

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:
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Justification of the dissertation topic

The topic of this research is both timely and scientifically relevant. The development of sustainable remediation technologies to manage the complex and widespread problems of groundwater pollution is becoming increasingly important, to comply with EU and specific Member State environmental protection legislation. Remediation technologies should be robust in performance and versatile in design for application in different pollution contexts and hydrogeological settings. While the technology evaluated (permeable reactive barriers, PRB) is well known, it has to date been limited to specific contexts (pollutant groups) and a narrow range of reactive materials. The research in this thesis extends the potential of this technology concept more widely, by considering the utility of different low-cost waste materials for the *in situ* remediation of organic-inorganic contaminant mixtures. It addresses an important development gap in the design of existing PRBs.

Characteristic and overall evaluation of the dissertation

The thesis is presented as 7 chapters preceded by an abstract. The work includes a short introduction, literature review, 4 chapters of original experimental and modelling-based research, and conclusion with recommendations. A list of references cited and appendices is also provided.

Chapter 1 presents a short introduction to the project concept, with a clear aim and supporting objectives. These are appropriate, logical and coherent to achieve the project aim. Relevant hypotheses, which underpin the research programme, are presented. The thesis outline is conveyed as a flowchart, documenting the connection between all laboratory, field and modelling studies undertaken.

Chapter 2 is an extended literature review of the subject matter covered in the thesis. It provides a detailed appraisal of the state-of-the-art in PRB technology, considering operational aspects, material properties, pollutant attenuation mechanisms, construction and design issues and potential applications. While it is comprehensive in scope, it is repetitive and the information poorly organised in parts (e.g. section on aerobic vs anaerobic biobarriers). It could be focused more in certain sections to critical analysis of the literature rather than reporting of previous studies. References are not always presented in ascending order of date.

Chapter 3 presents a feasibility study for PRB implementation at two contrasting field sites, drawing on material previously published in 3 book chapters. The investigative procedures described and followed in the case studies are standard and not new, but the analysis is undertaken comprehensively and rigorously. It includes detailed evaluation of geological, hydrogeological and hydrochemical data from each site, with statistical analysis. These case studies have value in illustrating the technical basis for site assessment supporting remediation decision-making for PRB installation. While not novel, the work presented is confirmatory and necessary to support later lab and field studies. References cited in the text need to be re-ordered in ascending date order.

Chapter 4 describes laboratory batch tests to evaluate the suitability of reactive materials for use in a PRB to treat groundwater contaminated with benzene and lead (Pb). The work presented has been published/submitted for publication in international journals. The chapter discusses many heavy metals and the BTEX group of chemicals as potential groundwater contaminants, but the analysis focuses only on benzene and Pb. The justification for this is based on the toxicity, ubiquity and low water quality standards for these chemicals. A batch test methodology is described to screen and select specific materials for use on PRB designs. The batch tests evaluate the materials in isolation and as mixtures using test solutions of benzene and Pb prepared in de-ionised water. Results are used to assess the environmental compatibility of the materials, their selection in subsequent column studies and appropriate mixtures (ratios) for evaluation in the latter.

Chapter 5 explores the use of column studies to deduce the attenuation mechanisms and performance of the test materials for benzene and Pb removal. The column studies are a logical supplement to the batch tests described in Chapter 4, by providing observations of the influence of coupled geochemical-transport processes in a dynamic flow domain. This more closely represents the operational conditions expected in a field-scale PRB. Such tests provide important information on the effect of hydraulic residence time and other PRB design parameters. The design of the column tests is based on the batch test results, with use of similar material mixtures.

Chapter 6 describes numerical modelling studies conducted to interpret results from the column experiments using PHREEQC, a public domain reactive transport code. The material presented has in part been submitted for publication. The modelling is used to both understand the fate and transport of Pb in the column studies and explore the long-term performance of one test material (zeolite) in proposed PRB contexts. The modelling approach follows standard convention, by considering both transport and geochemical reaction modules to simulate the conceptual problem. It examines material properties, hydraulic characteristics and mineral phase transformations that may limit Pb concentration in a PRB composed of zeolite.

Chapter 7 provides a summary of the thesis, overview of key approaches and findings as they apply to each chapter, and general conclusions which lead to recommendations for further work. The content is coherent with the material presented beforehand in the individual chapters. The conclusions and recommendations are consistent and appropriate with the main findings of the work. These acknowledge some limitations of the current work and propose new research to address them in more detail. The reference list is comprehensive, up-to-date and relevant for the research undertaken.

Evaluation of the results and most important achievements of the dissertation

The results presented in the thesis have been collected in a methodical, diligent and comprehensive way, with due consideration of relevant supporting literature. There are several novel aspects of the research. This includes the combined approach of using

laboratory-scale batch and column tests with geochemical modelling to interpret the findings. This is a logical and informative strategy, which provides additional insight of the mechanisms controlling contaminant behaviour in the materials tested and supports up-scaling to a PRB design. The focus on testing various low-cost waste materials as possible candidates for reactive barrier designs is also novel, in that it ensures re-use of such materials in a highly productive way, supporting the development of sustainable remediation technologies for common groundwater pollution problems. The research is conducted at an empirical (rather than mechanistic) level, using mixtures of the candidate materials in laboratory batch and column experiments, to deduce relevant biogeochemical processes controlling the removal of benzene and Pb under different conditions and the hydraulic performance of the mixtures. The important achievements of the research are (i) the systematic evaluation of the properties and capability of several important industrial waste materials as substrates for sustainable PRB designs, (ii) the performance evaluation of these materials as mixtures in candidate PRBs using model contaminants (benzene and Pb) that commonly occur in groundwater impacted by industrial activities, (iii) detailed quantitative interpretation of the column studies using a numerical reactive transport code, (iv) the development of a rational basis (considering both experimental and modelling perspectives) to design a PRB from these reactive materials to treat such contaminants *in situ*, and (v) the publication of this research in peer-reviewed international journals, including a literature review on the state-of-the-art in PRB design and applications.

Critical comments

1. The research focuses only on benzene and Pb as representative organic and inorganic contaminants of a wide range of potential pollutants ("heavy metals" and "BTEX") which commonly occur in groundwater that must be treated by a PRB. This is a weakness of the work, since these compounds usually occur in mixtures with other similar compounds and also each other, as indicated in the objectives of the overall research and initial literature review. Their behaviour in groundwater is therefore influenced to a significant extent by interactions with other organic and inorganic compounds in such mixtures. The focus on only these two compounds must be justified and the limitations of the results clearly explained. This narrow focus potentially limits the application of the research to situations in which these two pollutants occur individually or as co-contaminants. Extrapolation of the laboratory results to explain the behaviour of these compounds in mixtures with other similar chemicals must be questioned, based on the investigative methodology used, and needs to be explained fully.
2. The experimental procedures used in the batch tests (Chapter 4) need further justification. For example, the "synthetic groundwater" used appears to comprise a model solution of the two contaminants made up in de-ionised water. This matrix does not represent natural groundwater, which contains a range of other major ion species. It is therefore not a realistic fluid composition to use. Published studies show that such background ions can affect the sorption of heavy metals, due to competition effects, resulting in lower sorption of metals than that which occurs in model systems containing the chemical of interest only (direct reference is made to this effect on p.84, second paragraph). The solutions used in the batch tests should ideally be made up in a composition that represents the chemistry of a typical groundwater. The rationale for using de-ionised water in this respect, and subsequent limitations/transferability of the results from these tests to the field-scale, should be clarified.
3. Further explanation should be provided on the quality control aspects of the batch tests in Chapter 4. Firstly, the selection of 20:1 as a solid:solution ratio should be justified, considering published observations that sorption of chemicals can vary as a function of

the solid:solution ratio used in batch tests. As a minimum, evidence should be presented that the ratio used was optimum and the reasons given for this. Secondly, an assumption is made that biodegradation of benzene in the batch tests conforms to first-order kinetics and half-lives are calculated as a result. Evidence should be presented to support this assumption, for example, time-series data showing that benzene loss, corrected for sorption, is first-order with respect to the substrate concentration. In addition, the electron acceptor supporting such biodegradation should be demonstrated. Thirdly, the sequential extraction procedure used characterises four fractions (ion-exchangeable, carbonate-bound, Mn/Fe-oxide-bound and residual/organic-bound) for metal retention. However, the physico-chemical characterisation done separately includes the material organic matter content and cation exchange properties, but not the carbonate or Mn/Fe-oxide content. Standard methods are available to specifically measure carbonate and metal oxide content of geological materials. Without an independent measure of the Mn/Fe-oxide content of the materials, the sequential extraction data for the same nominal fraction cannot be assumed. This omission should be explained and reconciled with the test results.

4. Sorption of benzene to the test materials is attributed to a linear isotherm model. This has specific assumptions, including sorption reversibility. Other sorption models (e.g. Langmuir, Freundlich) exist, but these have not been considered in the experiments. No desorption tests were completed to check the validity of this assumed model. The assumption of a linear sorption model and lack of evaluation of other possible sorption models in the experiments should be explained.
5. The batch test results suggest that heavy metal (Pb) retention occurs mainly by ion-exchange for the reactive materials investigated. This is unusual, as Pb is very insoluble in most neutral pH groundwaters and would be expected to precipitate as a metal hydroxide (+Eh) or sulphide (-Eh) under corresponding aerobic and anaerobic (SO₄-reducing) conditions and neutral pH. The results obtained in the batch tests may relate to the specific experimental conditions used (e.g. low pH, de-ionised water without competing anions promoting metal precipitation). The implications of the test conditions on the results of the Pb sorption studies should be explained in this context.
6. Reference is made on p.85 to the precipitation of Pb carbonate (cerrusite) as a mechanism to explain Pb retention in the batch tests. This is interpreted from the sequential extraction tests, which are themselves operational definitions for specific phase associations and therefore subject to error/uncertainty. Other options to interpret this data include direct analysis of potential mineral precipitates using XRD and equilibrium geochemical modelling of the test solutions after reaction. This can be done, for example, using PHREEQC to deduce if conditions exist to support PbCO₃ precipitation in the batch tests. The latter is relatively easy as the fluid composition from these tests is precisely known. The limitations of the sequential extraction methodology in assigning association of Pb with specific mineral phases in the test materials should therefore be considered, given that (i) no direct measurement of such phases was undertaken, and (ii) with reference to the test solution composition. This comment also applies to other mineral phases (e.g. Mn/Fe-oxides).
7. Tracer experiments are used in the column studies to determine the hydrodynamic characteristics of the test mixtures. The tracer tests appear to have been done separately from those using the (reactive) benzene and Pb solutions. It is more correct to add a tracer to the reactive solute mixture and inject this as a combined test solution. In this way the exact resident time, dispersivity and sorption parameters can be accurately deduced for the chemicals of interest from the combined tracer and reactive

solute breakthrough profiles. The procedure avoids changes in transport properties of the column media that may occur when separate tracer and reactive solute solutions are run. This can make interpretation of attenuation processes more complicated. For example, the column residence time was estimated using flow rate and column porosity (p.99). A more accurate method is to use the tracer breakthrough profile, since this accounts for the kinematic (not total) porosity of the porous media. Residence time estimated using the tracer breakthrough will be shorter than that estimated using column total porosity and flow rate. This difference can affect calculations of reaction kinetics. Some comment on the reason for separate tracer and reactive solute tests should be provided.

8. Biodegradation of benzene in the column studies can be deduced when the breakthrough profile does not reach C/C_0 1.0 under constant injection. This occurs in Figure 5.5a-c. A mass balance should be done for these columns, to estimate the benzene loss via biodegradation (assuming constant input). This can then be related to material design mixtures and attenuation performance in a quantitative way.
9. A mass balance should be done to check if the Pb loss in the column studies was via ion-exchange reactions. This can be undertaken using the data presented in Figure 5.6 and comparing total mass of cations released vs Pb retained by the mixtures. Differences in the mass balance allude to other attenuation processes and reactions controlling these species.
10. The conceptual model developed in Chapter 6 for the numerical modelling of results from the zeolite column studies is much more complex than that reported from the analysis of the experimental studies. For example, a Freundlich adsorption model is proposed to explain the retention of Pb by zeolite in a surface complexation reaction. Some comment is needed on the justification of this specific adsorption model, considering the experimental results, and whether the experiments could have explicitly tested this hypothesis to obtain the necessary parameters for such modelling.
11. Results are presented (Fig 6.5) in section 6.3.1 from the numerical modelling of column studies containing zeolite permeated with a Pb solution. There are some significant differences between the experimental and predicted breakthrough of chemical species shown, for example, Ca, K and Na. The reasons given for this difference are exclusion of other removal processes, such as precipitation of carbonates, sulphides, oxides or other minerals (p.131). The numerical model used (PHREEQC) has a well developed thermodynamic database and mineral assemblage which allows reactions involving these species and mineral phases to be explored to resolve the reasons for the differences observed. It is therefore possible to improve the fit between experimental and predicted behaviour, and understand the reactions contributing to this discrepancy. This can be undertaken using a "trial and error" analysis to better fit the model to the experimental data. It is also important to do this to validate the conceptual model for the experiment. As presented, the numerical modelling provides a poor interpretation of the results for this column experiment and should be further explained/improved. It is likely that mineral phases and/or reactions have been omitted from the analysis, or perhaps important input data is missing or in error. Further information to resolve this can be obtained from (i) the mineralogical/chemical characterization of the zeolite material, (ii) "calibration" and refinement of the geochemical reactions (ion-exchange, dissolution/precipitation), (iii) checks on the accuracy of input parameters used in the numerical analysis, and (iv) a review of the conceptual model that underpins the experiment.

12. Further numerical modelling is done in section 6.3.3 and 6.3.4 to explore the long-term performance of the zeolite for Pb attenuation and the effects of a limited number of parameters on Pb removal. Firstly, it is not clear how the range in some parameters was decided. For example, why pH 1.4, 1.88, 2.5, 2.88, 5.2 and 13.2 were compared, or why a Pb concentration range of 10-200 mg/L was chosen. The rationale for selecting these ranges should be explained. Secondly, while this analysis provides some understanding of the processes contributing to Pb fate and transport in the column experiments, it does not really explain how a field-scale PRB containing zeolite would perform. The limitations of the experimental approach are stated by the candidate (p.134-135), but some scenario modelling using the experimental results and measured parameters (e.g. K_d values) could be done for a typical contaminated groundwater-PRB design problem, to consider variations in material properties, contaminant waste stream and groundwater conditions that may reasonable occur. The extra information required for this is easily obtained from the field site hosting the research and this additional analysis would be highly informative to address aspects of upscaling and PRB design performance under near *in situ* conditions. Currently, this potentially novel aspect of the modelling work is missing and the section is therefore under-developed. The results of additional parameter evaluation using the model (p. 137) are also not fully explained.

Conclusion

The dissertation provided is sufficient for evaluation as a PhD thesis. It is generally well written and presented with clear figures and tables. The work is supported by a thorough analysis of the current literature. The rationale for the research is clear and the importance of the chosen topic in the field of groundwater pollution remediation is well demonstrated. It justifies the scope (field, experimental and modelling studies) of activities conducted. The candidate has demonstrated a very good understanding of the context in which the research is undertaken and developed appropriate research questions with hypotheses to explore in the field, experimental and modelling studies completed. The field and laboratory studies have been completed by the candidate to a high standard and are interpreted at an empirical level. Overall, the candidate shows the appropriate skills to perform independent research, including preparation of scientific papers and other articles for peer-reviewed publications. In general the results support the conclusions of the dissertation, but the modelling work is less developed, with limitations in the interpretation. There are clear limitations in directly transferring the results of the experimental and modelling studies to field-scale application of PRB designs. These relate mainly to the design of the batch and column experiments, and scope of modelling undertaken. The limitations identified above should be addressed in any corrections made to the thesis and subsequent publications arising from it. Notwithstanding these, the candidate has achieved the research goal, in the context of the aim, objectives and hypotheses presented.

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 the PhD dissertation, because of its sufficient scientific and practical value in the area of environmental engineering and geochemistry. I therefore recommend it to be the subject of the public defense.

Signature

