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Evaluation
of the PhD dissertation of Mr Franklin Obiri-Nyarko, MSc, entitled:
'Simultaneous removal of heavy metals and BTEX from contaminated groundwater by Permeable Reactive Barriers'

Promoter:
Associate professor, dr hab. inż. Jolanta Kwiatkowska-Malina

This evaluation report was prepared based on the decision of the Faculty Board of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Krakow from 29 September 2014.

Justification of the dissertation topic importance

Permeable Reactive Barrier systems are an important tool to treat polluted groundwater or to protect clean groundwater from pollution. These remediation systems have a lot of advantages above other remediation systems. Practical experience is available with these remediation systems, however this experience is limited. There is a strong need for improvement of existing and further development of innovative Permeable Reactive Barrier systems. The thesis addresses a very important environmental problem of groundwater contamination. Compared to the literature information and the state-of-the art information the thesis provides relevant additional scientific and technological information. The thesis can also be considered as a useful handbook in this interesting scientific and technological field.

Characteristic and overall evaluation of the dissertation

The evaluated thesis consists of 7 chapters, including a general introduction and a general summary, as well as summary in Polish and 5 appendices (in total 194 pages). The text is supported by 38 figures and 26 tables. The extensive bibliography

consisting of more than 400 references, mainly in English, with most of them from last years (2000-2013) is above an average concerning PhD dissertations, and it indicates that the candidate has got acquainted with the state of the art of the subject of his thesis.

Chapter 1

Chapter 1 starts with a short introduction of the environmental problem of contaminated groundwater and the need to protect groundwater water from contamination. A short introduction of the application of Permeable Reactive Barriers which may offer a cost-effective alternative in the abatement of groundwater polluted with BTEX and heavy metals, is given. The aim and topic of the thesis is given. Research objectives and research hypotheses are mentioned. The outline gives a clear overview of the various aspects of the research, the content of each chapter and the relationship between these chapters.

Chapter 2

In this chapter, an overview of Permeable Reactive Barriers including the current state of the technology, the merits and limitations, the reactive media used so far and the mechanisms employed to transform or immobilize contaminants is presented. The chapter also looks at the design, construction and the long-term performance of Permeable Reactive Barriers.

The chapter is clearly written and discusses the history of the remediation technology of polluted groundwater by means of reactive barrier materials, the advances and innovations obtained with this process since the early nineties and the two types of multi-barrier systems (sequential multi-barrier system and simultaneous multi-barrier system). Attention is also given to the costs, the complexities in the design of such multi-treatment systems, the difficulties in monitoring them, the use of geochemical modelling tools that can be used to study and predict the possible mineral phases that may be formed, and changes in geochemical parameters. Also advantages and limitations of the Permeable Reactive Barrier technology are discussed. The various reactive media used in Permeable Reactive Barrier systems for removal of various types of pollutants from groundwater are described in detail. Attention is also given to the design of these systems.

In general it can be concluded that this chapter provides a very well-balanced overview of the key aspects of Permeable Reactive Barrier systems for treating polluted groundwater and the state of the art of this treatment system. It can be considered as an appropriate basis for considering this system for practical application and for set up of research into the improvement of existing reactive barrier systems and the development of new systems.

This chapter is based on a paper published as: Obiri-Nyarko et al., (2014). An overview of permeable reactive barriers for in-situ sustainable groundwater remediation, Chemosphere 111: 243-259.

Chapter 3

Chapter 3 deals with a feasibility study on sustainable remediation of BTEX and heavy metals contaminated groundwater using Permeable Reactive Barrier systems.

In this chapter the way how the technical feasibility of applying a Permeate Reactive Barrier system as a remedial option could be determined for two completely different polluted sites, are presented. Historical activities resulted in the contamination of the groundwater at these sites, and Permeable Reactive Barrier has been considered as one of the remedial options. The chapter clearly describes the assessment methodology consisting of a site description, the hydrogeological conditions at the site, the concentration of the contaminants, the evaluation of the occurrence of natural attenuation. Most attention is given to the aspect of the natural attenuation where a few assessment methods are discussed. These assessment methods were applied to the two sites.The assessment shows that it is feasible to use Permeable Reactive Barrier system to remediate the contaminated groundwater at one site, but not at the other site.

The chapter is clearly written and straight forward, the illustrations are clear. It is an interesting illustration how such a feasibility study can be executed, however, the innovative character is limited.

This chapter is a compilation of three book chapters that have been published.

Chapter 4

Chapter 4 deals with a screening procedure of reactive materials for permeable barriers to treat groundwater contaminated with benzene and Pb based on batch

tests. The reactive materials investigated in this study were Zero Valent Iron (ZVI, as a control), and a number of other materials: clinoptilolite (zeolite), brown coal, compost, mulch, and diatomaceous earth. These materials are locally available, inexpensive and can be obtained in large quantities. This will help reduce the general costs of the technology. Based on an assessment of their properties it was presumed that a mixture of some of them will have good removal properties for these components and may probably also improve the hydraulic performance of the Permeable Reactive Barrier system. The laboratory batch studies performed allow to screen the performance of individual reactive materials and mixtures of reactive materials for the removal of benzene and Pb from groundwater.

The chapter is very well organized. The experiments are well motivated and elaborated. Relevant literature information is included both in the motivation and the set-up of the experiments and also in the explanation of the results. Figures, equations and tables are in general clear. Some aspects which might be relevant in the evaluation of the long-term behaviour of a Permeable Reactive Barrier are discussed but have not been investigated experimentally, as can be understood looking to the very broad research program. However, a clear motivation of the chosen treatment time in the batch experiments has not been given. The possibility of biodegradation of benzene is discussed, however, taking into account the very specific conditions necessary for biodegradation, it is not very clear why biodegradation is expected in the short-term batch experiments.

This chapter is a modified version of two papers: Obiri-Nyarko et al. (2014), Removal of lead and benzene from groundwater by zeolite and brown coal: isotherm and kinetic studies, in: Environmental Pollution and Remediation (in press), and is also submitted as: Obiri-Nyarko et al. (2014), Screening reactive materials as possible permeable barriers to treat Pb and benzene contaminated groundwater, Water Science and Technology (under review).

Chapter 5

Chapter 5 deals with evaluating materials for Permeable Reactive Barriers to treat groundwater contaminated with benzene and lead. In this chapter, continuous laboratory column experiments are presented that were performed to evaluate the performance of the reactive materials selected in Chapter 4 of this thesis. The effect

of the reactive materials on pH, their hydraulic performance and effectiveness in the removal of benzene and Pb under dynamic conditions was investigated.

The column experiments are clearly described. The major parameters governing the transport and fate of water polluted with Pb and benzene through the column with reactive materials, such as: advection, hydraulic conductivity, molecular and turbulent diffusion, adsorption, desorption, retardation, biodegradation, tortuosity, pore size distribution and precipitation reactions, are briefly discussed. In fact all relevant parameters are considered. Main results are presented in clear figures. The obtained experimental results are discussed and related to the physical, chemical and biological phenomena that might play a role. From the results presented in this chapter the effectiveness of the reactive materials for removal of Pb and benzene from polluted water, the mechanisms of the removal process and the hydraulic performance of the materials could be derived. Based on these characteristics a clear comparison of the performance of the various barrier materials are made. The chapter shows that an appropriate performance of column experiments is a suitable tool for the selection of reactive barrier materials.

Chapter 6

In this chapter, the need and possibility of using numerical models to predict the long-term performance of Permeable Reactive Barriers is discussed. Laboratory batch and column studies seldom allow for sufficient understanding of long time behaviour of the relevant process that occur in Permeable Reactive Barriers systems. A number of geochemical models capable of simulating long-term geochemical phenomena are available. One of these models is PHREEQC that has been focused on zero valent iron (ZVI). In this chapter column experiments executed with zeolite as the permeable reactive material and Pb as the pollutant are described. The possibility of using PHREEQC to predict the transport of Pb through a Permeable Reactive Barrier of zeolite has been investigated. Using relevant data regarding the characteristics of the column experiments, the chemical reactions that occur, thermodynamic data and transport parameters the possibility of using PHREEQC for the prediction of the short and long-term performance of a zeolite Permeable Reactive Barrier for removal of Pb was illustrated. It was found that the theoretical predictions are comparable with the results of accelerated column experiments. The research presented in this chapter is clearly described and convincing.

Chapter 7

Chapter 7 gives a brief summary and addresses all aspects that have been studied in this research work. It presents a short overview of the main conclusions and gives a set of recommendations. In general it can be concluded that the brief summary gives a well–balanced finalization of this PhD thesis.

Evaluation of the results and most important achievements of the dissertation

The thesis provides a very useful overview of almost all aspects relevant for the assessment of the application of Permeable Reactive Barrier systems. Besides it shows very well how to screen appropriate reactive materials that might be applied and how to use simulation models for assessment of the long-term behavior of Permeable Reactive Barrier systems. It described simple batch and continuous lab-scale experiments that can be used for such a screening. It gives also a clear elaboration about the way the simulation tool PHREEQC can be used. Literature information is very well integrated and used in both the theoretical and experimental part of the thesis. This is also shown by the intensive literature overview of Permeable Reactive Barriers. The scientific and technological significance of this thesis work is also illustrated by the number of publications in scientific journals and in conference proceedings.

Critical comments

Almost all relevant aspects are addressed in the thesis. What is missing, is a somewhat more detailed discussion about four aspects indicated below.

- Biologically conversion of organic pollutants, such as benzene, in a Permeable Reactive Barrier system, is only briefly discussed in the thesis. Biological biodegradation requires very specific environmental conditions and is in general a very slow process. The required conditions strongly depend on the type of organic pollutant. Chlorinated hydrocarbons can also be converted in toxic intermediates. It is therefore hardly possible to assess the biodegradability of an organic component in short-term batch or continuous column experiments.

- The organic reactive barrier material such as compost can be partially biodegraded into CO_2 and H_2O, depending on the properties of the water to be treated. In that case the hydraulic conductivity can change and also the ab(d)sorption potential of the reactive material.
- Compaction of the reactive material may also influence the performance. What parameters influence the compaction?
- What might be possible tools to suppress turbulent diffusion and channeling in the Permeable Reactive Barrier systems?

It should be remarked that in the formulated aim of the thesis these aspects have not been mentioned explicitly. Therefore, the critical comment should primarily considered as missing aspects that might be addressed in future research on Permeable Reactive Barriers.

Conclusions

After analyzing the PhD thesis of Mr. Franklin Obiri-Nyarko I state the following:

- the provided dissertation is sufficient for its evaluation,
- the importance and actuality of the problem fully justify the adoption of the topic as the research and utility problem of the dissertation,
- the presented results are adequately interpreted and fully support the conclusions of the dissertation,
- the research goal was fully reached and research hypothesis proven,
- The PhD candidate has shown appropriate skills to perform independently scientific experiments,
- the overall quality of the thesis work can be qualified as good.

In summary, the study has shown that it is important to perform a feasibility study prior to the installation of a Permeable Reactive Barrier system. The study has identified a mixture of brown coal and compost as possible materials for the simultaneous removal of benzene and Pb in a Permeable Reactive Barrier system and provided insight into the mechanisms utilized thereof. The simulation model PHREEQC was shown to be useful in the prediction/interpretation of the

experimental results and the long-term performance assessment of the Permeable Reactive Barrier system.

From a theoretical point of view it can be concluded that the PhD thesis addresses/discusses, often in much detail, the various aspects which are relevant in the assessment of the application of Permeable Reactive Barriers for the treatment of polluted groundwater. The theoretical evaluation gives a lot of background information regarding these aspects. The experimental part is primarily focused on the removal of BTEX and Pb from polluted groundwater by means of a Permeable Reactive Barrier system. Experimental results and theory are clearly integrated. Besides a lot of theoretical and practical information is given.

The innovative character of the thesis is mainly expressed by the batch and continuous column experiments that can be executed to assess the feasibility of a reactive barrier material. The thesis contains also an extended literature review about Permeable Reactive Barrier systems.

Some aspects that have been addressed hardly or only briefly are biological degradation of organic pollutants, compaction of the reactive material, chemical or biological degradation of an organic reactive material and suppressing turbulent diffusion and channeling in the Permeable Reactive Barrier systems.

Considering the above I conclude that the dissertation of Mr Franklin Obiri-Nyarko entitled: 'Simultaneous removal of heavy metals and BTEX from contaminated groundwater by Permeable Reactive Barriers', fulfills the requirements of PhD dissertations, because of its high scientific and application value in the area of environmental engineering and geochemistry. I will recommend the thesis to be the subject of the public defense.

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