FID (CP-3800) equipped with a Rt-U plot column for the detection of ethene, ethane and acetylene or a split-splitless injector followed by a Rt-X column (Restek) and a DB-1 column (J&W Scientific) for analysis of CAHs. Hydrogen production at each sampling point was analyzed using a GC-TCD (Interscience). At each sampling point the redox potential (ORP) and pH were measured using a redox/pH meter (Radiometer).

Viscosity test was done with Haake viscosity measurement device. The test was set up in 100 ml bottles with normal blue caps. The bottle contained 0.6 g of guar gum, 100 ml miliQ water with a final concentration of guar gum 6 g/l. 0.4 ml of enzyme was added in bottle and was continuously shaken at 12°C. After 2 hours viscosity was measured.

RESULTS

Batch dechlorination tests

Without guar gum, the MZVI degrades the CAHs efficiently as shown in figure 1. Results show that PCE, TCE, cDCE and 111-TCA were degraded 73 %, 97 %, 63 % and 100 % respectively by MZVI.

Figure 2 shows the evolution of ORP and pH in time. ORP values were decreased significantly from + 257 mV at the beginning to - 485 mV indicating reducing conditions. pH was increased from 6 to 9.

The corrosion rate of MZVI was 195,38 mmol/kg/days and has been calculated based on the measured hydrogen pro-

duction in batches.

The results of PCE, TCE, cDCE and 111-TCA degradation using MZVI stabilized with the lowest (2 g/l) and highest (6g/l) concentration of guar gum before and after adding 0,4 ml of LEB-H enzyme are given in figure 3.

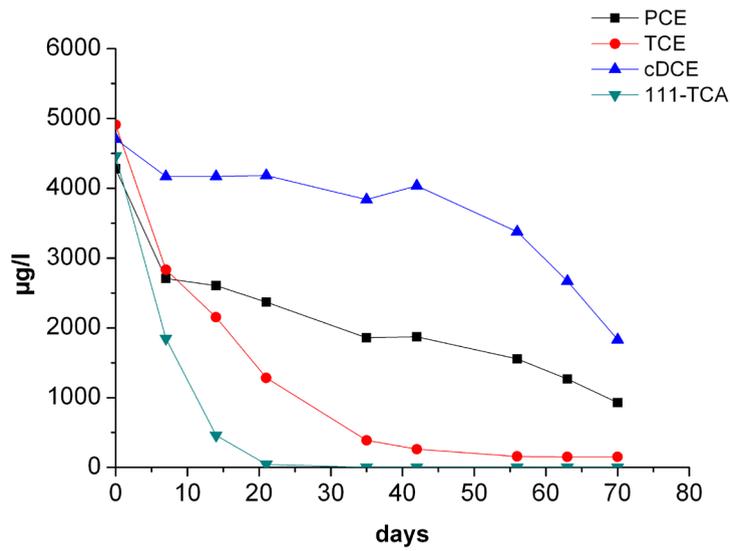


Figure 1. Evolution of the CAHs concentrations and breakdown products with time (days)

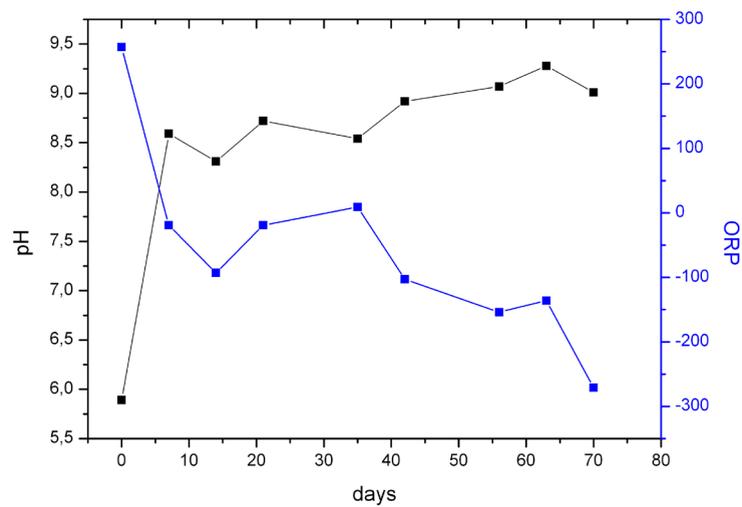


Figure 2: Change of pH and ORP values in time (days)

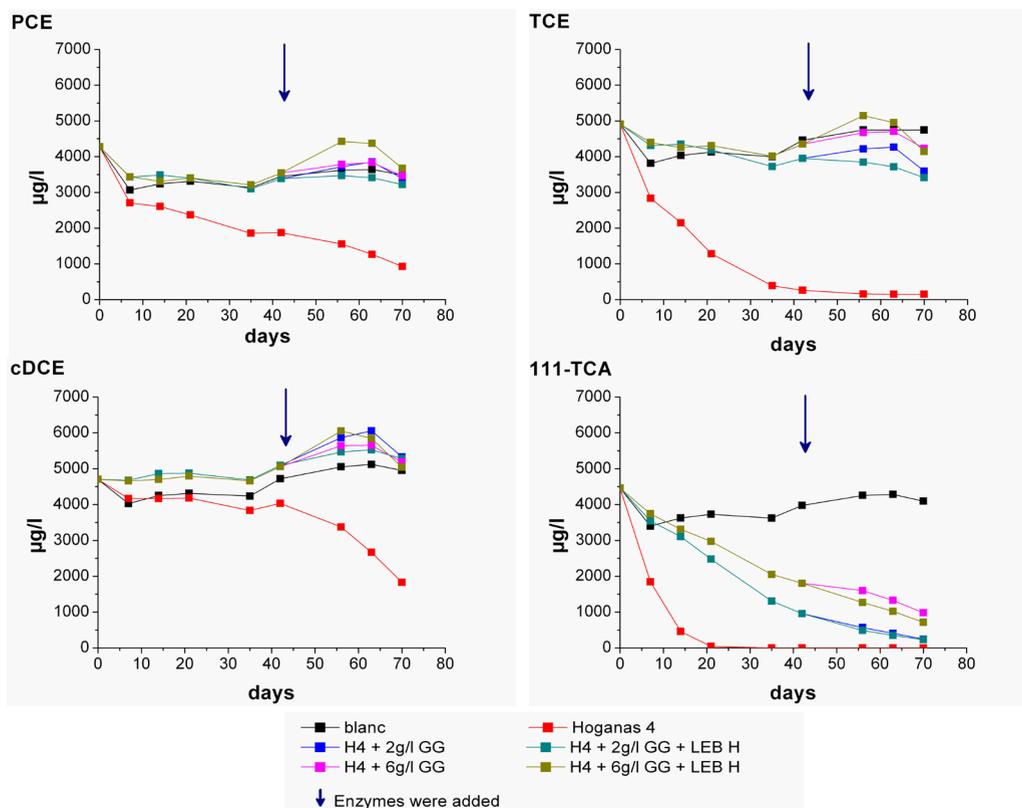


Figure 3: PCE, TCE, cDCE and 111-TCA reduction by stabilized MZVI

In comparison with the control (MZVI without guar gum), the presence of the guar gum had a significant negative influence on CAHs removal from simulated groundwater by MZVI particles. In the presence of all concentrations of guar gum PCE and cDCE degradation by MZVI did not occur. TCE degradation have been started slowly for the MZVI stabilized with the lowest concentration of guar gum. Results showed that MZVI in the presence of stabilizers is only effective in degrading 111-TCA, although also here a delayed degradation was observed. Mass balance results have not shown adsorption of 111-TCA on guar gum. The final degradation products were mainly 1,1 DCA, 1,2 DCA, ethane and ethane. Significant concentrations of VC have not been observed. DCA reacts further with ZVI to form ethane and chloroethane (Arnold and Roberts, 2000). CA concentrations were not found in batches. This could be explained if it assumed that the formed daughter product is a short-time intermediate or it would be hardly formed. Comparing with 6 g/l and 4 g/l of guar gum added for MZVI stabilization the lowest concentration of guar gum (2 g/l) has the less impact on MZVI reactivity towards this pollutant, than other two.

To improve reactivity of MZVI that was stabilised by guar gum, the same amount of enzymes were added in two of four batches after 42 days for guar gum degradation. The main assumption was that reactivity of MZVI towards CAHs mixture should increase after guar gum breakdown. As could be seen in figure 3, after adding enzymes, the reactivity of MZVI towards PCE and TCE remained limited. Towards cDCE stabilized MZVI still did not show any reactivity. With 111-TCA a limited improvement of the reactivity was observed after addition of the enzymes.

Figure 4 shows the relationship between apparent viscosity and shear rate for guar gum solution before and after adding LEB-H enzyme at 12 °C (average ground water temperature in Belgium). Degraded guar gum shows a typical non-Newtonian shear-thinning behaviour. The apparent viscosity decreased with the increase of shear rate. These data prove that LEB-H enzyme is able to degrade guar gum.

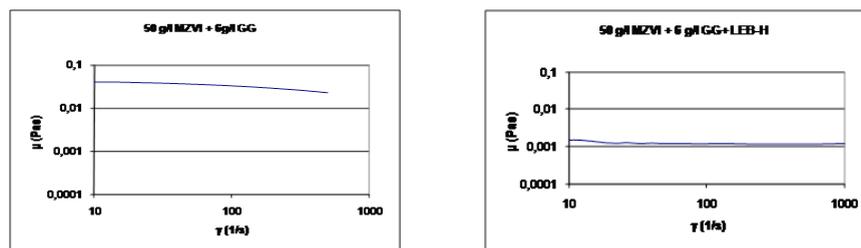


Figure 4: Apparent viscosity (μ) vs shear rate ($\dot{\gamma}$) for guar gum solution without and with LEB-H enzyme

In a next step, the sugar containing water was removed by replacing the liquid phase in the batches with new simulated groundwater. This mimics the flushing of the sugar containing water by the groundwater in situ. After this event, the reactivity was examined again (results not shown). It was found that the reactivity of MZVI stabilized with 2 g/l of GG increase somehow, after guar gum flushing, but not drastically. To explain influence of sugar flushing on iron reactivity experiment will be continued and corrosion rate of iron and half-life of contaminants will be calculated after several time points.

CONCLUSION

Presented lab-scale study demonstrated that MZVI could be used for in situ remediation of CAHs. Comparing to nano scale iron particles, micro scale iron particles are less reactive, but still cheaper, more available, easier to handle and with a longer life time. To improve mobility and prevent MZVI sedimentation use of stabilizers is necessary. The present study was designed to determine effect of guar gum on MZVI reactivity towards chlorinated aliphatic hydrocarbons in simulated ground water.

Main conclusions of this research are that reactivity of MZVI is negatively influenced by the presence of different concentrations of guar gum. For 111-TCA, degradation rate was reduced but good removal was still observed. For the other tested CAHs (PCE, TCE, cDCE) only a very slow or no degradation was observed, even with the lowest tested guar gum concentration. The addition of enzymes to degrade the guar gum and refreshment of the liquid phase only had a minor positive impact on the reactivity of the guar gum stabilised MZVI.

New experiments have been started with a different MZVI to verify the obtained results and to find a clear explanation. In addition, alternative stabilisers will be evaluated.

ACKNOWLEDGEMENTS

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REFERENCES

- Arnold, W. A., Roberts, A. L. 2000. Pathways and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. *Environ. Sci. Technol.*, 34(9):1794-1805.
- Comba S., Sethi, R. 2009. Stabilisation of highly concentrated suspensions of iron nanoparticles using shear-thinning gels of xanthan gum. *Wat. Res.*, 43(15):3717-3726.
- Gillham, R.W., O'Hannesin, S.F. 1992. Metal-catalysed abiotic degradation of halogenated organic compounds. IAH Conference Modern trends of Hydrogeology, Hamilton, 94-103.
- Gillham, R.W., O'Hannesin, S.F. 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water*, 32:958-971.
- Haest, P.J., Springael, D., Smolders, E. 2010. Dechlorination kinetics of TCE at toxic TCE concentrations: Assessment of different models. *Wat. Res.*, 44:331-339.
- He, F., Zhao, D., 2005. Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water. *Environ. Sci. Technol.*, 39:3314-3320.
- He, F., Zhao, D., Liu, J., Roberts, C.B. 2007. Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater. *Ind. Eng. Chem. Res.*, 46:29-34.
- Kawamura, Y., 2008. Guar gum – Chemical and technical assessment (CTA). 69th JECFA. 1-4.
- Matheson, I.J., Tratnyek, P.G. 1994. Reductive dehalogenation of chlorinated methanes by iron metal. *Environ. Sci. Technol.*, 28:2045-2053.
- Prommer, H., Aziz, L.H., Bolano, N., Taubals, H. Schuth, C. 2008. Modelling of geochemical and isotopic changes in a column experiment for degradation of TCE by zero-valent iron, *J. Contam. Hydrol.*, 97:13-26.
- Tiraferri, A., Chen, K.L., Sethi, R., Elimelech, M. 2008. Reduced aggregation and sedimentation of zero-valent iron nanoparticles in the presence of guar gum. *J. Colloid Interf. Sci.*, 324:71-79.
- Vecchia, E.D., Luna, M., Sethi, R. 2009. Transport in Porous Media of Highly Concentrated Iron Micro- and Nanoparticles in the Presence of Xanthan Gum. *Environ. Sci. Technol.*, 43(23):8942-8947.
- U.S. EPA. 1999. Field Applications of In Situ Remediation Technologies: Permeable Reactive Barriers. U.S. Environmental Protection Agency Office of Solid Waste and Emergency Response Technology Innovation Office Washington, DC. EPA 542-R-99-002:6-7.
- Zhang, W.-X. 2003. Nanoscale iron particles for environmental remediation: an overview. *J. Nanopart. Res.*, 5:323-332.

Session 2

The challenge of combining pollutant removal process - mixed pollution

ISMP of a Zn-contamination in combination with enhanced attenuation of VOCs by injection

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INTRODUCTION

NTP was contracted to perform groundwater remediation at a former cable and wire production plant in Venlo, The Netherlands to reduce off-site migration of heavy metals (mainly zinc) and chlorinated hydrocarbons (mainly tetra-chloroethene, PCE). The selected approach was based on in-situ chemical reduction and it included two elements:

- treatment of impacted groundwater migrating off-site along the north- east site boundary, the aim being to reduce the contaminants at the toe of plume to below the Intermediate Values (Dutch T-Values); and
- treatment of impacted groundwater in a localized contaminant source are to reduce contaminant mass loading that reaches the above boundary treatment zone.

The groundwater plume has spread over a distance of about 200 m from the source area. Zn-concentrations of more than 22 mg/l were measured, while a PCE-concentration was detected at a level of 280 µg/l. No significant concentrations of TCE, DCE or VC were measured at the site. Soil mainly composed of coarse sand and a relatively high groundwater velocity of about 120 m/year showed no natural attenuation of VOCs to take place at the site. In total a soil volume of about 75.000 m³ was contaminated at the site over a depth of about 6 to 12 m bg.

Figure 1 shows a top view and cross section of the groundwater contamination at the site, showing a rather narrow plume, caused by the high groundwater velocity.

speed, the required residence time and a safety factor 3. From this, a thickness of the reactive zone of 1.6 meters (= 120 m/year * 1.6 day * 1/365 * 3) was calculated.

REACTIVE ZONES

As indicated, two reactive zones had to be created: in the source zone and at the site boundary. Installing the reactive zone in the source zone directly affects the current spread of the highest heavy metal concentrations. The reactive zone at the site boundary removes further risks of off-site migration to the down gradient area. The reactive zone was designed over a breadth of 8 m were about 2.000 kg of EHC-M™ was injected from about 6 to 13 m bg. The reactive zone at the site boundary covered a total width of 40 m along the site, were about 10.000 kg of EHC-M™ was injected (about 125 kg/injection).

Figure 2 shows a top view of the reactive zones with the injections placed at the site.

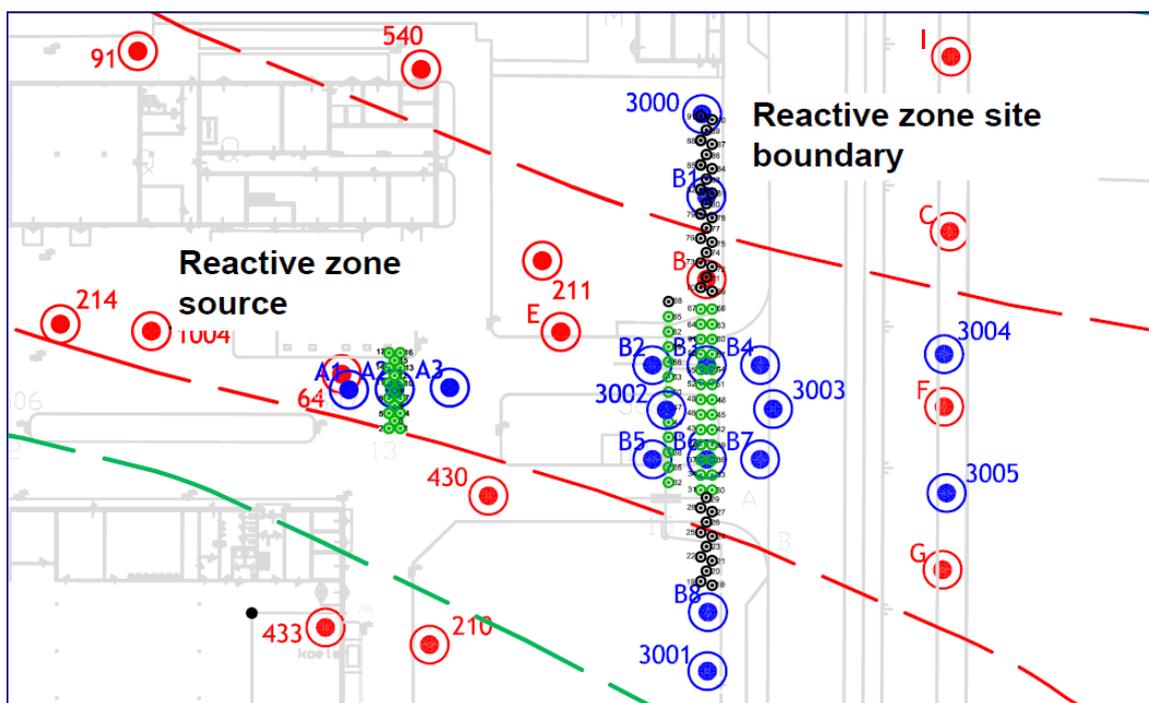


Figure 2: Reactive zones at the site

PERFORMANCE TWO YEARS AFTER INSTALLATION

Trends in the source and boundary reactive zone during the last two years have shown a significant decrease of the influent Zn and PCE concentrations to below clean-up goals (Zn and PCE; 433 and 20 µg/l). Monitoring data collected to date indicate that the implemented remedial approach provided the required plume control within a period of two years in all monitoring wells for Zn and PCE. Monitoring data collected for row B2-B3-B4 are shown in figure 3.

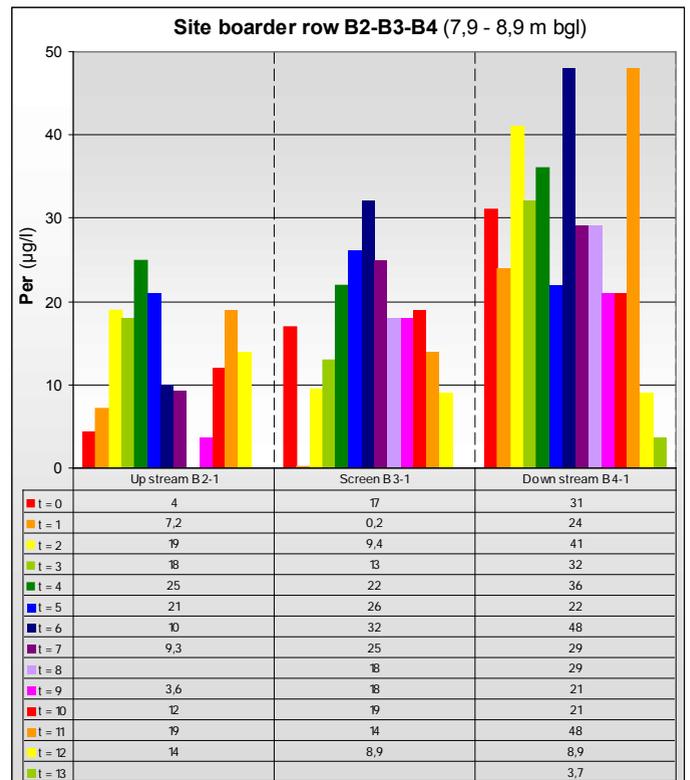
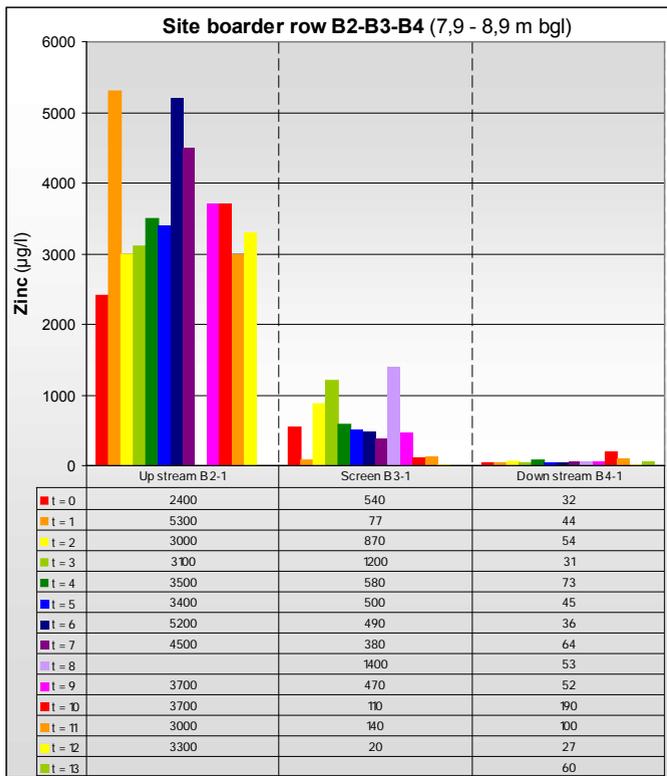


Figure 3: Concentrations in monitoring wells B2-B3-B4

After the remediation targets were met the site will now be monitored for another 5 years to show stability of the obtained concentration levels.

Design of a multibarrier for the treatment of landfill leachate contamination: laboratory column evaluation

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Due to an ongoing increase in waste generation and a limited waste incineration capacity, landfilling is worldwide still the most common way of solid waste disposal. Landfill leachates can lead to large groundwater contamination plumes, covering several to hundreds of hectares, if they are not properly collected and treated. Within the framework of the European Life project MULTIBARDEM, a laboratory-scale multifunctional permeable reactive barrier (multibarrier) was designed for the removal of ammonium (NH_4^+ : $313 \pm 51 \text{ mg N L}^{-1}$), adsorbable organic halogens (AOX: $0.71 \pm 0.25 \text{ mg Cl L}^{-1}$), chemical oxygen demand (COD: $389 \pm 36 \text{ mg L}^{-1}$), and toxicity from leachate originating from the 40-year-old Belgian landfill Hooze Maey.

The complexity of the contamination required a sequential setup combining different reactive materials and removal processes. All target contaminants could be removed to levels below the regulatory discharge limits. Ammonium was efficiently oxidized to NO_x^- in a first microbial nitrification compartment, which was equipped with diffusive oxygen emitters to ensure a sufficient oxygen supply. A downgradient clinoptilolite-filled buffer compartment, exhibiting a total ammonium removal capacity of $6.62 \text{ mg N (0.47 meq) per g}$ of clinoptilolite, was included to ensure a robust ammonium removal in case of temporary insufficient microbial activities. Both ammonium removal mechanisms were combined in a specific configuration that allowed microbially-mediated regeneration of ammonium-saturated clinoptilolite in the multibarrier system. A microbial denitrification compartment, fed with sodium butyrate as a carbon source, was used to remove NO_x^- formed in the first compartment. Maximum nitrification and denitrification rates at $12 \text{ }^\circ\text{C}$ indicated that hydraulic retention times of $\sim 62 \text{ h}$ and $\sim 32 \text{ h}$ were required in the columns to remove 400 mg N L^{-1} by nitrification and denitrification, respectively. Leachate toxicity decreased to background levels together with the removal of ammonium and its oxidation products. AOX and COD were efficiently removed by sorption in an additional compartment filled with granular activated carbon.

A pilot-scale configuration of the designed multibarrier concept, operating at the landfill Hooze Maey, is currently under evaluation.

Enhancing biotic and abiotic reductive dechlorination in ZVI-PRB combined with a slow releasing carbon source (PHB)

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Zero Valent Iron (ZVI) is the most commonly employed reactive medium to address chlorinated hydrocarbon contamination in PRB. ZVI abiotically transforms chlorinated hydrocarbons eventually into nonchlorinated harmless end products (e.g., ethene and ethane), via reductive dechlorination reactions. Unfortunately, some important chlorinated hydrocarbons are not degraded in the presence of ZVI, as it is the case for 1,2-dichloroethane (1,2-DCA). A promising approach is then to couple ZVI with a slow-release carbon source in order to stimulate the biological activity (either within the PRB or downgradient) capable of degrading those contaminants which commonly escape the ZVI-based barrier.

Along this line, the aim of the present research is to verify the feasibility of Poly-Hydroxy-Butyrate (PHB), an insoluble biological polymer, fully biodegradable under anaerobic condition, as a slow-release carbon source in ZVI barriers to sustain biological activity. Moreover, the effect of PHB, and its fermentation products (e.g. VFAs) on ZVI reactivity and longevity was also specifically investigated. Experiments were performed by laboratory columns, packed with mixtures of sand, granular commercial ZVI (Connelly GPM's Iron aggregate ETI CC-1004) and PHB in different combination fed with a solution, containing the ZVI reducible 1,1,2,2-TeCA and the ZVI recalcitrant 1,2-DCA at nearly 10 mg/L.

During the first phase of the experimentation the possibility to use PHB as carbon source in typical PRB conditions has been proved as it was rapidly fermented, without external inoculum. PHB fermentation products, acetic and butyric acid, were detected at high concentration (up to 2 g/l). Such high VFA concentration induced a significant increase in ZVI reactivity towards 1,1,2,2-TeCA and its by-products; moreover, a considerable increase in long time performance was also observed. Over the whole first phase 1,2-DCA dechlorination was not observed.

In the second phase an appropriate DCA-dechlorinating culture, has been inoculated both in the reactive ZVI zone and in a downgradient sand. Dechlorinating biological activity, was clearly observed along the different zones, strongly supporting the use of PHB as feasible slow release carbon source in the ZVI environment and the effectiveness of coupling the process with specialized DCA-dechlorinating culture.

Demonstration of the multibarrier technology for leachate containing water at the landfill Hooge Maey: 2 Pilot systems

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Two pilot-scale field demonstrations of the sequential multibarrier concepts were installed at the Hooge Maey landfill site in summer 2008 and summer 2009, respectively. In the landfill, the waste and leachate are well isolated from the environment without contaminating the groundwater. For demonstration purposes, leachate diluted with some groundwater is pumped from the landfill drainage system through the 2 multibarrier systems. The sequential multibarrier concept, based on laboratory-scale column experiments, combines microbial degradation (nitrification-denitrification) and sorption processes for the removal of adsorbable organic halogens (AOX) and chemical oxygen demand (COD).

The multibarrier concept in **pilot 1** consists of the following 5 sequential compartments which are installed vertically in a partly buried 9 m long steel container: (1) an aerobic nitrifying zone, (2) a sorption zone with clinoptilolite, (3) a second nitrifying zone, (4) a zone with granular activated carbon (GAC) for the removal of AOX and COD by sorption, and (5) an anoxic denitrifying zone. Compartment 2 and 3 were included as a buffer system to remove ammonium when biology would be temporarily less efficient. AOX and COD were efficiently removed by sorption in a compartment filled with granular activated carbon, till breakthrough. The nitrification compartments, equipped with diffusive oxygen emitters, converted ammonium microbially to nitrate and nitrite, which at their turn are converted to N₂ in a downgradient denitrification compartment, supplied with an external carbon source. Ammonium was removed up to 90% and more, but the process was less efficient during winter periods. During that time, remaining ammonium concentrations were largely removed by ion-exchange in a compartment filled with clinoptilolite, until saturation of the material occurred.

Pilot 2 was intended to be an improved, simplified and cheaper version of the first pilot, and consists of 3 horizontal sequential parts, being (1) sorption part to remove AOX & COD, (2) an aerobic biological nitrification part, and (3) anoxic denitrification part.

The latest monitoring results of both pilots will presented at the conference.

Session 3

Poster session

Wetlands with *Phragmites australis* degradation material as reactive zones applied to remediation of groundwater contaminated by nitrates

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Wetlands are examples of habitats that can be used directly to decrease nutrient loading from groundwater that discharges to surface waters through riparian zones and, thus, improve its quality. Nitrogen removal in a riparian area is commonly attributed to denitrification and plant uptake [1] [2]. Denitrification is a solution that is based on the growth of facultative microorganisms present in the site under anoxic conditions. Electrons needed for chemical reduction are originated from the oxidation of organic matter present in wetland soil which also acts as a source of cellular carbon.

The objective of the present study is to assess at laboratory scale the denitrification capacity of a wetland soil in which *Phragmites australis* reed species have been present during years. Soil containing this vegetal material was obtained from a wetland from Ebro river that is placed in the Sebes Natural Reservation of Flix, (Tarragona, Spain). The sampled zone is a 40 ha *Phragmites australis* field used for horse grazing and birdlife place.

Two batch experiments that used wetland soils collected at two depths (0-5 and 5-10 cm) were conducted at ambient temperature without stirring in closed bottles and without head space with water/soil ratios of 13 and 20 ml·g⁻¹ dry. Previous characterization of these two soil samples showed the capacity to leach 350 and 580 mg organic C·g⁻¹ dry soil in 24 h. The batches were spiked with 50 mg·L⁻¹ nitrate after 24 h from the beginning of the experiment.

An elimination of 99,4% nitrate was observed after 48 hours of experiment. Nitrite concentration increased as nitrate was removed, reaching a maximum concentration of 8,6 mg·L⁻¹, but it was finally eliminated below detection limits (0.01 mg·L⁻¹). These results showed a fast denitrification of waters with this kind of material, mainly due to organic matter release, presence of microorganisms and anoxic conditions.

From these results, a continuous system was built. The system consisted of a LDPE box (600 length x 400 width x 320 mm depth) filled with siliceous sand (0.25-0.3 mm diameter) and an input and output zone filled with marmolite (5-7 mm diameter). Input solution was pumped by using a peristaltic pump. The output consisted of a drainage made with 10 mm-diameter tube placed in the bottom of the output zone. The level of the output was fixed to control the depth of the solution in the setup. The input zone has a piezometer with a plastic tube where level could be measured. An hydraulic conductivity of 36.6 m/day was determined by varying the difference of levels between input and output and measuring the output flow rate. Experiments with tracers allowed obtaining the dispersivity and the flow velocity by using analytical advection and dispersion models to the obtained curves.

A continuous solution of nitrate in deionized waters (25 mg NO₃⁻·L⁻¹) was pumped to the system. Residence time of 32 h and pore velocity of 17.7 mm·h⁻¹ were calculated for this setup. After 168 h; 2 cm of the superficial sand was replaced with 280 g of wetland soil used in batch experiments. This material was showered twice a week in order to mimic rain episodes by using 615 ml of deionized water and output nitrate was monitored every 24 h.

Results showed that denitrification was less than 8 % and organic carbon below 2 mg C·L⁻¹. Comparison between batch and flow experiments seemed to point to lack of a continuous concentration of organic matter as electron donor, micro-organism acclimatization or the presence of aerobic conditions in the continuous setup. Future work will be addressed to incorporate *Phragmites australis* plant in order to assess its denitrification capability.

The present research work has been co-funded by the EU-project "AQUAREHAB (FP7 - Grant Agreement Nr. 226565)" and project PAIS (Ground Water Pollution from Agricultural and Industrial Sources: Contaminant Fate, Natural and Induced Attenuation, and Vulnerability) funded by Spanish Ministry of Science and Innovation (MCINN CGL 2008-06373-

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REFERENCES

- [1] Haycock, N. E., G. Pinay, et al. (1993). "Nitrogen-Retention in River Corridors - European Perspective." *Ambio* **22**(6): 340-346.
- [2] Mayer, P. M., S. K. Reynolds, et al. (2005). Riparian buffer width, vegetative cover, and nitrogen removal effectiveness: a review of current science and regulations, EPA/600/R-05/118, U.S. Environmental Protection Agency.

Verification of Transport of Zero-Valent Iron Colloids in Porous Media

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In order to remove contaminants from the groundwater, several methods are available. A relatively new and promising method is the injection of a zero valent iron colloid suspension in the subsurface using injection wells. The goal is to deposit the iron in the pores space and hence form an injected reactive zone. However, little is known about the transport behavior of zero valent iron colloids during the injection. A better understanding of the transport behavior is necessary to design a field application such that the reactive zone will be continuous in space and sufficiently wide. So far, the spreading and distribution of the iron colloids in the subsurface during injection could not be proven due to the lack of appropriate measuring techniques.

In the ongoing work, measuring devices with a very high sensitivity based upon magnetic susceptibility have been developed to non-destructively determine the concentration of nano-scale iron during and after the injection in columns and in a large-scale container experiment. In a field application the injection in a well would result in a radial flow field around the well. The large-scale container experiment was constructed to create such a 2-D radial flow field. The experiment was equipped with the newly developed measuring technique providing a quantitative measurement of breakthrough curves.

Several column and container experiments were conducted to determine the parameters controlling the mobility of iron colloids in the subsurface during injection. Within the ongoing EU research project SQUAREHAB the measuring technique is being improved and optimized to make detection and verification also possible in the field.

Development of rehabilitation technologies and approaches for multipressured degraded waters and the integration of their impact on river basin management.

Bastiaens L.¹ & AQUAERHAB consortium

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AQUAERHAB is an EU financed research project (FP7) that started May 1st 2009 with 19 project partners (VITO-Belgium, KULeuven-Belgium, GEUS-Denmark, HMGU-Germany, CTM-Spain, TUDelft-Netherlands, Sapion-Belgium, ISO-DETECT-Germany, USTUTT-Germany, Wageningen univ.-Netherlands, Ben Gurion Univ-Israel; Masarykova univ. -Czech Republic, UNESCO-IHE-Netherlands, Univ. Sheffield-UK, POLITO-Italy, Hoganas-Sweden, Univ. Copenhagen-Denmark, INERIS-France, Environmental Institute – Slovak Republic).

The overall quality status of fresh water resources is determined by (1) the kind and quantity of contaminants that are released in the water system and (2) the migration of the pollutants (via groundwater and run-off) towards different rivers, lakes, and seas. The migration of pollutants towards vulnerable receptors (drinkingwater reserves in the subsurface, surface waters, water wells) is of particular concern. Within the AQUAERHAB project, different innovative rehabilitation technologies for soil, groundwater and surface water will be developed to cope with a number of priority contaminants (nitrates, pesticides, chlorinated compounds, aromatic compounds, mixed pollutions...) within heavily degraded water systems. Methods will be developed to determine the (long-term) impact of the innovative rehabilitation technologies on the reduction of the influx of these priority pollutants towards the receptor. A connection between the innovative technologies and river basin management will be worked out. In a first stage of the project, the technologies and integration of their impact in river basin management will be developed in three different river basins (Denmark, Israel, Belgium). In a second stage, the generic approaches will be extrapolated to one or two more river basins.

One of the outcomes of the project will be a generic river basin management tool that integrates multiple measures with ecological and economic impact assessments of the whole water system. The project will aid in underpinning river basin management plans being developed in EU Member States, and will demonstrate cost effective technologies that can provide technical options for national and local water managers, planners and other stakeholders (drinking water companies, industry, agriculture, recreation and nature conservation) to revive highly polluted areas.

Effect of carbon sources on CAH degradation kinetics in the aquifer of the Zenne site

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Chlorinated Aliphatic Hydrocarbons (CAHs) are significant groundwater contaminants due to their widespread use as solvents. The possibility of lowering the cost of remediating chloroethene contaminated soils by stimulating anaerobic dechlorination activity has made it an attractive option. The aim of this study is to investigate stimulation of CAH degradation potential by aquifer microbial community using different carbon sources in batch cultures. In this study, aquifer materials and ground water samples were taken at three different locations from a CAH polluted Zenne site in Vilvoorde-Machelen, Belgium. CAH degradation was studied under both natural attenuation and stimulated conditions. Stimulated conditions were obtained by the addition of lactate or molasses as carbon sources. Next to this, sediments and also two different types of sediment extracts (obtained after sedimentation or centrifugation of the extracts) were added to the flasks. By adding different types of sediments, dissolved organic carbon and/or CAH-degrading-bacteria are added to the flasks. No degradation was observed in un-amended controls and reductive dechlorination of VC, DCE and TCE was only observed in the tests amended with the different electron donors. Different degradation profiles were obtained for the different locations but overall, sediment and lactate amended microcosms had the highest degradation potential. Sequential degradation models employing first-order rate constant and Monod kinetics were also used to simulate the degradation processes under the experimental conditions. This will enable to quantify the effect of carbon sources on CAH degradation potential.

Full scale horizontal ZVI PRB in combination with enhanced anaerobic bioremediation

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Previous activities at a razor blades and cutleries plant situated in Apeldoorn, the Netherlands resulted in severe soil and groundwater contamination by metals and chlorinated solvents (VOCs). The groundwater VOC plume had migrated underneath adjacent private properties over a distance of about 200 m from the source area. A large fraction of VOCs that had infiltrated to the groundwater was absorbed into a peat layer.

Highly contaminated unsaturated soil and shallow aquifer material in three areas were remediated by excavation and backfilling using a mixture of zero valent iron (5 % vol.) and sand (Figure 1). In total, about 7.000 m³ of soil material was removed. Next to the excavated areas, three rows of infiltration wells were installed perpendicular to the groundwater flow direction (Figure 1) to treat a soil volume of about 35.000 m³ to a depth of about 15 m bg. Even though dewatering was used during those activities, concentrations of up to 19 mg/l DCE were measured in those wells after completion of this remedial stage.

In-situ chemical reduction (ISCR) of cVOCs was used for remediation of the residual VOC plume by continuous recirculation of groundwater through the ZVI-backfilled zones and enhanced bioremediation. Periodic injections of EHC-A (Adventus), composed of a ferrous iron and soluble organic carbon compounds, was used to stimulate indigenous dechlorinating microorganisms. Two years after the in-situ remediation began, all VOC concentrations measured were below clean-up goals and the remediation activities were stopped in September 2009. Based on the observed success of this remedial approach, the site is now being prepared for redevelopment to take place.

Use of different zero-valent iron particles for CAHs degradation

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Last decades remediation of groundwater polluted with chlorinated aliphatic hydrocarbons (CAHs) has been studied intensively. A promising remediation technique for in-situ removal of CAHs is reductive dehalogenation by zero-valent iron (ZVI) particles.

The general aim of our study is to find injectable Fe-based particles with good reactivity and transportability properties for innovative in-situ remediation technology. This paper focuses on the reactivity aspect.

This lab-scale study presents the reactivity of different ZVI particles with respect to CAHs for in-situ remediation applications. Batch experiments were carried out to study degradation rates of CAHs from simulated groundwater. Twenty-three different commercially available and new fine Fe-based materials were tested for their degradation potential towards different chlorinated compounds: perchlorethylene (PCE), trichloroethylene (TCE), cis-dichloroethylene (cDCE) and 1,1,1 trichloroethane (111-TCA). Tests were comprised nanoscale zero-valent irons (nZVI), microscale zero-valent irons and fine iron-sulfides supplied by different suppliers. FeS were produced at VITO using sulfate reducing bacteria cultures. Granular ZVI was included in the tests as a reference material. Degradation intermediates cDCE, VC, 1,1 DCA were also analyzed. Corrosion rates of tested irons have been calculated by hydrogen production in batches. Dechlorination rates of tested irons were also calculated using the pseudo-first order rate equation.

After 15 weeks of experiment the results have shown that 8 ZVI particles are capable for PCE, TCE, cDCE and 111-TCA removal of > 85%. The fastest reduction rates were by nZVI. 3 micro scale irons were showed sorption tendency. Iron sulfides have had possibility for slow degradation of PCE and 111-TCA. Only one iron was capable for degradation of daughter product 1,1 DCA. 1,1 DCA represents pollutant and its degradation is important for further experiments.

On the basis of the batch studies results promising reactive materials were recommended for a more detailed characterization and evaluation for in-situ remediation applications.

This study is co-funded by European Union project SQUAREHAB (FP7 - Grant Agreement Nr. 226565)

Abstract Submission for the PRB-RZ Symposium: Application of In-Situ Precipitation to Remediate Heavy Metals Contamination in Groundwater

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Groundwater contamination with trace metals is a recurring major problem for mining and metallurgical sector worldwide, threatening drinking-water reserves, ecosystems and adversely affecting people's health. The treatment of strongly polluted contaminant plumes requires time-demanding and financial efforts in order to limit the size of the affected regions. Traditional approaches, such as pump&treat, are moreover not sustainable since large amounts of toxic waste sludge are produced. A promising new alternative has been found in the in situ bioprecipitation (ISBP) process. It is induced chemically by adding suitable agents, or bacterially by simulating the activity of certain micro-organisms that reduce sulphate to sulphide when provided with a suitable electron donor.

Although the ISBP process has been proven by laboratory tests and "widely" used in passive treatment of acid mine drainage water, the implementation of this technology to remediate in-situ groundwater is still pending. An extensive pilot program funded by the EU Life program was executed to design an in-situ remediation system (metals precipitation) for historic groundwater contamination with heavy metals underneath three non-ferrous industrial sites.

Based upon batch and column tests, glycerol was proven to be the most suitable chemical agent for the ISBP process. Its critical concentration (minimal concentration at which the ISBP process starts) and reaction time were evaluated as well. Tracers tests, data acquisition and groundwater & hydrochemical models were performed to simulate, monitor and optimize the injection design.

Based on the site characterization, modelling and lab tests, a field test was designed by installing a grid of injection wells surrounded by monitoring wells. Continuous injections were performed and resulted in a distinct decrease of Cd and Zn concentrations in the monitoring wells as well as lowered sulfate concentrations. Analyses were performed to control the effectiveness of the metal precipitation and growth of bacteria.

It is anticipated that the ISBP process is active and responsible for metal decrease when the following process occurs:

- metal concentrations decrease,
- sulphate concentration decrease,
- ORP (oxidation-reduction potential) decreases, and
- TOC increases (as glycerol is a carbon source, the TOC values can be used as indicator of the dispersion of the glycerol).

In general, in situ bioprecipitation has been successfully demonstrated by this field test resulting in the removal of metals from the groundwater. However, to ensure a sustainable process, the stability of the formed precipitates is currently under study. This research project could present an economical and sustainable technique to reduce footprint and to remediate metal contaminated aquifer from mining & metal operation sectors.

Four Years Performance of the first continuous iron PRB in KATWIJK, The Netherlands

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Chlorinated hydrocarbon contamination is present in the shallow groundwater at a former drum cleaner site in Katwijk, the Netherlands, located north of The Hague. The groundwater contamination plume had migrated within about 100 m from a public garden located down gradient. Based on a remedial options review, a zero valent iron (ZVI) PRB was identified as the best method of controlling plume migration and protecting the down gradient receptors.

On July 10, 2006, the PRB was constructed at the site by NTP Milieu with supervision by ETI (Canada, Adventus Group) and Grontmij. A continuous trenching machine excavated a trench over a length of 180 meters and to a depth of 5.5 meters bgs. This construction method allowed for simultaneous excavation and backfill using a mixture of 20% granular ZVI (0.3-2 mm diameter) and 80% sand. The ZVI material was manufactured by Gotthart Maier (Germany). To provide an additional treatment capacity, 40% ZVI was used in the centre of the plume over a length of 30 meters. Wing sections of 30 meters in length and composed of HDPE plastic were installed on both sides of the PRB to reduce the amount of ZVI. The average residence time within the PRB is estimated at about 67 hours. The monitoring results during the last four years have shown a significant decrease of cis 1,2-dichloroethene and vinyl chloride down gradient of the PRB. Detailed performance monitoring data will be presented at the conference.

Clinoptilolite as Microbial Mediated Regenerable Reactive Material for Remove Ammonium from Landfill Leachate in a Multibarrier

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This study focuses on multifunctional permeable reactive barrier (multibarrier) technology, combining microbial degradation and abiotic ion exchange processes for removal of ammonium from landfill leachate contamination. The sequential multibarrier concept relies on the use of a clinoptilolite-filled buffer compartment to ensure a robust ammonium removal in case of temporary insufficient microbial activities. An innovative strategy was developed to allow in-situ clinoptilolite regeneration. Laboratory-scale clinoptilolite-filled columns were first saturated with ammonium, using real landfill leachate as well as synthetic leachates as feed media. Other inorganic metal cations, typically present in landfill leachate, had a detrimental influence on the ammonium removal capacity by competing for clinoptilolite exchange sites. On the other hand, the metals had a highly favorable impact on regeneration of the saturated material. Feeding the columns with leachate deprived from ammonium (e.g. by microbial nitrification in an upgradient compartment), resulted in a complete release of the previously sorbed ammonium from the clinoptilolite, due to exchange with metal cations present in the leachate. The released ammonium is then available for microbial consumption in a downgradient compartment. The regeneration process resulted in a slightly increased ammonium exchange capacity afterwards. The described strategy throws a new light on sustainable use of sorption materials for in-situ groundwater remediation, by avoiding the need for material removal and the use of external chemical regenerants.

This work was co-funded by the EU Life project MULTIBARDEM (LIFE06 ENV/B/000359) and has recently been accepted as a paper in ES&T.

Nanozox™, an innovative application of ozone in water treatment

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Ozone is a powerful and widely used chemical for disinfection and oxidation purposes. In drinking water and wastewater processing, ozone has been classically employed as a dissolved molecular form. Verhoeve Groep, however, has recently developed an innovative ozone-based water treatment application, called Nanozox™. This technology is based on the generation of nano-scale and micro-scale gaseous ozone bubbles surrounded by hydrogen peroxide in the water to be treated. The combination of both powerful oxidants in the form of tiny gas bubbles results in a slow bubble rise velocity, an increased reactive surface area, and thus a strongly increased reactivity.

Nanozox™ is an effective method to treat a broad range of organics, including chlorinated solvents, petroleum hydrocarbons, oxygenates (MTBE), 1,4-dioxane, PAHs, cyanide and thiocyanate, pharmaceuticals, and endocrine disruption compounds. In addition, it has an excellent bactericidal action. Different applications have been successfully demonstrated on both a pilot-scale and full-scale level, including colour removal from regenerant solutions and removal of pharmaceutical compounds in hospital wastewater. In a Dutch zoo, the technology is used to disinfect seal basin water at a flow rate of 250 m³ per hour, to avoid algal growth. In addition to wastewater treatment applications, Nanozox™ can also be used to treat contaminated groundwater in pump-and-treat applications. In this context, a full-scale system was applied at a former MGP plant to remove a cocktail of BTEX, PAHs and SCN from the contaminated groundwater. Results of different applications will be presented.

Design of a multifunctional permeable reactive barriers (Multibarrier) for treatment of a VOCl, BTEX & MTBE contamination plume

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Mixed contamination plumes are more difficult to treat than single compounds, as a combination of remediation techniques is mostly required. The present study focuses on the feasibility of a multifunctional permeable reactive barriers, called multibarriers, to cope with these mixed pollutants. Multibarriers can be defined as a combination of permeable reactive barriers and zones in which different pollutant processes are active. The specific multibarrier configuration is function of the pollutant mixture. Earlier, we showed that multibarriers were feasible to remediate an artificial mixture of BTEX, chlorinated ethenes and heavy metals (Dries, 2004). Here we report the design of a multibarrier-concept for a real site.

At a Belgian industrial site the groundwater is polluted with chlorinated compounds (VOCl_s), benzene, toluene, ethylbenzene and xylenes (BTEX), methyl-tert alcohol (TBA) and Methyl Tert-Butyl Ether (MTBE). A lab scale feasibility test was performed to evaluate whether a sequential combination of a permeable reactive barrier (PRB) and a reactive zone (RZ) is suitable to reduce all the present pollutions below the regulatory limits. The PRB consists of zerovalent iron (ZVI) and is able to degrade the chlorinated compounds via reductive dehalogenation. In the reactive zone aerobic biodegradation of BTEX-compounds and MTBE is stimulated. The lab scale column test was set up with representative groundwater and aquifer material from the site. All chlorinated compounds were rapidly dehalogenated to ethene and ethane in the ZVI-part, while a breakthrough of BTEX-compounds was observed after a 'sorption' phase. On the other hand, as predicted by its high water solubility and low sorption tendency, MTBE very rapidly moved through the ZVI-barrier without any decrease in concentration. The effluent of the ZVI-columns was pumped in two parallel aquifer-containing columns (biotic and abiotic one), simulating the aerobic reactive zone. While passing through the aquifer columns, the BTEX-concentration decreased, explicable by sorption and aerobic biodegradation. The TBA and MTBE-concentration could be reduced only after addition of an MTBE/TBA-degrading inoculum.

Part of the project was performed in collaboration with DEC and Sertius.

Impact of microbiology on performance of Zero Valent Iron based Permeable Reactive Barriers and Reactive Zones: A comparative study

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Use of ZVI in PRBs (Permeable Reactive Barriers) and RZs (Reactive Zones) have been increased in recent years. Both technologies can successfully deal with wide range of contaminants in groundwater over having their own benefits and also practical constrains. The long term performance and life of PRBs and RZ is still a research interest. Although lot of studies confirm the development and impact of microbial communities in PRB itself but less studies have been done on bio(geo)-chemical changes in downstream sediment, which is very likely to be affected due to sudden change in equilibrium. In this work we studied the performance and efficiency of both technologies in laboratory column experiments using 1- granular-ZVI (PRB) and 2- micro-ZVI (RZ). Four flow through glass columns were setup, comprising biotic and abiotic conditions at controlled flow and temperature conditions. Simulated groundwater containing sulfate, metals (Zn, Ni, Cd, and Fe) and metalloids (arsenic) was used in continuous upflow mode. Regular analysis of pH, redox, metals, arsenic and sulfate was followed in the different reactive zones within the column. Samples were also taken for microbial community identification. More specifically, the goal of this study is (1) to understand the impact of ZVI on biotic metal removal in continuous systems and (2) to understand the impact of PRB's and RZ on the downstream sediment, which is directly affected due to changes in pH and redox state. Also the treated water coming out of PRB/RZ has very less or negligible contaminant levels, which can possibly results into leaching of contaminants from downstream sediments into the groundwater again. The production of gas mainly H₂ also can affect geochemical activities and can also be beneficial in accelerating microbial mediated redox processes (sulfate reduction, Iron reduction). This is also likely to start in downstream sediment as the availability of H₂ and also natural organic matter in soil. Furthermore, stable isotope fractionation has recently emerged as a critical tool in monitoring insitu activities, especially in characterizing biotic and abiotic processes. Preference of using lighter element by microbial cells marks a significant change in isotope ratio, which can be easily monitored following isotopic compositions of S and O of sulfate and Fe isotopes. This technique is very useful in case of ZVI systems as physiochemical and biological activities occur simultaneously and hard to differentiate in underground systems. Latest results from columns will be discussed in presentation.

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Emulsified metallic nano- and micro-iron particles for in-situ Remediation of Chlorinated Ethenes in Groundwater

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Nano-size metallic iron particles (ZVI) can be injected in the groundwater to achieve in-situ reductive dechlorination of chlorinated solvents (CAH). It has been found that they tend to aggregate and they may not only react with target pollutants, but also with other reducible matter in the soil. Attempts have been made to enhance the specificity and effectiveness of nano-iron particles by suspending them in emulsified vegetable oil (EZVI). CAH present as NAPL in source areas may be taken up in iron containing vegetable oil micelles, allowing for a more targeted reaction of ZVI with the pollutants.

In this work we have evaluated various forms of emulsified reactive metal particles for in-situ reductive dehalogenation. The metal particles included nano-size ZVI as well as two types of micro-scale ZVI and one type of microscale iron sulphide (FeS). The latter may be used as an alternative for ZVI.

In a first stage we have evaluated different recipes for emulsifying the reactive metal particles. For this we tested two types of vegetable oil, two types of non-ionic surfactant and water in varying ratio's. It was found that with some of them (including a published recipe) the emulsions did not incorporate the metal particles inside the oil micelles, while we did achieve incorporation with one new recipe. The stability of the emulsions varied for different recipes.

We have investigated the reactivity of the different combinations of metal particles, vegetable oil and surfactants by batch experiments for reductive dechlorination of TCE. Emulsified metal particles were less reactive than their non-emulsified counterparts. Nano-scale EZVI was more reactive than microscale EZVI. Nevertheless, significant degradation of TCE could still be achieved by some of the emulsified particles of nano-ZVI and micro-FeS. Emulsified metal particles for which the particles were not incorporated in micelles showed higher activity than their counterparts which were successfully incorporated.

Column tests were done to investigate the mobility in soil and effectiveness for reductive dechlorination of the best recipe of emulsified nano-iron. They included one control column with emulsified oil only and two columns with EnZVI, as well as two columns with straight nZVI and its control with water only elution. Emulsified nZVI exhibited a much improved mobility compared to the straight nZVI. Straight nZVI resulted in faster degradation of CAH, but the EnZVI also achieved enhanced removal of TCE when compared to the control with only emulsified oil.

This study was part of the FP7 UPSOIL project (GA 226956).

Multibarrier Comprising Abiotic and Biotic Removal Processes to Remediate Chlorinated Ethenes in Groundwater

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The multibarrier technology is an innovative in-situ technology to improve the quality of groundwater. It consists of a combination of permeable reactive barriers (PRBs) and reactive zones (RZ), in which different pollutant removal processes are combined. A research topic within the FP7 project SQUAREHAB (GA 226565) is a multibarrier consisting of 2 compartments to eliminate chlorinated aliphatic compounds (CAHs), being (1) a zerovalent iron barrier and (2) a biological reactive zone stimulated with injection of electron donor.

Earlier the multibarrier concept was found suitable for an industrial site in Belgium. For the ZVI-part, lab scale feasibility tests led to design parameters, which were used for the implementation of the full scale ZVI wall (200 m long) at the site.

Currently, based on lab scale experiments, focus is on determining corrosion rates of the zerovalent iron for the ZVI-part and CAH-degradation rates for the bioreactive zone. In the zone downgradient from the ZVI, aquifer samples and groundwater samples were taken at 4 different distances from the ZVI-barrier. For each of the locations batch degradation experiments were set-up to evaluate the distribution of the VOCL-biodegradation capacity. New approaches to determine degradation rates with innovative molecular and analytical methods are being evaluated. The gathered data are required input for a model, which allows to evaluate the impact of the multibarrier technology on the water quality in time and in space. The aim of the model is to realise a more accurate design of PRBs and RZ, including information on the longevity of the technology. The general guidelines that will be produced for an optimal multibarrier design, will be applied to other multibarrier systems later on in the SQUAREHAB project.

Every 3 to 4 months, a monitoring campaign of the groundwater in and near the multibarrier is taking place, which will allow to extrapolate results from the lab into the field and calibrate numerical models.

Session 4

Progress in basic research

Transport of highly concentrated slurries of iron colloids for groundwater remediation: experimental and modeling

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ABSTRACT

Colloidal suspensions of engineered nanoparticles have been studied in recent years for waste water and in-situ groundwater remediation. In particular, injectable Fe-based materials (nano- and micro-sized zero-valent iron particles, NZVI and MZVI) are an improvement on commonly used granular iron: they can be suspended in a slurry and directly injected into the source of contamination, overcoming most of the limitations of zerovalent iron permeable reactive barriers (PRBs). Moreover, colloidal particles show increased reactivity, thanks to their high specific surface area. To improve colloidal stability and transportability of MZVI and NZVI, the use of highly viscous shear-thinning carrier fluids have been suggested, and proved to be effective.

This work, co-funded by European Union project SQUAREHAB (FP7 - Grant Agreement Nr. 226565), presents experimental and modeling results for the transport of highly concentrated (up to 20 g/l) non-Newtonian (namely, shear-thinning) slurries of MZVI and NZVI in sand packed columns. Assessing the mobility of iron-based colloids is a key issue for field applications of these materials. A transport model is required to provide a reliable estimation of the radius of influence for the injection points, for a correct dimensioning of full scale remediations and to predict short- and long-term mobility of the iron particles injected in the subsurface. If compared to transport models developed for natural colloids and synthetic model particles (namely latex spheres), the model here presented incorporates more complex phenomena. Rheological properties of the shear-thinning carrier fluid, hydrodynamic parameters of the porous medium (porosity, permeability), and colloid concentrations (both suspended and deposited) are strongly inter-dependent, thus resulting in a complex set of coupled partial differential equations and constitutive relationships.

The model results highlight that deposition of relevant amounts of iron particles onto the soil grains significantly reduce porosity and permeability, thus resulting in clogging phenomena, especially for nanoscale particles. Moreover, mechanical filtration is shown to play a role under certain hydrochemical conditions, thus influencing the particle transport.

INTRODUCTION AND BACKGROUND

Colloidal suspensions of engineered nanoparticles have been studied in recent years for waste water and in-situ groundwater remediation (Tiraferri, Sethi 2009, Zhang 2003). Injectable Fe-based materials (nano- and micro-sized zero-valent iron particles, named NZVI and MZVI) are an improvement on commonly used granular iron: they can be suspended in a slurry and injected directly into the source of contamination, overcoming most of the limitations of zerovalent iron permeable reactive barriers (PRBs) (Di Molfetta, Sethi 2006). **Moreover, they are characterized by specific surface areas up to a hundred times bigger, that dramatically increase reactivity if compared to millimetric iron.** Although iron colloids are very promising, a number of aspects are still burning topics of research, and the technique is not fully developed. Nevertheless, a quite broad range of field applications have been performed to date, exploring different delivery technologies, particle size, stabilizing agents, etc. (Comba et al. 2010b).

Because iron colloids are used suspended in slurries, one key issue for their field application is assessing the particle pathways of migration in the subsurface. Particle mobility is highly desired during injection and in the early stages of migration, to guarantee an acceptable spacing between injection points, and to ensure a uniform distribution of the iron slurry in the contaminated area. In the literature a number of studies concerning the scarce stability of NZVI aqueous suspensions is available (Saleh et al. 2008, Tiraferri, Sethi 2009). NZVI transport is mainly influenced (and limited) by particle-particle magnetic (attractive) interactions (Dalla Vecchia et al. 2009a), that lead to the formation of large aggregates, which are then filtered in the porous media. Moreover, magnetic attraction also influence the deposition onto the solid matrix, as deposited particles attract the suspended ones leading to ripening phenomena. Conversely, MZVI transport, although hardly affected by magnetic interactions, is mainly influenced by gravitational settling and straining of primary particles, due to their larger size. As a result, in transport tests unmodified NZVI and MZVI are almost completely retained within short distances from the inlet, leading to a progressive clogging of the porous medium (Schrick et al. 2004). To act against the strong particle-particle attraction of NZVI, stabilizing additives, that form a soft "shell" around the particles, have been studied, that are usually dosed in low concentrations during the synthesis

process, or after breakage of the aggregates before injection in the porous medium (Phenrat et al. 2008, Tiraferri, Sethi 2009). They mainly act via modification of particle surface properties, to increase repulsion forces between particles. However, if this approach can be successful when applied to nanosized particles, it fails when dealing with microsized iron, that exhibit a strongly limited mobility due to gravitational sedimentation. As an alternative, the viscosity of the dispersant fluid can be modified. (Dalla Vecchia et al. 2009b).

A xanthan gum solution is used in this study as a dispersant for NZVI and MZVI, for increasing stability of the dispersion. Xanthan solutions exhibit a shear-thinning behavior, i.e. viscosity is high at zero shear rate, and decreases with increasing shear rate till to the value of pure water. Consequently, xanthan can enhance stability of the iron dispersion when the product is stored (high viscosity prevents gravitational settling and aggregation of the particles) without hindering the injection. After the injection, when xanthan is progressively eluted, the brush layer of polymer molecules remains adsorbed on the particle surface, providing further steric stabilization.

The influence of the ionic strength is also explored, by comparing column tests performed using deionized water, and water with ionic strength adjusted to 12.5 mM. Ionic strength was found to have an impact on particle adhesion to and release from the porous medium, that can be explained with a modified DLVO theory. A novel modelling approach for the simulation of the transport of NZVI and MZVI shear-thinning (non-Newtonian) suspensions is finally proposed, and applied for the interpretation of the experimental results. The model further extend to non-Newtonian, highly concentrated colloidal suspensions the MNM1D model, previously developed for colloid transport simulation under transients in ionic strength (Tosco, Sethi 2009).

MATERIALS AND METHODS

Column tests

Detailed description of materials for the column tests here discussed was provided in a previous work (Dalla Vecchia et al. 2009b). Thus, only the most relevant data and experimental findings are summarized here. Commercial powders of MZVI (BASF-HQ, Germany) and aqueous suspensions of NZVI (RNIP-10DS from Toda Kogyo Corp., Japan) were used for column transport experiments. Iron particles at a concentration of 20 g/l were dispersed in xanthan solution (3g/l, Jungbunzlauer, Switzerland) in DI water, or in xanthan solution in water with adjusted ionic strength (12.5 mM), and injected in columns previously wet-packed with thoroughly cleaned silica sand (Sibelco, Italy) to a length of 0.46 m. Inlet and outlet concentrations were monitored measuring the magnetic susceptibility of the suspensions, which is directly proportional to iron concentration (Dalla Vecchia et al. 2009b). The pressure drop at the column ends was continuously monitored. Injection of iron + xanthan slurries (7 pore volumes) was followed by a flushing with pure water at the same ionic strength of the viscous slurry (DI or 12.5 mM). In the labelling of the tests (Figure 2) M indicates microiron, N nanoiron. 26 and 7 refer to the duration of the injection (7 or 26 pore volumes). X indicates that xanthan gum is used as a dispersant. IS indicates that the ionic strength of the solution was modified.

Modeling approach

Colloid transport is here modelled with a modified advection-dispersion equation. The influence of colloid transport on porosity, permeability, and fluid viscosity is explicitly embedded into the model through correlations from the literature, or here derived on purpose. Coupling of flow and transport is solved under the hypothesis that clogging of the porous medium is not a repeat process, thus handling the problem as a quasi-stationary phenomenon. In particular, the following aspects are included into the model (Tosco, Sethi 2010):

- Colloid transport equation. It was modelled with a dual-site (physico-chemical interactions plus straining) advection-dispersion-deposition equation.
- Darcy's law for Newtonian and non-Newtonian fluids. The "usual" form of Darcy's law is applied also for the case of non-Newtonian fluid, provided that the true pore fluid viscosity is replaced by the so-called "porous medium viscosity", that includes all non-Newtonian effects, and depends on both porous medium and fluid properties.
- State equations and hydrodynamic parameters. The following parameters were considered functions of the concentration of deposited or suspended particles, and/or of xanthan concentration:
 - Density of the pore fluid. It depends on the density of the carrier fluid (water or polymer solution), and on the density and concentration of suspended iron particles. Increasing particle concentration, the density of the mobile phase increases.
 - Porosity available for fluid flow. It depends on the concentration of deposited particles: increasing concentration of deposited particles, the medium porosity decreases.
 - Viscosity of the pore fluid. Dynamic viscosity of polymeric solutions is known to be a function of shear rate, polymer concentration and particles concentration via a modified Cross model (Comba et al. 2010a).
 - Permeability coefficient. Following Kozeny, the permeability of a porous medium depends on the third power of porosity, and on the square of the specific surface area of the matrix, through a constant. When colloids depose

on the soil grains, the pore space available for the fluid flow decreases, and the specific surface area increases, thanks to a further contribution of deposited particles. Therefore, both contributions are considered and the permeability coefficient is obtained by their combined effects.

The set of model equations is implemented in a finite-differences code, that represents the extension of the MNM1D model, previously developed for the simulation of colloidal transport under unfavourable deposition conditions in the presence of transients in ionic strength (Tosco et al. 2009). The newly developed model was applied for fitting of the experimental data.

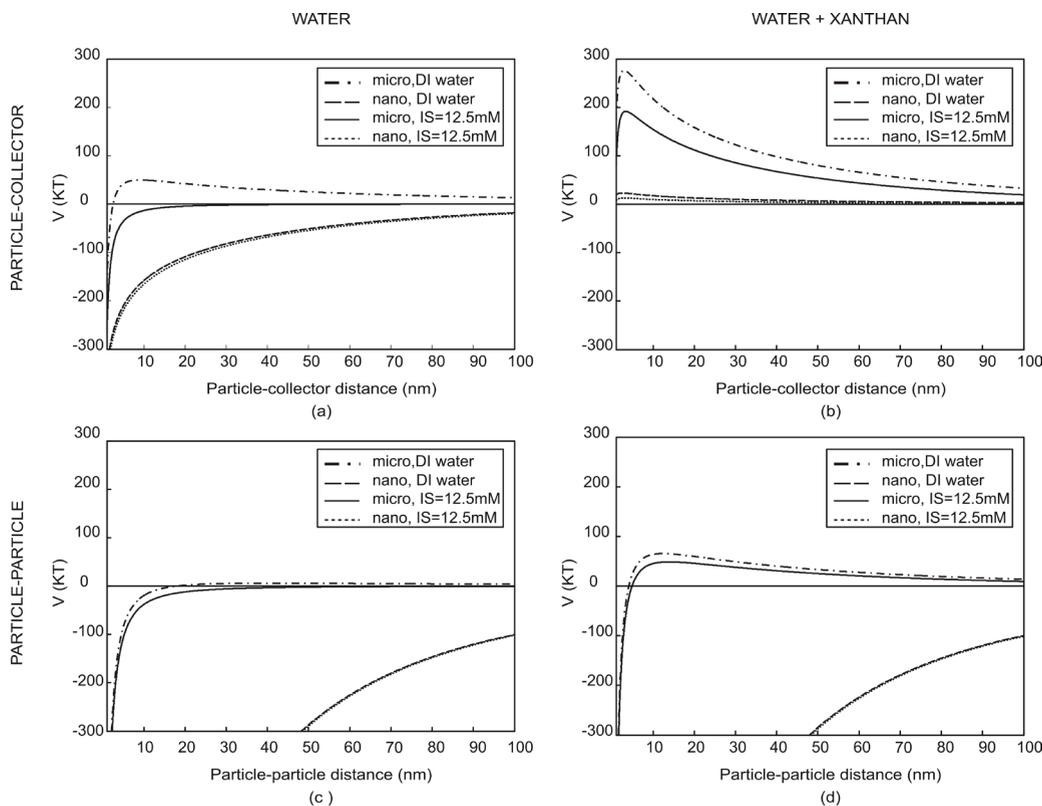


Figure 1: Particle-collector (a, b) and particle-particle (c, d) profiles of total interaction energy for microiron and nanoiron dispersed in water (a, c) and xanthan solution 3 g/l (b, d).

EXPERIMENTAL AND MODELING RESULTS

Estimation of interaction energy profiles

The total interaction potential is given by the sum of the following interaction forces following the extended DLVO theory (Tiraferrri, Sethi 2008):

- V_{vdW} the Van der Waals interaction, due to London-van der Waals attractive forces between faced bodies;
- V_{EDL} the electrical double layer interaction;
- V_{osm} the osmotic repulsion, due to osmotic forces generated by compression of the brush layer (polymer chains and liquid phase) that surrounds colloidal particles, when they approach each other;
- V_{el} the elastic repulsion, due to the presence of polymeric chains adsorbed on particles;
- V_{magn} the magnetic attraction (for NZVI only), that generates between surfaces with a residual magnetic saturation also in the absence of external magnetic fields.

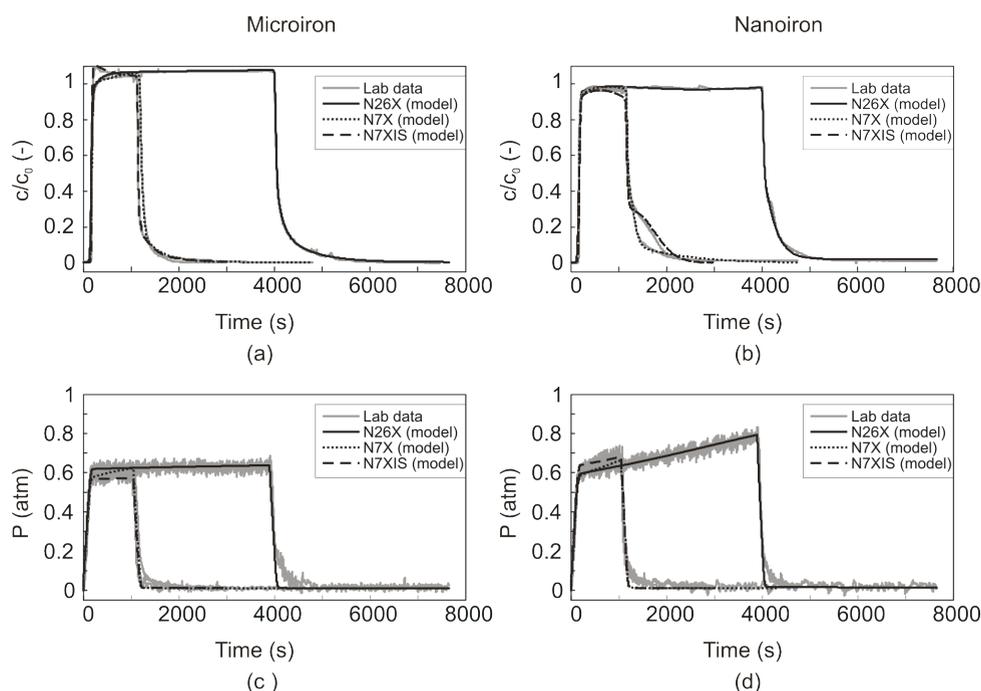


Figure 2: Experimental (grey) and model fitted (black) breakthrough curves (a, b) and pressure drop at column ends (c, d) for six transport tests with microiron (a, c) and nanoiron (b, d) dispersed in xanthan solution.

Breakthrough curves

Measured breakthrough curves of both microiron and nanoiron show a greatly increased transportability of the particles thanks to the use of xanthan gum, under both ionic strength conditions (data not shown here). Scarce mobility of unmodified iron particles has been reported by previous studies and was expected (Kanel et al. 2008). It is mainly attributable to the instability of unsupported iron dispersions, which leads to particle aggregation, in the case of MZVI, and to gravitational settling. Additionally, attractive interaction forces between the grains of the solid matrix and the suspended particles, both nano- and micro-scale, may contribute to filtration phenomena, as described by the DLVO profiles. The modelled curves reproduce accurately both breakthrough and pressure drop curves for all tests. Breakthrough curves for microiron tend to reach the influent concentration at the column outlet during injection, thus suggesting that a blocking phenomenon may take place, as confirmed by profiles of pressure drop at the column ends: after the initial step increase, due to the higher viscosity of xanthan with respect to pore water, no further increment is registered. Conversely, in NZVI tests the inlet concentration is never reached at the outlet ($C/C_0 < 1$). This behaviour can be attributed to ripening phenomena. The effect of ripening is a progressive clogging of the porous medium, which is confirmed by profiles of pressure drop at the column ends: after the initial step increment, during the slurry injection a slow but constant increase is found, suggesting a progressive reduction of permeability due to the clogging of the porous medium.

CONCLUSIONS

The experiments proved that xanthan gum can greatly enhance the mobility of both micro- and nanoscale iron, and is thus an excellent stabilizing agent and delivery vehicle of ZVI particles and has a high potential for use in real scale remediation interventions. Before this study, no model was available in the literature for the simulation of iron transport under the conditions described in the experimental section: although solutions exist for the simulation of clogging in deep bed filtration, or changes in pore space geometry due to mineral precipitation, none of these models can simulate the non-Newtonian nature of the carrier fluid, nor the influence of the concentration of suspended colloids on the fluid properties. The numerical model developed in this work, although implemented for the simulation of 1D laboratory column tests, could be extended to more complex geometries, thus becoming a useful tool for the design of the injection and early stages of migration of iron slurries in field applications.

ACKNOWLEDGEMENTS

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REFERENCES

- Comba S.; Dalmazzo D.; Santagata E.; Sethi R. 2010a. Rheological characterization of NZVI suspensions for injection in porous media. *Journal of Hazardous Materials* (submitted).
- Comba S.; Di Molfetta A.; Sethi R. (2010b) A comparison between field applications of nano, micro and millimetric zero-valent iron for the remediation of contaminated aquifers. *Water, Air, & Soil Pollution*, DOI: 10.1007/s11270-010-0502-1.
- Dalla Vecchia E.; Coisson M.; Appino C.; Vinai F.; Sethi R. 2009a. Magnetic Characterization and Interaction Modeling of Zerovalent Iron Nanoparticles for the Remediation of Contaminated Aquifers. *Journal of Nanoscience and Nanotechnology*, 9(5), 3210-3218.
- Dalla Vecchia E.; Luna M.; Sethi R. 2009b. Transport in Porous Media of Highly Concentrated Iron Micro- and Nanoparticles in the Presence of Xanthan Gum. *Environmental Science & Technology*, 43(23), 8942-8947.
- Di Molfetta A.; Sethi R. 2006. Clamshell excavation of a permeable reactive barrier. *Environmental Geology*.
- Kanel S. R.; Goswami R. R.; Clement T. P.; Barnett M. O.; Zhao D. 2008. Two dimensional transport characteristics of surface stabilized zero-valent iron nanoparticles in porous media. *Environmental Science & Technology*, 42(3), 896-900.
- Phenrat T.; Saleh N.; Sirk K.; Kim H. J.; Tilton R. D.; Lowry G. V. 2008. Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. *J Nanopart Res*, 10(5), 795-814.
- Saleh N.; Kim H. J.; Phenrat T.; Matyjaszewski K.; Tilton R. D.; Lowry G. V. 2008. Ionic strength and composition affect the mobility of surface-modified Fe-0 nanoparticles in water-saturated sand columns. *Environmental Science & Technology*, 42(9), 3349-3355.
- Schrick B.; Hydutsky B. W.; Blough J. L.; Mallouk T. E. 2004. Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater. *Chemistry of Materials*, 16(11), 2187-2193.
- Tiraferrri A.; Sethi R. 2008. Enhanced transport of zerovalent iron nanoparticles in saturated porous media by guar gum. *Journal of Nanoparticle Research*, Submitted.
- Tiraferrri A.; Sethi R. 2009. Enhanced transport of zerovalent iron nanoparticles in saturated porous media by guar gum. *J Nanopart Res*, 11(3), 635-645.
- Tosco T.; Sethi R. 2009. MNM1D: a numerical code for colloid transport in porous media: implementation and validation. *American Journal of Environmental Sciences*, 5(4), 517-525.
- Tosco T.; Tiraferrri A.; Sethi R. 2009. Ionic Strength Dependent Transport of Microparticles in Saturated Porous Media: Modeling Mobilization and Immobilization Phenomena under Transient Chemical Conditions. *Environmental Science & Technology*, 43(12), 4425-4431.
- Tosco T.; Sethi R. 2010. Transport of non-Newtonian suspensions of highly concentrated micro- and nanoscale iron particles in porous media: a modeling approach. *Environmental Science & Technology*, (under review).
- Zhang W. X. 2003. Nanoscale iron particles for environmental remediation: An overview. *Journal of Nanoparticle Research*, 5(3-4), 323-332.

The Effect of Chemical Oxidation on Heavy Metal Release and Microbial Community Diversity in Sediments

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ABSTRACT

The exponential growth of the human population and rapid growth in technology put stresses on the environment. The mixtures of organic and heavy metal that are present in sediments can have many toxicological and adverse effects on aquatic life, human health, and wildlife throughout the world. There are numerous remediation techniques that may be applicable on the treatment of sediment contamination and *in situ* chemical oxidation (ISCO) is one of them. In contrast to other remedial technologies, contaminant reduction can be seen in short time frames during ISCO which is an advantage. Different oxidants such as ozone, hydrogen peroxide, persulfate and permanganate can be applied depending on the type of the sediment treated and type of the pollution. In this study, the natural oxidant demands of three sediments was determined during permanganate and persulfate treatment, and the effect of these chemicals on the heavy metal release and on microbial community diversity was investigated. The quantitative microbial community changes were monitored with real time PCR (qPCR) and the diversity changes were observed by PCR-DGGE. The results revealed that natural oxidant demands of the sediments treated with persulfate were lower than the ones treated with permanganate. The demands ranged between 30-100 g/kg and 50-450 g/kg for persulfate and permanganate, respectively. Cr was released under the application of permanganate for three sediments; whereas, Zn and Pb were the problematic metals during persulfate treatment. The qPCR results showed that permanganate has strong effect on the numbers of total Bacteria, and more specifically on *Geobacter sulfurreducens* and sulphate reducing bacteria. On the other hand, the effect on numbers is less during persulfate treatment compared to permanganate.

Effect of ZVI Particle size on biostimulation of sulfate reducing bacteria for metal removal from groundwater: A batch study

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Use of metallic particles in environmental applications has been considerably increased in recent years. Zero valence state metals (Fe⁰, Zn⁰, Al⁰ etc) are surprisingly effective in groundwater remediation. As Iron is abundantly available, relatively inexpensive and normally non-toxic in nature, Zero Valent Iron (ZVI) gained much popularity in this area. ZVI is mostly used for abiotic removal of pollutants like arsenic and Chlorinated compounds. However, ZVI can also play a role in stimulating anaerobic biodegradation by depleting O₂, decreasing the redox potential and producing H₂ during anaerobic corrosion. This water derived H₂ can serve as potential electron donor to raise biomass yield and significantly accelerate sulfate reduction. But the efficiency, dose and performance of ZVI is highly dependent on surface area available hence on particle size.

The goal of this study was to evaluate the effect of ZVI on (1) the metal bio precipitation process and on (2) the stability of the formed metal precipitates. We studied three different yet most commonly used particle size of ZVI (Granular, Micro and Nano size) for heavy metal removal in a low pH sediment and groundwater via stimulation sulfate reduction and precipitation of metal sulfides. A batch experiment was performed comprising different conditions with ZVI with and without carbon source and also controls without ZVI or ZVI with formaldehyde to avoid microbial growth. Our laboratory experiment strongly support that ZVI can be very effective tool for inorganic contaminant removal and speeding up microbial mediated redox processes. Granular and micro Iron showed abiotic metal removal as well as stimulation of sulfate reduction in parallel. With nano iron sulfate reduction could not be induced despite of higher amount of H₂ production, though it is highly reactive and fast in a biotic metal precipitation. This suggests a possible toxicity or inhibition by nano particle towards certain bacterial cells, as suggested by several authors recently. Interestingly, our data show that the sulfate reducing population was inhibited, but not the whole soil microbiology as C-source was utilised. Molecular tools were also used to identify microbial community in different microcosms, which confirms that particle size also have a significant impact on microbial community selection and development. Our findings indicate that synergistic use of ZVI and SRB can lead to more stable precipitates and better contaminant removal.

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Micro-scale modelling of iron particles transport in saturated porous media

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ABSTRACT

Zero-valent iron micro- and nano-particles represent a promising technology for groundwater remediation, since they are characterized by high reactivity and can be easily injected in the aquifer system. Macro-scale mathematical models can be used to design and optimize the injection strategy. These models generally take into account micro-scale phenomena, such as particle-particle and particle-grain interactions, that significantly affect particle mobility. The aim of this work, co-funded by the European Union project AQUAREHAB (FP7 - Grant Agreement Nr. 226565), is to use Computational Fluid Dynamics (CFD) and Population Balance Models (PBM) at the micro-scale to derive more accurate (with respect to the empirical kinetics) "constitutive" equations to be implemented in the macro-scale model.

INTRODUCTION

As it is well known zero-valent iron micro- and nano-particles represent a promising technology for groundwater remediation for their ability to treat a wide range of contaminants. Their properties are strongly related to their large surface area, reactivity and mobility. In fact, iron micro- and nano-particles are extremely effective in contaminant degradation, allowing source treatment (rather than acting on the contaminant plume), as they can be injected directly in the subsurface in the form of aqueous dispersions. Recent experimental results have shown that some mobility limitations of iron particles, due to aggregation, can be overtaken by modification of the suspension viscosity by using biodegradable hydrocolloids, namely guar gum and xanthan gum (Dalla Vecchia et al., 2009), thus forming non-Newtonian fluids. The aim of this work is to use Computational Fluid Dynamics (CFD) and Population Balance Models (PBM) at the micro-scale to derive constitutive equations to be used in the macro-scale models typically employed to design the injection strategy.

Several two-dimensional computational grids, created in Gambit and obtained by Scanning Electron Microscopy (SEM) micrographs, are here employed to describe the real geometry of a small portion of the porous medium. Fluent 12.0 was used to model the flow field at the micro-scale, adopting different rheological models (Newtonian and non-Newtonian), effective superficial velocities, as well as sand sizes and porosities.

MODELLING APPROACH

CFD was here used to describe the flow of the dispersing fluid through the pores of a typical aquifer system. The Navier-Stokes and continuity equations were solved with Newtonian and non-Newtonian rheological models. In the range of superficial velocity, pore, sand and particle size investigated, the continuum hypothesis was always valid; if smaller pores (or bigger particles) were to be investigated then different modelling approaches would have to be used (such as Dissipative Particle Dynamics). Initially only four perfectly mono-disperse particle populations were studied with size equal to 1, 10, 100 and 1000 nm. Particles were modelled by resorting to an Eulerian model and further details will be given in the next sections.

Numerical details

Five computational grids, representative of different typical aquifers, were created with GAMBIT 2.4.6 starting from SEM images. Two-dimensional tetrahedral meshes were built with symmetrical boundary conditions; the final grids consisted of about 100 – 200.000 computational cells. The sand details are reported in Table 1, while an example of the SEM image and the corresponded grid are reported in Figure 1. The CFD code FLUENT 12.0 was employed to run steady-state simulations. Different superficial fluid velocities, v_s , ranging from 10^{-6} to 10 m/s, were considered. The selected conditions were representative of the natural flow conditions into the aquifers, as well as the injection conditions for the water treatment.

Table 1: *Grids characteristics.*

Grids	Mean sand size (μm)	Sand porosity (-)	x dimension (m)	y dimension (m)	Cells
02032	200	0.32	0.010	0.008	178560
02048	200	0.48	0.003	0.003	87768
03030	300	0.30	0.008	0.010	71220
03040	300	0.40	0.007	0.006	174555
03048	300	0.48	0.010	0.008	220528

A first-order upwind scheme was employed for spatial discretization, while for the pressure-velocity coupling the SIMPLE algorithm was employed. The effect of turbulence was considered for superficial velocities higher than 0.01 m/s. Turbulence was modelled by using the Reynolds-Averaged Navier-Stokes approach (RANS) with the standard k- ϵ model and with standard wall functions.

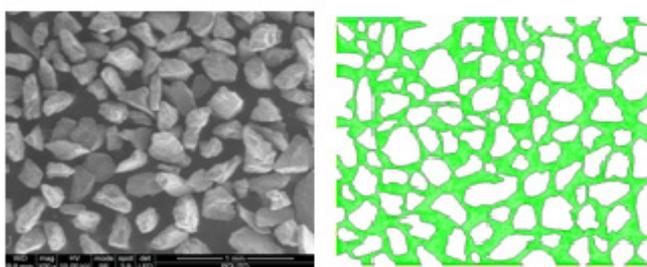


Figure 1: SEM image and corresponding grid.

Simulations were considered converged when the normalized residuals for each variable reached values smaller than 10^{-6} .

A first set of results were obtained considering a Newtonian fluid characterized by different viscosities, ranging from $\mu = 0.001$ Pas to 10 Pas. The second step in the flow field simulations was considering the Non-Newtonian behavior. In these cases Cross and the Ellis models were considered. For both cases the viscosities ranging from $\mu = 10^{-3}$ to 3.72 Pas, the time constant was kept equal to 10.2 s while the power law index assumed the value of 0.32.

RESULTS

Flow field for Newtonian rheology

The contour plots for the fluid velocity magnitude at four different superficial velocities are reported in Figure 2. As it is possible to see, the flow field is characterized by a non-homogeneous trend, especially at very low and very high velocities. In all the investigated cases, the profile is characterized by regions at high fluid velocity close to regions at low velocity.

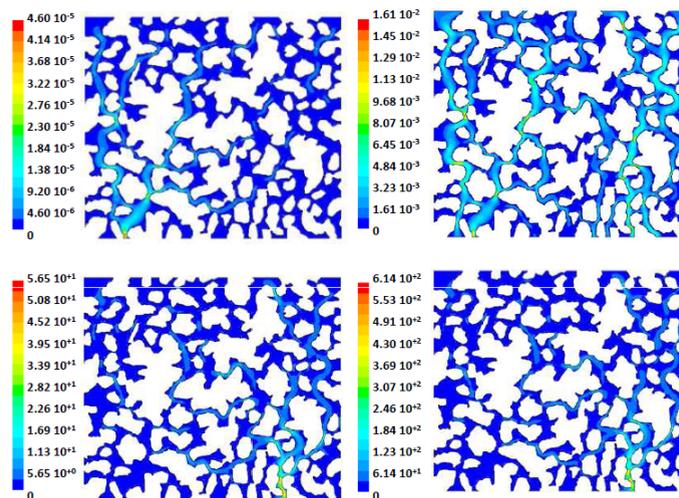


Figure 2: Contour plots of velocity magnitude for water (0304) (from left to right and top to bottom) 0.000001 m/s, 0.001 m/s, 1 m/s and 10 m/s.

When the superficial velocity is increased the flow field, in all the different grids, radically changes and the presence of by-passes is evidenced. It is interesting to notice that increasing the superficial velocity the flow pattern becomes highly irregular, its variation with the imposed superficial velocity becomes non linear, and the convergence criteria are hardly met, probably signalling the presence of time-dependent irregular oscillations, that could represent the onset of turbulence.

For all the selected geometries and under the operating conditions investigated the obtained pressure drop, ΔP , experienced by the fluid while flowing through a porous domain of length L , was normalized, $(\Delta P/v_s^2)(D_p/L)(\epsilon^3/(1-\epsilon))$, with respect to the superficial velocity, v_s , the grain size, D_p , and the porosity of the porous medium, ϵ . These normalized pressure drops were then reported versus the sand Reynolds number (Re_p), $(\rho D_p v_s/\mu)(1/(1-\epsilon))$, where μ is the fluid viscosity, and results are reported in Fig. 3 (symbols) together with the theoretical Ergun equation (continuous line).

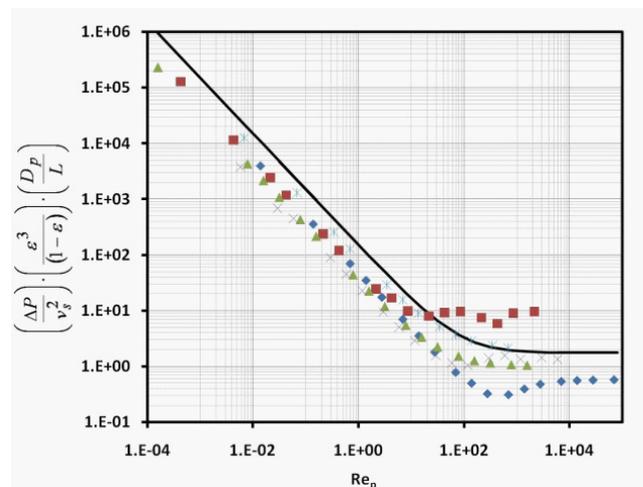


Figure 3: Comparison between the normalised ΔP versus the Re_p obtained by CFD simulations (symbols: \blacklozenge 02032; \blacksquare 02048; \blacktriangle 03030; \times 03040; \ast 03048) and the value calculated by Ergun equation (line).

As it is possible to see the simulation results, obtained with different grids and under different operating conditions, collapse into a single line in good agreement with the Ergun equation. It is also important to highlight that, although the Ergun equation is a very simple law, it describes fairly accurately the behaviour of Newtonian fluids flowing through porous media, and can therefore in this context be considered as an exact solution to be used for model validation. Therefore, the good agreement between CFD simulations and the predictions of the Ergun equation proves that the computational grids selected, although being two-dimensional projections of three-dimensional porous media, as well as the overall approach, are adequate to describe the investigated systems.

Flow simulations with Non-Newtonian fluids

The behaviour of Non-Newtonian fluids, by employing the Ellis and Cross models, was also considered in this work and results are detailed in Fig. 4, where the apparent viscosity, $(k/v_s)(\Delta P/L)$, is reported versus the shear rate $v_s/(k\epsilon)^{1/2}$,

calculated by using the permeability k previously obtained with the Darcy law applied at low superficial velocity.

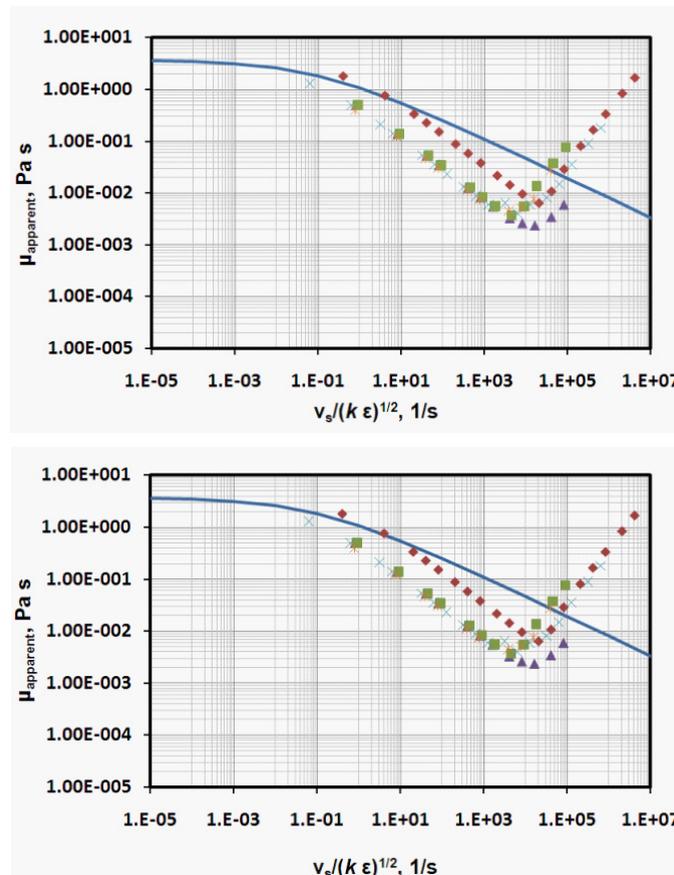


Figure 4: Comparison between the apparent viscosity versus the shear rate obtained by CFD simulations (symbols: ◆ 02032; ■ 02048; ▲ 03030; × 03040; * 03048) and the rheological models considered: Ellis model (top) and Cross (bottom).

As it is possible to see once again CFD predictions obtained for different grids and under different operating conditions collapse into one single line, proving the validity of the approach. It is also interesting to notice that, as observed in a number of experimental studies, at low superficial velocities, there is a perfect overlap between the pressure drops (either measured or simulated) and the rheological model. However, the two grow apart when the superficial velocity increases, probably due to some flows instability.

Flow simulations of Newtonian fluids in the presence of particles

The presence of the particles was eventually considered by employing User Defined Scalars (UDS) and Functions (UDF). Particles were modelled by resorting to an Eulerian approach, tracking the moments of the particle size distribution (PSD). Particle diffusivity was calculated by employing the Stokes-Einstein approach; four different mono-disperse particle populations, of size equal to 1, 10, 100 and 1000 nm, and only particle-grain interactions, were considered at this stage.

In real systems particles flow with the fluid and due to collisions (mainly due to Brownian motions) with the grain walls may remain attached (i.e., attachment). As a result of the attractive Van der Waals forces and the repulsive and drag forces exerted by the fluid, some particles may detach from the grain walls and return in the fluid flow (i.e., detachment). These interactions, governed by the standard DLVO theory (Lyklema, 2003), are quantified in an Eulerian approach by an attachment efficiency, bounded between zero and one, that is a function of surface potentials of particles and grain walls, as well as of the ionic strength of the solution.

In what follows this efficiency will be considered equal to one, which is equivalent to the assumption that all the particle-grain collisions (due to Brownian motions) are effective. Different values will be considered in our future work (as resulting from the DLVO theory), but is indeed interesting to start considering this limiting case. It is also important to remind that although particle clogging can indeed be considered (Bensaid et al., 2010) it will, at this at this initial stage of the work, be neglected.

In Figures 5 and 6 the contour plots of the normalized particle concentration in the suspending fluid is reported at

four different superficial velocities, equal to $10^{-6}, 10^{-5}, 10^{-4}$ and 10^{-3} m/s, and for two different particle sizes, 1 and 1000 nm, for a grid with grain size $200 \mu\text{m}$ and porosity 0.32 (grid label 02032 of Tab. 1). As it is seen, as particles enter the domain flow with the fluid but as soon as, thanks to diffusion due to Brownian motions, collide with the grain walls, remain attached and their concentration in solution goes to zero. As the superficial velocity is increased, convection prevails, and particles can enter deeper into the domain before being attached to the grain walls. It is interesting to highlight that as the particle size increases (compare Figs. 5 and 6 for the same superficial velocity) the mobility of the particles and therefore their collision rate onto the grain walls, are reduced, resulting in higher particle concentrations in solution.

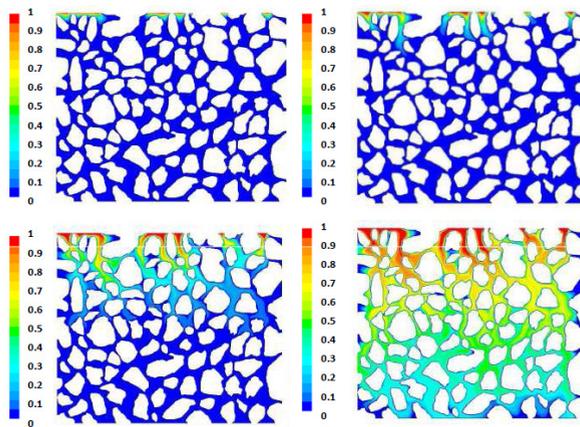


Figure 5: Contour plots of particles through the sand $D_p = 200 \mu\text{m}$ and porosity 0.32, particle size 1 nm. From top to bottom, and from left to right: spatial velocity $10^{-6}, 10^{-5}, 10^{-4}$ and 10^{-3} m/s.

From the analysed geometries and for the operating conditions investigated, it is possible to estimate the rate of particle attachment per unit volume to the grain walls. Results show that this rate depends on the local superficial velocity, porosity of the medium, and grain (collector) size, in a very complex way. Results are compared with the classical filtration theory (Fan and Zhu, 1998) and will be used to formulate more reliable deposition/attachment kinetics.

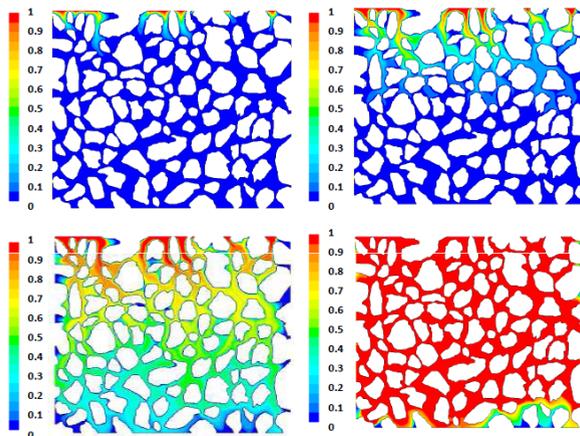


Figure 6: Contour plots of particles through the sand $D_p = 200 \mu\text{m}$ and porosity 0.32, particle size 1000 nm. From top to bottom, and from left to right: spatial velocity $10^{-6}, 10^{-5}, 10^{-4}$ and 10^{-3} m/s.

CONCLUSIONS

Two-dimensional CFD simulations are here used to describe the flow of Newtonian and non-Newtonian fluids in porous media carrying particles interacting with each other and with the grain walls. The objective of the work is to extract constitutive laws to be used in macr-scale models. Preliminary results show good agreement between the permeabilities predicted by the CFD model and by the empirical Ergun equation, proving the validity of the approach. The CFD code is then coupled with PBM to simulate the presence and the evolution of the particles, including for example grain attachment. Preliminary results show that the classical filtration theory (based on the collector concept) needs to be improved to realistically describe the phenomena involved. Future work includes the investigation of particle-particle aggregation, of three-dimensional geometries, as well as the use of alternative more efficient approaches, able to overcome the limitation of the continuum approach adopted here.

ACKNOWLEDGEMENTS

The authors wish to thank Mauro Raimondo for the SEM analysis.

REFERENCES

- Bensaid, S., Marchisio, D.L., Fino, D. 2010. Numerical simulation of soot filtration and combustion within diesel particulate filters, *Chem. Eng. Sci.*, 65: 357-363.
- Fan, L.S., Zhu, C. 1998. *Principles of gas-solid flows*, Cambridge Univ. Press, Cambridge.
- Comba, S., Sethi R. 2009. Stabilization of highly concentrate suspensions of iron nanoparticles using shear-thinning gels of xanthan gum. *Water research*, 43: 3717-3726.
- Zhang, WX. 2003. Nanoscale iron particles for environmental remediation: an overview. *Jour. Nanoparticle Res.*, 5: 323-332.
- Dalla Vecchia E., Luna M., Sethi R., 2009. Transport in Porous Media of Highly Concentrated Iron Micro- and Nanoparticles in the Presence of Xanthan Gum, *Environmental Science & Technology*, ISSN: 0013-936X, DOI: 10.1021/es901897d
- Lyklema, J. 2003 *Fundamental of interface and colloid science*, Elsevier Academic Press.

Geochemical modelling of Fe⁰ permeable reactive barriers

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Effective application of Permeable Reactive Barriers (PRBs) requires a solid understanding of the site-specific hydrogeological and biochemical conditions. Secondary mineral precipitation has been shown to reduce reactivity and efficiency of permeable reactive barriers and the interactions between biological and chemical processes may also influence the long-term efficiency of such systems.

In this study a multi-component transport model based on PHAST USGS has been developed using batch and column experiments data provided by VITO. The use of lab-scale data has been particularly important to understand the main chemical processes, reducing model prediction uncertainty and increasing accuracy of longevity assessment. Moreover the influence of each measurement on the model parameters has been estimated in order to identify the optimal experimental design. A simplified application of the calibrated model on a real PRB will be also shown.

Industrial Scale Bimetallic Nano-alloys With High Potential For In Situ POP Abatement

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ABSTRACT

Biorem Engineering has developed an industrial-scale production technology to produce formulations of bimetallic nano-alloys, with the capability to degrade a broad spectrum of persistent chlorinated pollutants. The formulations are well-suited for injection applications (source zone abatement) and for incorporation into reactive barriers (risk control measures). The bimetallic nature of the alloy results in a rapid and complete dehalogenation of a range of chlorinated solvents, pesticides and PCB congeners under environmental aquifer conditions. The small size of the individual particles offers an increased reactive surface area and improves dispersibility in the subsurface environment. Alloyed particles consisting for > 95% of zero valent iron and organic carbon were most suited for dechlorination of VOC compounds, with excellent conversion yields Vinyl Chloride, Chlorinated Ethanes, PCE, TCE and DCE towards ethane and ethene. Our research indicates that other catalytic technologies, based on zero valent iron, were not or only slightly reactive for many of these chlorinated solvents.

For ease of handling and improved dispersibility of the nano-alloy into a reactive zone (RZ), we developed a method to formulate the bimetallic alloy into a homogeneous, concentrated slurry.

We also have in-house capacity to formulate bimetallic particles into porous granules, with a diameter size of about 5 mm. These granules are suitable for application into a PRB and have the additional advantage that oxidation products are shielded from the inner pores of the granules allowing longer and better reactivity over-all.

Our patented process results in efficient nano-alloy production, resulting in a competitive technology for source-zone abatement and effective implementation into reactive barriers.

The production and formulation of highly active bimetallic nano-alloys for *in-situ* applications in soil remediation on industrial scale is economically feasible by this competitive technology.

INTRODUCTION

Catalytic reactivity tests were performed where the Biorem alloy was compared to both the precursor powders in terms of hydrodechlorination catalysis potential for three chlorinated solvents, 1,1,1-trichloro ethane (1,1,1-TCA), vinyl chloride, 1,1-dichloroethane (1,1-DCA) and for dechlorination of a polychlorinated biphenyl congeners.

MATERIALS AND METHODS

1,1,1-TCA Lab scale Tests

The tests with 1,1,1-TCA, vinyl chloride and 1,1-DCA were executed in 100 ml closed penicillin bottles with Viton stoppers, containing 50 ml milliQ water that was de-aerated and into which 10 mg/L 1,1,1-TCA had been spiked from a 1,1,1-TCA stock solution in methanol. De-aeration was done by flushing for example with argon gas, no oxygen was present in the water volume. The headspace of the penicillin bottles contained 100 % Ar gas at the start of the experiment. All experiments were set up in duplicate. The powders were added to the respective penicillin bottles in the following concentration: 2000 mg/l Biorem catalytic alloy, or both components alone in the same proportion.

Assays were incubated at 28 °C.

Analyses were done in samples of the headspace. Ethane, ethene, 1,1,1-TCA, vinyl chloride and 1,1-DCA were measured in the headspace by GC-FID analysis (Varian).

For 1,1,1-TCA, vinyl chloride and 1,1-DCA a capillary column (Varian FactorFour Low Bleed VF624 ms, 30 m x 0,25 mm) was used. The temperature of the injector was 200 °C with a split ratio of 5. The setup of the temperature program was 30 °C for 2 minutes, increasing to 40 °C at 1 °C/min and finally to 105 °C at 5 °C/min. The carrier gas was helium at a flow rate of 3 ml/min. The temperature of the FID detector was kept at 250 °C. The detection limit was 10 µg/l .

Ethane and ethene were separated on a Varian Poraplot Q column, 25 m x 0,53 mm. GC injections were made at 30 °C. This temperature was maintained for 3 min, followed by an increase to 80 °C at 30 °C/min and finally to 150 °C at 10 °C/min. The temperature of the injector was 200 °C with a split ratio of 5. The carrier gas was He at a flow rate of 10

ml/min. The temperature of the FID detector was 240 °C.

PCB 118 Lab scale Tests

The tests with PCB 118 were executed in 100 ml closed penicillin bottles with Viton stoppers, containing milliQ 30 ml water. PCB 118 was added from a methanol stock solution to a final concentration of 1 mg/l . All experiments were set up in duplicate. The Biorem catalytic alloys were added to the respective penicillin bottles in the following concentration: 2000 mg/l. The suspensions were anaerobised by consecutive cycles of underpressure and Ar overpressure. PCBs were analyzed with a gas chromatograph (GC), Varian 3800 (Varian, Middelburg, The Netherlands) equipped with an electron capture detector (ECD). N₂ was used as carrier gas at a flow rate of 1,3 ml min⁻¹. One µl of the extracted sample was injected splitless. For detection of PCBs and their dechlorination products, temperature was held for 2 min at 100 °C, increased to 160 °C with a gradient of 15 °C min⁻¹, followed by 5 °C min⁻¹ to 270 °C and held at 270 °C for 10 min. The pressure in the capillary column was 1,09 kg/cm².

Full scale test on PCB

The Biorem catalytic alloy was used in a reactive zone by injection with the Bio Float in a lake sediment (www.biofloat.com). The Bio Float allows a continuous injection of the product into sediment with cm-precision. The Bio Float is a amphibious vessel with turbines for controlled movement; with a silo, pumps and tubing for distributing the formulation, an injection system that continuously distributes the product over the sediment and an on-board 3D positioning system and high-frequency sonar.

To treat contaminated sediment, polluted with PCBs via a reactive zone, a new injectable 3-component formulation was developed. The formulation consists of: (a) a biopolymer, produced from agricultural feedstock and completely biodegradable, (b) a small quantity (12%) of biodegradable solvent and (c) a catalytic nano-alloy that catalyzes hydrodechlorination reactions. The alloy consists for more than 95% of zero valent iron, a co-catalyst and organic carbon. The total amount of injected slurry was 2g/kg dry matter (DM).

Samples were taken from a 3 zones: a control zone (untreated), a sandloam zone and a clay zone. PCBs were analyzed after a acetone/hexane extraction with a gas chromatograph (GC), Varian 3800 (Varian, Middelburg, The Netherlands) equipped with an electron capture detector (ECD). N₂ was used as carrier gas at a flow rate of 1,3 ml min⁻¹. One µl of the extracted sample was injected splitless. For detection of PCBs and their dechlorination products, temperature was held for 2 min at 100 °C, increased to 160 °C with a gradient of 15 °C min⁻¹, followed by 5 °C min⁻¹ to 270 °C and held at 270 °C for 10 min. The pressure in the capillary column was 1,09 kg/cm².

RESULTS

Lab scale feasibility testing PCB 118

The lab scale results from the microcosm tests are shown in figure 1.

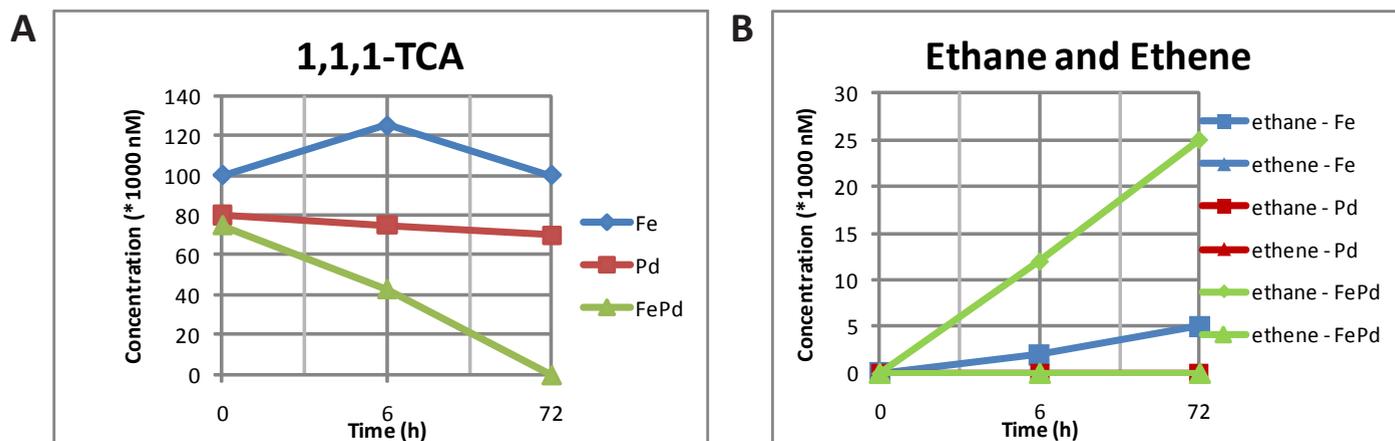


Figure 1: (A) Concentration of 1,1,1-TCA in function of time in the presence of 3 different catalytic compositions : Zerovalent iron powder, Biorem catalytic nanoparticles, and the Biorem catalytic alloy. (B) Concentration of dechlorinated reaction products of 1,1,1-TCA in function of time in the presence of the same catalytic compositions as in (A).

It can be seen that zerovalent iron powder and Biorem catalytic nanoparticles are an ineffective catalyst for 1,1,1-TCA dechlorination, whereas the combination of both in the Biorem catalytic alloy results in complete removal of 1,1,1-TCA

within 72 hours and with formation of significant amounts of ethane in the headspace, indicative of complete and effective hydrodechlorination. With the nano-alloy, complete dechlorination of vinyl chloride was observed within 72h, and 1,1-DCA was dechlorinated by 58% within 72h (results not shown).

Lab scale feasibility testing PCB 118

The lab scale results are shown in figure 1. It can be seen that removal of PCB 118 by hydrodechlorination was more effective with the Biorem catalytic alloy than with the Biorem catalytic nanoparticles, even when the nanoparticles were saturated with molecular hydrogen gas and no H₂ was added to the Biorem catalytic alloy.

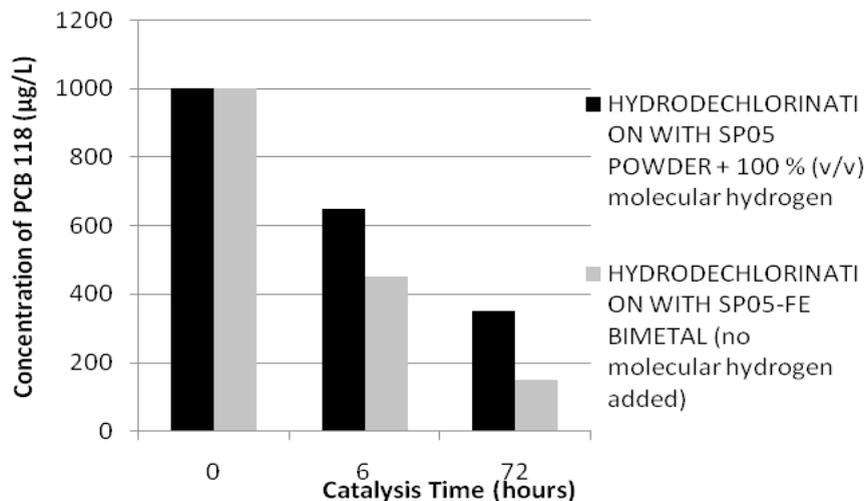
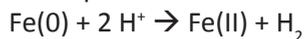


Figure 2 : Concentration of PCB 118 in function of time in the presence of 2 different catalytic compositions : Biorem catalyst nano-particles under H₂ atmosphere, and an Biorem catalytic alloy under Ar atmosphere.

The reason is probably the more effective hydride formation on the catalytic surface due to the presence of iron in the catalytic alloy “mixed sites”, according to the following reactions.

On (anoxic) iron surface the following reaction takes place:



On the catalytic surface, the following reaction takes place:



Due to the alloying of Pd and Fe, hydrogen can be more effectively charged onto the palladium surface (De Windt et al, 2005).

Injection

The full scale results are shown in Table 1. The in situ PCB degradation as established by the injection of a biopolymer and the Biorem catalytic alloy into the sediment.

Table 1: Concentration of the sum of the 7 Ballschmitter PCBs in function of time in different sediment zones under effect of the Biorem catalytic alloy. The threshold limit for remediation was set on 190 µg/kg DM.

Sediment zone	Time (days)	Concentration Σ 7 Ballschmitter PCBs (µg/kg DM)
Area S8 (sand-loam)	0	1600
	13	1149
	33	679
	53	36
Area C9 (clay)	0	440
	13	226
	33	147
	53	137
Control	0	269
	10	210
	23	273
	48	202

The degradation of the PCBs involved a 3 phase system: (a) the biodegradable polymer was metabolic converted into hydrogen by the endogenic microbiota, and charged the Biorem catalytic alloy, (b) the solvent increased the availability of the contaminant from the soil or sediment particle and (c) the Biorem catalyst degraded the PCBs by hydrodechlorination.

In a sand-loam sediment zone, a hotspot of 1600 ppb of Ballschmitter PCBs was degraded in 53 days to 36 ppb.

In a zone with clay-like sediment, a lower concentration of 440 ppb was measured, however the nature of the sediment resulted in a more persistent sorption of the PCBs onto the soil particles.

Due to the action of the biodegradable solvent, the PCBs could be degraded below the risk threshold value within 33 days.

After a total of 53 days, the PCB concentration had decreased to a concentration below the risk threshold level, which was set at 190 ppb.

CONCLUSIONS

Biorem Engineering has developed a successful technology for on-spot remediation of sediments contaminated with persistent contaminated organic pollutants, such as polychlorinated biphenyls, dioxins, chlorinated solvents and furans. The degradation takes place under ambient environment conditions.

The innovative catalytic products can be produced on large industrial scale by Biorem Engineering and can be applied by a contractor for in situ reductive chemical remediation of heavily contaminated sited.

ACKNOWLEDGEMENTS

We wish to express our sincere thanks to Ghent University for co-development and testing of this technology. We also thank our worldwide partners for adding value every day to our collaboration.

REFERENCES

De Windt W., Aelterman P., Verstraete W. 2005. Bioreductive deposition of palladium (0) nanoparticles on *Shewanella oneidensis* with catalytic activity towards reductive dechlorination of polychlorinated biphenyls. *Environmental Microbiology*. 7(3): 314-325.

www.biofloat.com

www.bioremengineering.com (under construction, operation mid July 2010)

Session 5

Lessons learned from the field & Economics

Stretching limits of Reactive Zones: 3 examples

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Reactive zones are applicable in an increasing range of situations. Three examples are evaluated.

1 Reactive zone for after-care

After dig & dump remediation of chlorinated carbon contaminated soil, eternal pump and treat of chlorinated carbon contaminated groundwater was necessary as aftercare at a site. By the end of the life cycle of the water treatment plant, an economical evaluation was performed whether eternal pump & treat was the best option to remediate the groundwater. Based on the results, a plan was designed to economize the eternal aftercare to a finite remediation period of preferably a few decades. The plan consists of creating a reactive zone at the contaminated parts of the site by injection of large quantities of electron donor by a direct push method. An elaborate process monitoring is planned including concentrations measurements as well as hydrogen and molecular DNA analyses. Preceding the full-scale treatment, a pilot, with injections and high definition monitoring was performed to define a site-specific sphere of injection influence, in order to fine-tune the injection plan.

2 Reactive zone for improving soil remediation

On a chlorinated carbon contaminated groundwater site, remediation was performed by pump and treat. Because concentration levels did not descend as quick as anticipated, an economical evaluation was executed. Based on the results, a plan was designed to economize soil remediation at the site and bring the period of active remediation to an end in preferably a few years by installing a reactive zone. Because of the difficult site lay-out with buildings, an extended full scale pilot was performed with an elaborate process monitoring. Two separate electron donor blends were tested for study benefits. The monitoring results show clearly different characteristics of both blends. Degradation was enhanced considerably in spite of low quantities of dechlorinating organisms, presumably due to relative high groundwater temperatures.

3 Proof of concept for integration of soil energy storage with reactive zone application

High groundwater temperatures can be used to enhance biodegradation of aromatic and chlorinated compounds in groundwater where soil energy storage is applied. If necessary, also electron donor or receptors can be provided in the soil energy zone. This concept of the combination of bioremediation and soil energy storage was worked out and is tested now. The first preliminary results are available and will be presented.

Permeable Reactive Barriers for Ground Water Remediation at Contaminated Former Manufactured Gasworks Plants and Related Sites: Design Features, Performances Achieved, and Outlook

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ABSTRACT

For three permeable reactive barriers (PRBs), which have been operated at former manufactured gas plants (MGPs) and related sites in Germany and Austria over around 3-10 years now, it has been found that virtually all of them have performed well or even perfectly over their operational term so far. "Efficiently controllable" ("EC")-PRBs, Drain and gate (D&G) PRBs or modified funnel-and-gate systems (F&G) to treat polycyclic aromatic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene and xylenes (BTEX) in more or less accessible reactive zones, have successfully been operated at different sites across Europe so far. They are packed with granular activated carbon (GAC) or equipped with a biological treatment zone, where added nutrients and/or microbes enhance microbiological degradation (Bio-PRBs). Moreover, during the second working period of the German PRB research and development (R&D) cluster "RUBIN" from 2006-2010, it could be verified that even emerging novel contaminants, such as heterocyclic PAHs (NSO-PAHs), can effectively be retained and/or destroyed in such PRBs as well. This contribution covers main results of ongoing investigations on longevity and long term efficacy of two GAC-PRBs in Germany and Austria. Major overall conclusions from the work of RUBIN (Birke et al., 2005a; RUBIN, 2010), as well as from the German PRB handbook (Birke et al., 2006a), which was published in 2006 and is currently being updated, are included. First performance data of a recently erected pilot scale Bio-PRB at Offenbach, Germany, are also discussed.

Economical Potential of Multibarriers as a Sustainable Method for In-Situ Groundwater Pollution Treatment

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ABSTRACT

A multibarrier is a sustainable in-situ passive solution to contain and treat contaminated groundwater. It consists of a tailor-made combination of different types of permeable reactive barriers and reactive zones in which pollutant removal processes are active. In the Multibardem LIFE-project, executed by a consortium of Belgian and Austrian research and industrial partners (2006-2010), multibarrier concepts were demonstrated at two locations:

- Location 1: Hooge Maey in Antwerp (Belgium) - Municipal and industrial landfill site;
- Location 2: Altlast site 024 in Austria – Industrial site.

Monitoring of the installed multibarriers showed promising results. However, to stimulate adoption of this new technique in full-scale applications, not only the environmental performance is important but also economical aspects. Because of the tailor-made nature of multibarriers, a detailed site characterization is necessary before implementation. Design of the multibarrier depends on such factors as groundwater pollution characteristics; hydrogeological, geochemical, microbial and geotechnical data; as well as the site's physical setting. Other factors that may be of importance are regulatory or land use requirements, as well as the desired time frame for remediation. A rough cost comparison between multibarriers and conventional P&T remediation shows that installation costs for multibarriers are typically higher whereas operational costs are lower. Multibarriers therefore are cost-efficient solutions for long-running remediations, typically in the order of 10 years or more.

Potential applications for multibarriers are mainly mixed groundwater pollutions from sources such as abandoned landfills, acid mine drainage or industrial sites. For multibarriers to be a viable option for groundwater treatment, a number of preconditions must be fulfilled, including maximum depth of groundwater pollution, required subsurface characteristics, time and regulatory requirements. Even with these constraints, the potential market for multibarrier applications is considerable, with thousands of sites representing a market value of several million Euros worldwide.

INTRODUCTION

A multibarrier is a sustainable in-situ passive solution to contain and treat contaminated groundwater. It consists of a tailor-made combination of different types of permeable reactive barriers and reactive zones in which pollutant removal processes are active. Degradation and/or immobilization of pollutants occurs as the groundwater flows through the system.

In the Multibardem LIFE-project (2006-2010), Multibarrier concepts were demonstrated at two locations with different geological conditions:

Location 1: Hooge Maey in Antwerp (Belgium) - Municipal and industrial landfill site

Location 2: Altlast site 024 in Austria – Industrial site

The results from these pilot studies are promising, indicating that pollutant removal with multibarriers is possible. However, for multibarriers to become a viable alternative to traditional groundwater treatment systems such as Pump&Treat (P&T) installations, multibarriers must also be cost-effective. Multibarriers are highly dependent on site and pollution characteristics. Since differences in design have an impact on installation and operational costs, a general economical evaluation of multibarriers is very difficult.

Therefore, a rough cost comparison between a multibarrier and P&T was performed for a hypothetical situation. An attempt was also made to give a more general view on the potential market for multibarrier applications.

MULTIBARRIER DESIGN

The multibarrier design process typically consists of the following steps:

- Site characterization;
- Design, based on laboratory feasibility tests;

- Installation;
- Operation, Maintenance and Monitoring.

Each of these steps entails specific costs. A short description of the different steps, and how they were applied to the hypothetical case study is given below.

Site characterization

Because of the passive nature of multibarriers, very little adaptation is possible after installation. This in contrast to more active systems, where parameters such as flow rate and hydraulic residence time are more easily adapted. Thorough site characterization is therefore necessary prior to the design and installation of a multibarrier, and is likely to be more costly than for traditional systems. Site characterization must include at least the following parameters:

- **Groundwater contamination characteristics** such as type and concentrations of contaminants, competition, redox conditions, pollution depth; these will determine the possible treatments;
- **Hydrogeological data** such as flow velocity, hydraulic conductivity and preferential pathways are vital for the design and installation of multibarriers. For example, groundwater flow velocity will determine the HRT and therefore size of the multibarrier; whereas the groundwater flow direction is important for optimal placement of the multibarrier;
- **Groundwater geochemistry** (apart from pollution characteristics) may influence the efficiency and long-term performance of the treatment process;
- **Microbial data** (if biological treatment is considered);
- **Geotechnical characterization:** soil properties and multibarrier material properties define the ability of the multibarrier system to maintain its structural integrity for the design lifetime;
- **Physical setting:** multibarrier design is influenced by topography, surface and underground structures and utilities, etc.

For the hypothetical case, an 8 m thick aquifer layer, starting at 2 m bgs, was considered with an underlying aquitard. The aquifer was assumed to consist of sand to loamy sand with a permeability of $K_s = 10^{-6}$ m/s and a groundwater flow velocity of 0.1 m/day. Continuous leakage of leachate from an old uncontrolled landfill in the groundwater resulted in a 350 m wide leachate-contaminated groundwater plume. Ammonium was selected as the primary target pollutant, because this is considered the most significant contaminant of landfill leachate on the long term (Kjeldsen et al., 2002) and considered to be present at 50 mg N/L in the groundwater plume. A top view of the hypothetical case is shown in Figure 1.

Design

Conceptual design of a multibarrier is based on laboratory feasibility tests to determine the removal efficiency of the selected processes, required hydraulic retention time (HRT) and lifetime of the reactive media. Execution of pilot tests, if possible, can increase the reliability of the design parameters.

For the hypothetical case, multibarrier design was based on the results from the pilot test on the Belgian landfill site. The ammonium removal was based on a combination of microbial degradation processes (nitrification-denitrification) and ion exchange processes (using granular clinoptilolite). In the pilot-scale multibarrier, performed in a partly buried steel container (Van Nooten et al., 2009), HRTs of 53 h and 26 h were required for the removal of 50 mg N/L by nitrification and denitrification, respectively.

The multibarrier system was therefore designed as follows:

- Funnel and gate system, with 3 gates of each 25 m wide for a funnel-to-gate ratio of ~ 5 ; 10 m depth;
- Each of the gates has a total length of 5m, including a 3 m long nitrification compartment (average porosity: 0.5) and a 2 m long denitrification compartment (porosity: 0.4);
- Nitrification compartment equipped with diffusive oxygen transfer systems, half filled with granular clinoptilolite (to remove remaining ammonium concentrations by ion exchange when microbial activity is insufficient) and half filled with coarse sand;
- Denitrification compartment equipped with a butyrate injection system;
- Complete gate filling is mixed with diluted microbial sludge originating from a wastewater treatment, as inoculum for nitrifying and denitrifying bacteria.

Construction

Depending on the multibarrier design, construction methods such as excavation, continuous trenching or vertical hydrofracturing may be used. In case of excavation, additional stability measures such as sheet piling, secant walls, casings, etc may be necessary, which increase the cost significantly. For reactive zones, installation costs are limited to the installation of injection systems.

For the hypothetical case, installation was considered to consist of excavation using sheet piling for stability. Due to the fact that excavation is needed below the groundwater table, groundwater extraction (with transport and disposal of the extracted groundwater) is also included. The reactive materials are placed in the multibarrier using cranes.

Operation, maintenance and monitoring

Operational costs for multibarriers are lower than for traditional techniques such as P&T, because of the reduction of electricity and maintenance costs. Costs for chemicals may also be reduced, especially for reactive barriers. For reactive zones, addition of nutrients, oxygen or others may increase the operational cost.

Monitoring costs on the other hand are likely to be higher for multibarriers compared to traditional systems. Continuous monitoring is needed to assure efficient removal of pollutants. Regulatory monitoring requirements are also likely to be higher than for traditional “proven” methods such as P&T, although this will likely decrease as the technique becomes better accepted.

For the hypothetical case, monitoring requirements were based on the Flemish guideline for monitoring of iron PRBs (OVAM, 2005). This included installation of 20 monitoring wells, with an average monitoring frequency of 6 months. Electricity and maintenance costs were assumed to be 20% of that for the P&T system. The addition of oxygen was an important cost factor for the pilot test. For a full scale application, it was assumed that these costs can be reduced significantly.

PUMP AND TREAT DESIGN

A pump & treat hydraulic barrier in the gate was designed as follows:

- Distance between pumping wells of 50m;
- 8 pumping wells screened between 2 and 10 m bgl;
- Pumping rate of 35 m³/day (total flow rate 280 m³/day);
- Total of piping distance between the pumping wells and the potential waste water treatment plant of 500 m;
- Installation of 2 monitoring wells per pumping well, screened between 2 and 10 m bgl (different depths).

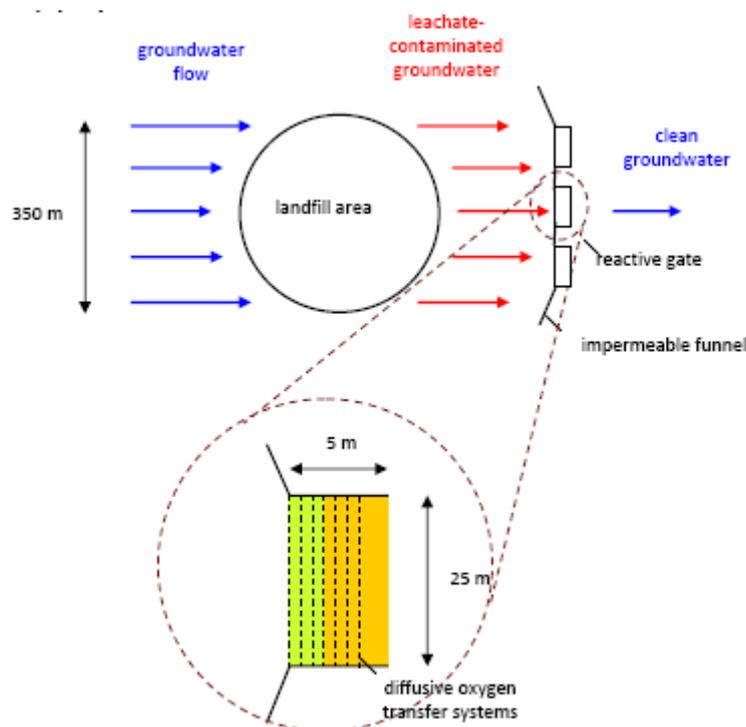


Figure 1: Top view of hypothetical groundwater pollution

COST COMPARISON

Rough estimates were made for the installation, operational and monitoring costs for both systems. Site characterization and design costs were estimated at 15% for the multibarrier system, and 10% for the P&T system. Because of the hypothetical nature of the case study, a number of costs were very difficult to assess. Some costs that were not included are:

- Contingency measure costs;
- Replacement costs for reactive media, pumps, etc.

The obtained costs were discounted using a discount rate of 5%, over a period of 50 years. The results (see Table 1) indicate that, as expected, installation costs are higher but operational costs are lower for multibarriers compared to P&T systems. This results in multibarriers becoming cost efficient for long-running remediations. For the hypothetical case study, the required period is 10 years.

It must be stressed that the cost calculations performed for this hypothetical case study are very rough estimates. For real applications, site specific cost estimates will be needed.

Table 1: Results of cost comparison

	Total 5 years	Total 10 years	Total 15 years	Total 20 years	Total 50 years
Pump & Treat	1.792.367,98 €	2.280.558,04 €	2.663.067,73 €	2.962.774,08 €	3.796.565,00 €
Multibarrier	2.037.874,65 €	2.245.447,93 €	2.408.087,03 €	2.535.519,02 €	2.890.038,15 €

MARKET STUDY

As shown above, multibarriers can be cost efficient for long term groundwater remediations, if the necessary preconditions are present.

Some important preconditions are:

- Depth of groundwater table and groundwater pollution: especially for multibarriers installed by excavation, costs and feasibility of the installation are strongly influenced by the groundwater depth. As a guideline, a maximum depth of 10m is proposed.
- Hydrology: homogeneity of the aquifer, presence of impermeable layers, groundwater velocity are all factors that will determine the feasibility and costs of multibarrier systems
- Time: multibarriers are passive and hence slow systems. For situations where rapid treatment of pollution is needed, multibarriers will therefore not be a viable option
- Regulatory requirements: these will likely be very stringent as long as multibarriers are a new technique, but will hopefully become similar to requirements for traditional systems with increasing experience.
- ...

Based on these preconditions, the potential market for multibarrier applications is mainly situated in the following fields:

- Abandoned landfills
- Industrial sites with historical pollution
- Acid mine drainage sites

The potential market for multibarriers in these fields is enormous. For example, in the EU alone, approximately 150.000 abandoned landfill sites exist, with associated remediation costs estimated at 40-50 billion Euro (Loesberg, 2007). If multibarriers could be used for only 1% of these sites, the potential market value is 500 million Euro. For industrial sites and acid mine drainage sites, the potential market is similar.

CONCLUSIONS

A multibarrier is a tailor-made combination of permeable reactive barriers and reactive zones for passive in situ treatment of groundwater pollutions. To determine if multibarriers are a viable option for a specific site, a detailed site characterization is necessary. Multibarrier design will depend on the information gathered during this assessment, such as groundwater pollution characteristics, hydrogeological, geochemical, microbial and geotechnical data, as well

as the site's physical setting. Other factors that may be of importance are regulatory or land use requirements, as well as the desired time frame for remediation.

Compared to conventional P&T remediation, installation costs for multibarriers are higher whereas operational costs are lower. Therefore multibarriers become cost-efficient for long-running remediations, typically in the order of 10 years or more.

Potential applications for multibarriers are mainly mixed groundwater pollutions from sources such as abandoned landfills, acid mine drainage or industrial sites. The worldwide market for these applications is considerable, with market value of several million Euros.

Regulatory requirements are likely to be more stringent for multibarriers in the near future. With increasing applications, and increasing knowledge about long term reliability, these requirements will hopefully become similar to those for traditional treatment systems.

REFERENCES

OVAM, March 2005. Code van goede praktijk: Reactieve ijzerwanden.

Kjeldsen, P., Barlaz, M. A., Rooker, A. P., Baun, A., Ledin, A., Christensen, T. H., 2002. Present and long-term composition of MSW landfill leachate: a review. *Crit. Rev. Environ. Sci. Technol.* 32: 297-336.

Van Nooten, T., L. Diels, L. Bastiaens., 2009. A laboratory-scale mixed multibarrier for removal of ammonium from landfill leachate contamination. *International Journal of Environmental Engineering* – accepted for publication.

Loesberg, C., 2007. SUFALNET – Sustainable Use of Former and Abandoned Landfills. Presented at Final SUFALNET conference, Brussels, Belgium, 14 November 2007.

Multidisciplinary approaches for in-situ remediation of complex groundwater pollution: Experiences from the field

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ABSTRACT

Verhoeve Groep is an international contracting company specialized in the treatment of complex groundwater pollutions by combining a broad range of (in-situ) techniques. The company is widely experienced in various in-situ chemical oxidation (ISCO) applications, including the patented Perozone[®] technology, for removal of source and plume zones of organic contaminants. This technology relies on specially designed laminar spargepoints[®] for the subsurface injection of tiny and highly reactive ozone bubbles surrounded with a coating of hydrogen peroxide. Source zone removal is often followed by biological plume treatment (BIO) using biological reactive zones.

In this paper, a Dutch full-scale field case is presented, where Perozone[®] as a chemical oxidation technique was followed by the installation of an anaerobic biological reactive zone (ISCO-BIO) for the removal of trichloroethylene (TCE) at a former industrial area. The results indicate that combining both treatments was an effective approach to reduce TCE and its degradation products to concentrations below the intervention values. Despite the highly oxidizing soil conditions induced by Perozone[®], reducing conditions could be rapidly reached by injection of two carbon sources. Injection of V-CS[®], a carbon source designed by Verhoeve Groep and TNO/Deltares, resulted in a continuous and long-lasting delivery of electrons.

INTRODUCTION

Preservation and remediation of groundwater resources are currently of major importance as human activities need ever-more clean water resources. On a European level, the EU soil framework directive requires that in 2015 groundwater quality in the EU member states meets a good chemical condition, without negative effects on surface water and terrestrial ecosystems. In real terms, this implies that thousands of sites are considered for remediation. These developments are important drivers for the development of groundwater remediation technologies. The extensive size and complexity of many contaminated sites often require a multidisciplinary in-situ remediation approach to reach clean-up goals in a cost-effective way.

Verhoeve Groep is an international contracting company with a broad experience in the treatment of complex groundwater pollutions by combining a wide range of in-situ techniques. Source zones of organic contaminants such as chlorinated hydrocarbons (e.g. PCE, TCE), petroleum compounds (e.g. BTEX) and mineral oil can be removed with in-situ chemical oxidation (ISCO) techniques (Huling and Pivetz, 2006). Verhoeve Groep is licensed to use the patented Perozone[®] technology (Kerfoot, 2003), and applies this advanced ISCO technique in addition to other techniques such as injection of Fenton's reagent and permanganate. Perozone[®] technology relies on specially designed laminar spargepoints[®] for the subsurface injection of tiny ozone bubbles surrounded with a coating of hydrogen peroxide (Figure 1). The gas bubbles exhibit a very high reactivity and the gas injection technique ensures a better oxidant spreading compared to liquid oxidant injections.

Verhoeve Groep frequently combines source zone removal with biological plume treatment (BIO) using biological reactive zones. Next to the use of common and commercially available groundwater additives for biostimulation, Verhoeve Groep recently developed a new substrate for anaerobic reductive biodegradation, called V-CS[®], in cooperation with TNO/Deltares (the Netherlands). V-CS[®] combines easily degradable with long-lasting carbon sources to ensure a continuous and prolonged delivery of electrons during reductive biodegradation treatments.

In this paper, a Dutch full-scale field case is presented, where Perozone[®] technology was followed by the installation of an anaerobic biological reactive zone (ISCO-BIO) for the removal of TCE at a former industrial site.

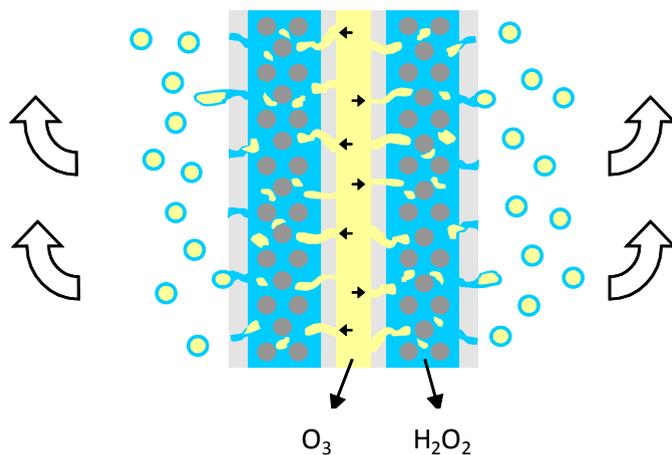


Figure 1: Schematic overview of the subsurface injection of tiny ozone bubbles surrounded with a coating of hydrogen peroxide via laminar spargepoints®.

TECHNICAL ASPECTS

Site description

The soil remediation project described in this paper took place at a former industrial site in Tilburg, the Netherlands. The site was contaminated with TCE due to leakage of basement storage tanks. In the late 80's, the contaminated soil was excavated to 4 m bgs, under buildings which were still uninhabited at that time (Figure 2).

The excavation was followed by more than 10 years of pump-and-treat of which the efficiency stagnated due to the presence of DNAPL. Residual contamination was left in a soil volume of 23000 m³, with maximum TCE concentrations in ground and groundwater of up to 150 mg/kg DS and 16 mg/L, respectively.

The soil to be treated consisted of alternating layers of fine sand and humic sand (4.0-10.3 m bgs) with an underlying peat layer (10.3-11.5 m bgs). The groundwater level varied around 3 m bgs.

Remediation concept

The aim of the remediation project was to reduce the contaminant concentrations to below the intervention value within 5 years. In a first stage, Perozone® technology was applied to mobilize and oxidize the bulk of the TCE contamination with the aim to reduce the groundwater concentrations to <1 mg/L. A multiple-phase extraction (MPE) system was used to support the ISCO approach by extracting pure product that was mobilized by the Perozone® treatment.

A second stage involved the installation of a biological reactive zone as a polishing step. Two substrates, i.e. protamylasse and V-CS®, were injected via the MPE filters to stimulate anaerobic dechlorination of residual TCE. The aim of the biological treatment was to reduce the concentrations of TCE, DCE and VC to <500 µg/L, <20 µg/L, <5 µg/L, respectively. Progress of the remediation was followed by sampling and analysis of groundwater from three monitoring wells (MW502, MW605, MW505) located in the contaminated source zone. All monitoring wells, injection filters and extraction filters are indicated on the schematic plan view presented in Figure 3.



Figure 2: Photographs showing the excavation of contaminated soil under uninhabited buildings.

RESULTS AND DISCUSSION

Perozone® treatment (ISCO)

For Perozone® treatment, 1500 kg ozone and 750 kg hydrogen peroxide were injected together in the contaminated soil between July 2007 and March 2008. The oxidants were dosed through 27 laminar spargepoints® which were spread in

the source zone comprising a soil volume of ~17000 m³ (Figure 3). The chemical oxidation treatment was followed by MPE between March 2008 and July 2008. In this period, 1675 m³ groundwater containing mobilized pure product was extracted through 37 MPE filters.

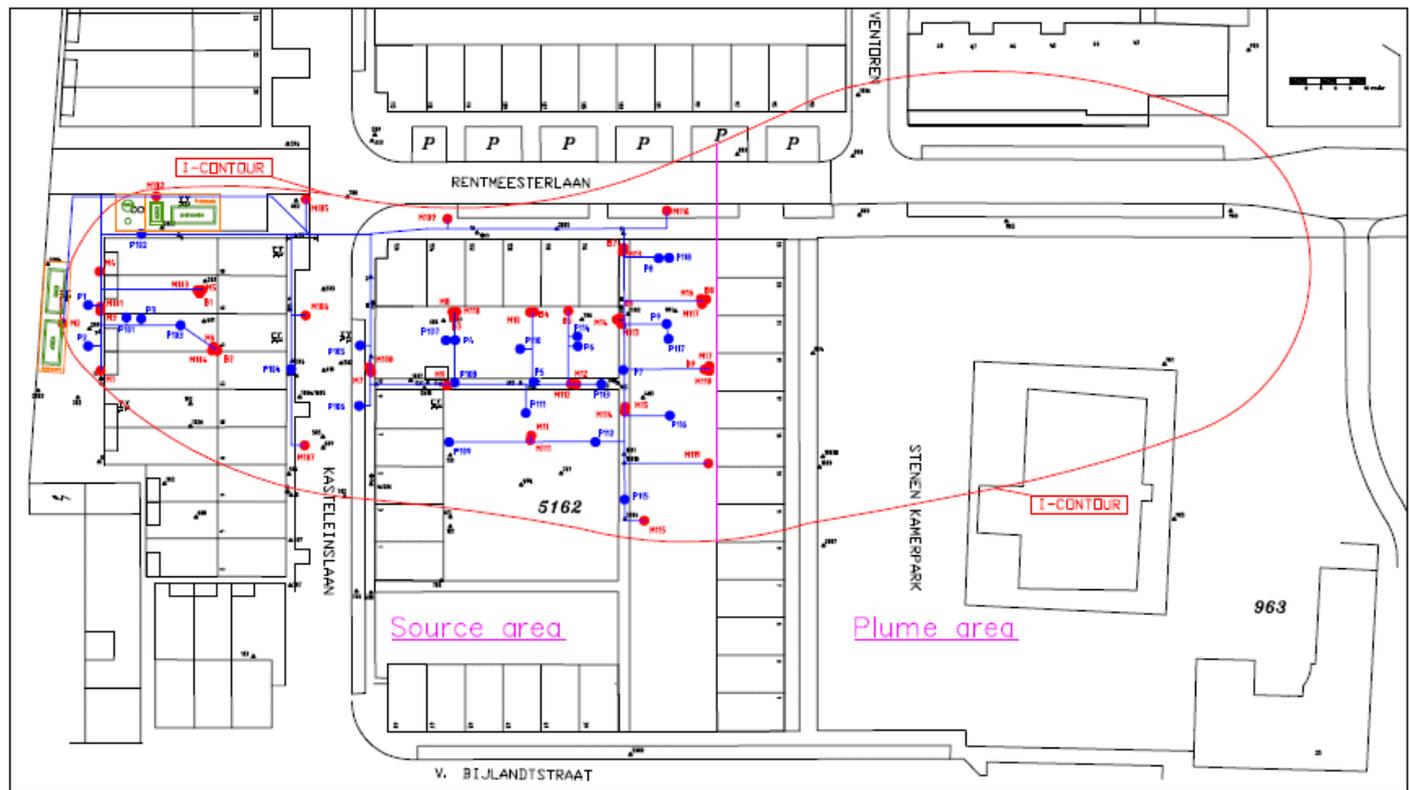


Figure 3: Schematic plan view of the contaminated area indicating the location of the process installations, laminar spargepoints® (red circles), MPE filters (blue circles), and monitoring wells (green circles).

Perozone® treatment clearly induced strongly oxidizing conditions in the contaminated soil, as indicated by the groundwater parameters. Dissolved oxygen (DO) concentrations increased from almost zero (anaerobic conditions) to elevated concentrations up to 15 mg/L (Figure 4a) and the redox potential increased to levels up to 290 mV (Figure 4b). The chemical oxidation treatment had a profound impact on TCE and DCE groundwater concentrations. In monitoring well MW502, TCE concentrations sharply decreased from 3400 µg/L to 250 µg/L (Figure 5a). DCE concentrations exhibited a similar trend. In monitoring wells MW505 and MW605, TCE and DCE concentrations were initially lower, ranging from 100 to 350 µg/L (Figure 5b and c). The concentrations increased as a consequence of Perozone® treatment, indicating mobilization of TCE and DCE which were presumably sorbed to strongly humic sand and peat layers. Mobilization of the contaminants was tackled by MPE performed immediately after the Perozone® treatment.

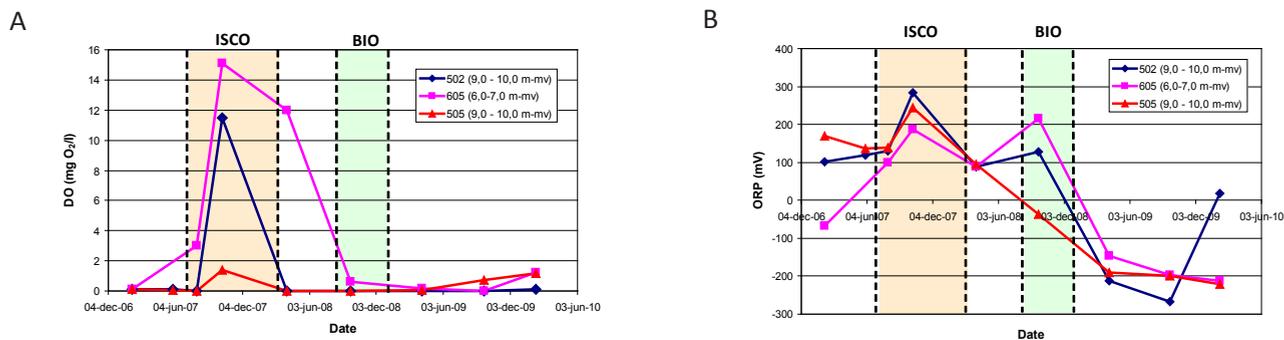


Figure 4: Overview of DO concentrations (A) and redox potential (B) of groundwater sampled from the monitoring wells.

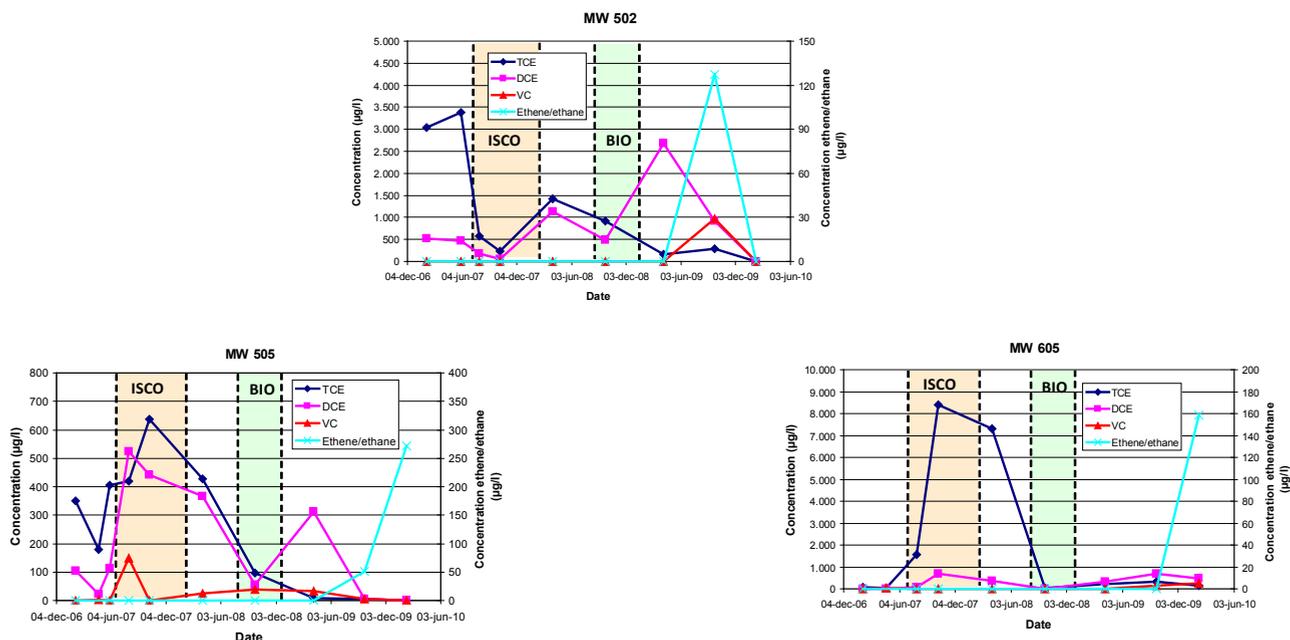


Figure 5: Overview of chlorinated hydrocarbon concentrations in groundwater sampled from the monitoring wells.

Biological treatment (BIO)

A biological reactive zone was created by injection of two carbon sources through the 37 MPE filters. In a first phase, 2500 kg protamylasse was injected in July and August 2008. Due to the preceding ISCO treatment and the resulting aerobic conditions, a significant portion of the substrate is consumed by aerobic respiration. After reaching anaerobic and reducing soil conditions, microbial reduction of other electron acceptors such as sulfate and ferric iron competes with microbial reductive dechlorination for carbon sources. Therefore, 9000 kg of a second substrate, V-CS[®], was injected in November 2008. V-CS[®] combines easily degradable with long-lasting carbon sources to ensure an continuous and prolonged delivery of electrons. To promote and accelerate complete reductive dechlorination of TCE, the soil was bioaugmented with groundwater rich in *Dehalococcoides ethenogenes* bacteria. The groundwater was extracted from the plume area and was injected together with nitrogen through the laminar spargepoints[®] to ensure a good spreading of the injectant in the treatment zone, similar to the Perozone[®] treatment.

Substrate injection rapidly induced reducing conditions, in the previously oxidized soil, as indicated by the decreased DO concentrations (almost zero) and redox potential (-150 to -250 mV) (Figure 4). Total organic carbon (TOC) concentrations in the groundwater increased to 400-1200 mg/L (Figure 6a). In March 2010, 16 months after the last substrate injection, TOC concentrations were still higher than 150 mg/L in monitoring wells MW505 and MW605, indicating a continuous and long-lasting effect of the substrates.

TCE concentrations were effectively reduced to <260 µg/L by microbial reductive dechlorination, which is below the remediation goal of 500 µg/L. Microbial degradation resulted in the formation of DCE and VC as degradation products. These products, of which VC is even more toxic than TCE, were subsequently reduced to harmless ethene, indicating complete dechlorination. Q-PCR analysis of DNA obtained from groundwater samples revealed a strong increase in *D. ethenogenes* species (up to 5 × 10⁵ gene copies per mL groundwater) (Figure 6b), which is related to the observed complete reductive dechlorination.

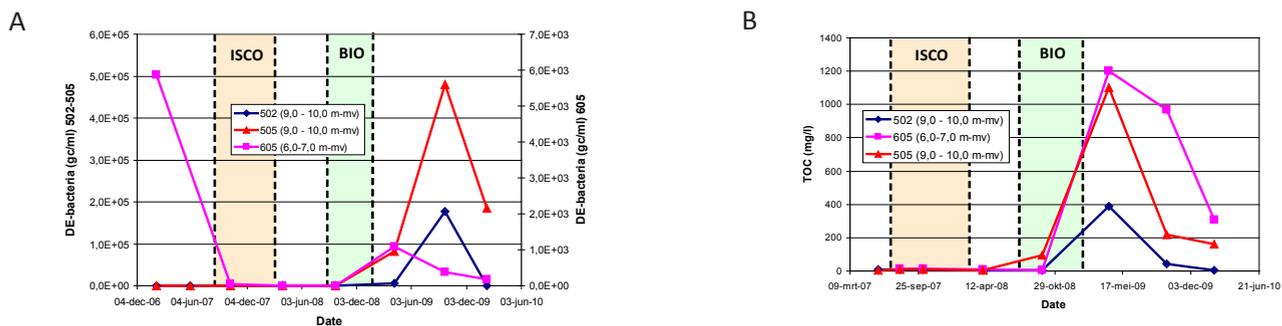


Figure 6: Overview of TOC concentrations (A) and *D. ethenogenes* gene copy numbers (B) of groundwater sampled from the monitoring wells.

CONCLUSIONS

The contaminated area was effectively remediated in-situ by the combination of a chemical and microbiological approach. In a first stage, TCE was oxidized using Perozone® technology. MPE was used to extract TCE pure product that was mobilized from strongly humic sand and peat layers as a consequence of the chemical oxidation. In a second stage, an anaerobic biological reactive zone was created by injection of carbon sources and groundwater rich in *D. ethenogenes* through the Perozone® and MPE filters which were used during the first stage.

The results indicate that reducing conditions were rapidly induced and that injection of V-CS® resulted in a long-lasting delivery of electron. Biostimulation and bioaugmentation resulted in a substantial enrichment of *D. ethenogenes* species and a complete reductive dechlorination. TCE and its degradation products were effectively reduced to concentrations below the intervention values.

ACKNOWLEDGEMENTS

We thank TNO/Deltares for cooperation in development of the V-CS® substrate, which involved both laboratory-scale and field testing.

REFERENCES

- Huling, S.G., Pivetz, B.E. 2006. In-situ chemical oxidation. EPA Engineering Issue, EPA/600/R-06/072, 1-60. Kerfoot, W.B. 2003. Groundwater and subsurface remediation. U.S. Patent Number 6,582,611.

Retrofitting an existing pump and treat system into a sustainable DNAPL remediation with a combined bioremediation and pumping system

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Remediation of chlorinated solvents is often challenging because of the presence of pure product in source zones. The persistence of DNAPL in the subsurface leads to a long remedial timeframe. In the last decade different techniques have been developed for more aggressive source treatment like chemical and thermal technologies. These technologies have proven their efficiency but generate high costs in the beginning of the project. As an alternative, enhanced reductive dechlorination (ERD) can be used. ERD is a well known technique for plume treatment, but applications in DNAPL source zones are limited. With ERD it is possible to significantly reduce the remedial timeframe of the remediation by enhancing dissolution from pure product to the groundwater, hereby making more contamination available for degradation by bacteria.

On a site in Northern Belgium a remedial system with pump and treat has been operated since 2002. The system has been able to significantly reduce contaminant concentrations in the plume but concentrations in the source zones remained high. The pump and treat system was able to contain the plume but would have to be operated for a very long time (over 30 years).

ERD has been chosen to accelerate cleanup to reduce remedial timeframe. Four ERD-barriers perpendicular to groundwater flow have been installed on the site. Downgradient a hydraulic barrier was kept in operation to contain the contamination. System construction was challenging because of the presence of an active facility on top of the contamination. By the installation of an automated injection system, activities on the site can go on during the remediation with minimal site interruption.

The system has been operating since September 2008 and mother product concentrations in the source zones have been reduced significantly. Concentrations of dichloroethene and vinylchloride have increased to concentrations much higher than would be expected on a molar basis, indicating that ERD is accelerating cleanup in the source zones. Downgradient of the source zones, complete transformation to ethene has occurred within a 1 year timeframe. It is expected that the site will be cleaned up within the 5 year time frame.

With this change in technology, we could significantly reduce the environmental footprint of the remediation:

- **Timeframe:** The reduction of the timeframe has an effect on the reduced use of resources (less water pumping, less use of electricity); the injection strategy to inject high volumes has a significant impact on the reduced remedial timeframe.
- **Use of natural resources:** Treated water from the hydraulic barrier was used for reinjection and addition of a carbon source. A waste product from sugar refinery (molasses) was used as a carbon source.
- **Maintenance and power usage:** due to the reduced timeframe power usage and maintenance of the total project have been reduced.

The application of ERD for source treatment also has cost advantages. Whereas there is an additional cost for the application of ERD, total project costs are reduced due to the decreased timeframe. Compared to more aggressive source zone treatment technologies like chemical oxidation or thermal treatment, the cost for ERD is lower.

At the conference, the results of DNAPL remediation with ERD, the site remediation strategy and a comparison between the environmental footprint of the previous pump and treat system and the current bioremediation system will be presented.

Session 6

Field trip to the landfill Hooge Maey (Antwerp)

MULTIBARDEM: a LIFE demonstration project of multibarriers as a sustainable approach for groundwater remediation

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MULTIBARDEM is an EU financed demonstration project (LIFE) that started November 1st 2006 with 7 project partners (VITO-Belgium, IHM-Belgium, Markis-Denmark, LFU-Austria, WPA-Austria, UBA-Austria and MWH-Belgium). The general objective of the MULTIBARDEM project was the demonstration of a multibarrier as a sustainable solution for preventing mixed contaminants spreading in the groundwater. More specifically, the MULTIBARDEM-Life project aimed the demonstration of Multibarrier concepts at two different locations with different geological situations. A multibarrier consists of a tailor-made combination of different types of permeable reactive barriers and reactive zones in which pollutant removal processes are active. The groundwater flows through the system during which the pollutants are degraded or immobilized. As such multibarriers prevent further spreading of the pollution to the downstream area. During the project, for a landfill site (Hooge Maey) in Belgium and an industrial site (Altlast 024) in Austria, multibarrier concepts were developed. The performance of the different multibarrier concepts was verified through lab scale simulations of the different multibarrier parts and their combination. For each site, promising multibarrier concepts were up-scaled to a pilot test in the field, which was designed and dimensioned based on the results from the lab scale tests. The last part of the project was dedicated to monitoring of the pilot systems and a general cost-benefit analyses. The project ends summer 2010.

INTRODUCTION

Groundwater is the main source of drinking water in Europe. Contaminated groundwater is one of the major concerns for the European society in the beginning of the 21st century. Especially the Water framework Directive (and its daughter Directive on groundwater) states that the water and groundwater quality must be improved before the year 2015. Recently, *in-situ* treatment is becoming more interesting for aquifer treatment as the technology is developing and becoming more reliable and accepted. A very attractive *in-situ* concept on the one hand is the “**Permeable Reactive Barrier (PRB)**” technology in which a trench is made perpendicular to the groundwater flow. This trench is filled with a coarse material in which a pollutant removal process (biological, chemical reduction, sorption, ...) is induced to remediate the passing groundwater. On the other hand “**reactive zones (RZ)**” are also an interesting *in-situ* technology, where, locally, pollutant removal processes are induced by injection of slurries/liquid containing reactive or degradation stimulating products (without excavation).

Mostly, PRBs and RZs are designed to abate specific pollutants. However, in many cases polluted groundwater contains a mixture of both organic and inorganic contaminants. The abatement of such pollutant mixtures is not possible with a simple barrier/zone based on removal of the pollutants by either physico-chemical or biological way. However, such pollutant mixtures might be treated using a combination of different reactive barriers/zones. Such a combination is defined as a **Multifunctional Permeable Barrier (MULTIBARRIER)**. Such an approach requests the efficient synergistic interaction and compatibility of different pollutant removal processes, often of microbial and physico-chemical key-components of the system. The MULTIBARRIER-concept was developed in the 5th Framework programme under the contract number QLK3-CT-2000-00163 and proven to be successful (Dries et al., 2005, Bastiaens et al., 2007). The objective of this LIFE-project was to demonstrate the MULTIBARRIER at 2 different locations in Europe with different partners. Therefore the following activities were planned:

- Evaluation of the different problems related to mixtures of pollutants at both sites.
- A challenge for the scientific partners was the design of a multibarrier concept for each site and to verify the performance of the concept via feasibility tests (lab-scale batch & column degradation experiments).
- In collaboration with the consultants these results were used to make a final design of the field scale MULTIBARRIER concepts taking into account the local situations concerning pollutants and (hydro)geology.
- Implementation 3 pilot demonstration in the field.
- Monitoring of the pilot systems to evaluate the performance of the system and the cost-benefit of a multibarrier relative to conventional pump-and treat.
- Dissemination of the results.

Project partners in the MULTIBARDEM LIFE project were VITO (Belgium), MWH (Belgium), IHM (Belgium), LFY (Austria), WPA (Austria), UBA (Austria) and Markis (Denmark). The project was coordinated by VITO.

SELECTED SITES & TESTED MULTIBARRIER CONCEPTS

Within MULTIBARDEM Multibarrier concepts (see figure 1) were developed for the following locations with different geological situations.

Location 1: Hooge Maey in Antwerp (Belgium) - Landfill site;

Location 2: Altlast site 024 in Austria – Industrial site.

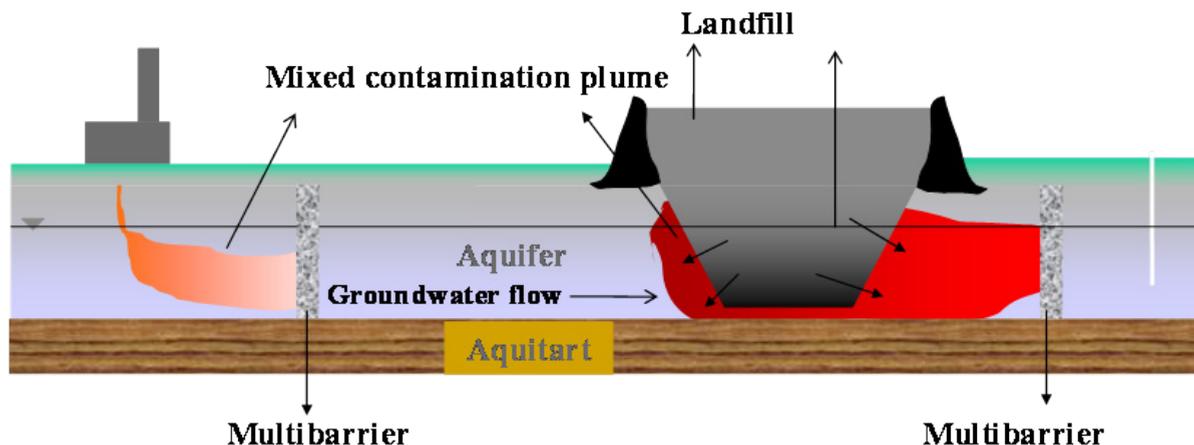


Figure 1: Schematic overview of 2 multibarrier-applications.

Landfill Hooge Maey (Belgium)

At the landfill, the water to be treated contained leachate, which is a complex mixed pollution. The main compounds of concern were ammonium, COD and AOX. The following pollutant removal processes were identified for this case:

- biological processes for removal of ammonium (nitrification & denitrification);
- abiotic processes to reduce concentrations of AOX, COD (sorption on activated carbon), and;
- abiotic removal of remaining ammonium & ion exchange on clinoptilolite).

Lab scale experiments showed (1) that all these pollutant removal processes were active at groundwater temperature (12°C) and (2) that a combination of these processes were suitable to reduce the pollutant levels below the required limits.

Two pilot systems were installed. Pilot 1 (MULTIBARRIER1) is a sequential multibarrier consisting of 5 different parts in which ammonium is biological removed via nitrification/denitrification processes, while AOC and COD are removed by sorption. In addition a clinoptilolite buffer-system for abiotic removal of ammonium (ion exchange) was included. The multibarrier concept was installed in a 9 m long container which was partially installed in the subsurface (Figure 2). Via a controlling unit, groundwater was pumped through the system and oxygen and a carbon source (butyrate) were added.

The second multibarrier (MULTIBARRIER2) was designed to treat the same water as multibarrier 1, and consisted of 3 sequential parts, being (1) sorption part to remove AOX & COD, (2) an aerobic biological nitrification part, and (3) anoxic denitrification part. It was intended to be an improved, simplified and cheaper version of multibarrier 1. A vertical concept was designed. Multibarrier 2 was installed next to multibarrier 1, and was controlled by the same controlling unit (figure 2).



Figure 2: Pilot multibarrier systems installed at the landfill Hooge Maey (Belgium).

Results of the lab scale tests and field test were published by (Van Nooten et al., 2008, 2010, PRB/RZ-2010).

Industrial site Altlast 024 (Austria)

The groundwater at the Austrian site contains a mixture of chlorinated hydrocarbons. The higher chlorinated compounds TeCE and 1,1,1-TCA are better degradable under anaerobic conditions, whereas 1,2-cis-DCE, 1,1-DCA and TCE are degradable aerobically as well or even better.

The following two multibarrier concepts were worked out to create a combination of aerobic and anaerobic zones, which is required to degrade the present mixture of chlorinated compounds: (1) pulse dosing of carbon source in the subsurface to create moving aerobic/anaerobic conditions via microbial oxygen consumption (Figure 3, right), and (2) Creation of anaerobic flow paths again by microbial oxygen consumption, but here with installing a solid slow releasing carbon source in some part of a PRB (Figure 3, left).

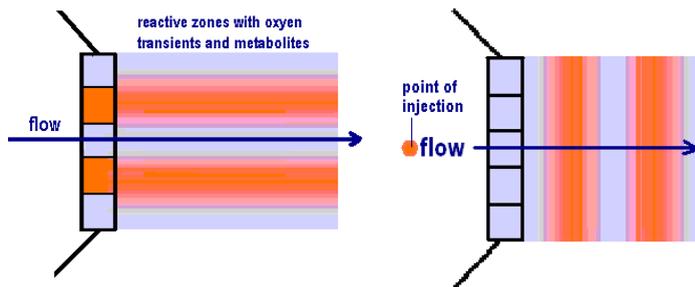


Figure 3: Creation of aerobic and anaerobic flow paths through a barrier by filling different materials into gate cells and/or different nutrient supply (left), and creation of fluctuations in oxygen concentration (concept of moving zones) by intermittent dosing of an energy source (right).

Both concepts were tested at lab scale and in the field and results were reported by Pümpel et al (PRB/RZ-2010).

CONCLUSIONS

Within the multibarrier project, tailor made multibarrier concepts were designed and tested for 2 different geological situations with a diverse groundwater pollution. Via lab scale experiments, the identified potential pollutant removal processes were verified and optimal combinations of the different pollutant removal processes in the multibarrier could be deduced. These tests were also used to derive kinetic parameters which are required to dimension the pilot scale tests. The step from lab scale to pilot scale testing was found very useful to evaluate the technical and economical feasibility of the technology, and to get a better idea of administrative issues required by local authorities. In general, the study indicated that multibarriers are technical feasible for a variety of situations, a tailor-made site-specific design is however recommended. At a short term, multibarriers are more expensive due to higher installation costs,

but at the longer term they become economically more favourable than conventional pump & treat technologies. To install multibarriers, support from the authorities is needed. The project is ending this summer and final conclusions will be formulated and distributed via our website www.Multibarrier.vito.be.

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REFERENCES

- L. Bastiaens, Q. Simons, J. Zwaenepoel, B. Meyns. **2007**. In-situ groundwater remediation of an MTBE-containing mixed pollution via a sequential PRB/RZ-approach. Proceedings 3rd International Symposium on Permeable Reactive Barriers and Reactive Zones, 8-9/11/2007, Rimini (Italy) - p. 19-22.
- Dries, J., L. Bastiaens, D. Springael, S.A. Agathos, L. Diels. Combined removal of chlorinated ethanes and heavy metals by zerovalent iron in batch and continuous flow column systems. **2005**. *Environ. Sci. Technol.* 39: 8460-8465.
- Pümpel, T., Pümpel, E., Jussel, B., Ausserleitner, M., Schramm, C., Hüther, T., Alge, G., Kolesar, C. .Biodegradation of CHC in an aerobic aquifer: Active nutrient dosing versus passive funnel & gate treatment. PRB/RZ-**2010**.
- Van Nooten, T.; Diels, L.; Bastiaens, L. Design of a multifunctional permeable reactive barrier for the treatment of landfill leachate contamination: laboratory column evaluation. *Environ. Sci. Technol.* **2008**, 42, 8890–8895.
- Van Nooten, T.; Diels, L.; Bastiaens, L. A laboratory-scale mixed multibarrier for removal of ammonium from landfill leachate contamination. (accepted for publication in *Int. J. Environ. Eng*, **2010**.)