THE POTENTIAL OF PERMEABLE REACTIVE BARRIER (PRB) TECHNOLOGY AS A REMEDIATION TOOL FOR CONTAMINATED MINE GROUNDWATER: LITERATURE REVIEW; PRELIMINARY LABORATORY ANALYSIS & ASSESSMENT

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THE POTENTIAL OF PERMEABLE REACTIVE BARRIER (PRB) TECHNOLOGY AS A REMEDIATION TOOL FOR CONTAMINATED MINE GROUNDWATER: LITERATURE REVIEW; PRELIMINARY LABORATORY ANALYSIS & ASSESSMENT

A report to the Water Research Commission by:

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on a project entitled:
"A preliminary assessment of PRB technology, within a risk assessment framework, to treat radionuclide and organic contamination in groundwater"

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EXECUTIVE SUMMARY

Significant financial resources have been directed towards (mine related) environmental restoration in South Africa - among the more difficult and expensive environmental problems,is contaminated ground and surface water. Water issues share a large part of the environmental stage in southern Africa because of the paucity and value of these limited resources.

The concept of a PRB is relatively simple. Reactive material is placed in a subsurface structure to intercept a plume(s) of contaminated ground water which must move through it as it flows, typically under its natural gradient, thereby creating a type of passive treatment system[2]. As the contaminant moves through the material, reactions occur that transform it to less harmful (non-toxic) or immobile species. The PRB technology under investigation may potentially have wide ranging applicability across a broad range of situations, from "active" mine and mining waste sites that border on residential areas, to abandoned mine sites that are utilized for housing or to which the population and biophysical environment are exposed. International research has shown that pilot scale studies (one of the recommendatory follow ups from this initial research work) could yield technology that may be a cost effective alternative to more traditional methods of contaminated water treatment and containment.

The broad aims of this research have been:

1. To assess the application potential of permeable reactive barriers (PRBs) under local conditions;
2. To determine at a laboratory scale, the efficacy and efficiency of PRBs in the removal of inorganic and organic contaminants from groundwater contaminated by mining.
3. To identify those local conditions to which this technology is most applicable, and where it has the highest application potential; and
4. To make recommendations concerning the usefulness of PRB technology, and the need for further research and development

Lessons learned from the United States and other countries in terms of the design, installation, monitoring and efficacy of PRBs are critical to review. Although the consensus amongst the authors of this report is that South African conditions probably provide unique, although not insurmountable, challenges to the use of PRB technology, many of the potential problems related to PRBs have been highlighted by the relative wealth of international literature on the topic.

The laboratory and analytical investigation component of this study focused on the potential use of Permeable Reactive Barriers (PRBs) to treat inorganic and organic contaminants in water. The investigation focused (Sections 2 & 3) initially on:

(i) a literature survey relating to organic and radionuclide contamination and treatment using PRBs.

(ii) assessing the feasibility and application potential of the technology under local conditions

Thereafter, two separate laboratory components (inorganic and organic) were undertaken wherein PRB situations were simulated in a laboratory – these components aimed to investigate:

(i) the efficacy of specific reactive media to treat radionuclide contaminated water (uranium as the primary radionuclide); and

(ii) the efficacy of specific media (different innocula and bacteria) to treat (biodegrade) organic contaminants in water.

Material (a spilled solvent/crud/soil mixture) from a single site in the Free State province (central South Africa) goldfields was used in the laboratory investigation, as well as uranium similar to the type encountered in the Far West Rand dolomitic gold mining environment. This material constituted the "test contaminant".

A risk assessment philosophy was used to guide and inform aspects of this research, particularly as it related to the initial identification of sites and contaminants that may be of interest in the context of PRB technology and its application in South Africa.

INORGANIC COMPONENT- RESULTS

The inorganic component of the research included a small but comprehensive modelling component that concluded that:

- The observed behaviour of the experimental column with steel wool as reactive barrier material was reproduced tolerably by reaction progress modelling.
- Pore structure and dynamics play an important role with respect to treatment efficiencies.
- The broadly available granular iron material does not work as well as steel wool in terms of uranium removal (although immobilisation efficiencies are suitable for an *in situ* scenario). Iron leaching in downgradient is, however, not as marked as for steel wool.
- The close fit between modelled and observed behaviour suggests that the chemical processes in the column may be well understood.

- The dolomitic water that was used as test remediation solution buffered potentially undesirable pH changes in the permeable reactive barrier.
- Based on the simulations, zero valent iron is a good material for use in a permeable reactive barrier for the remediation of uranium-contaminated dolomitic water.
- The optimum pH for operation of a zero-valent-iron PRB is around 8.0, to simultaneously ensure high rate of ferrous (dissolved) iron removal and to reduce clogging of the PRB by gelatinous ferric precipitates. These conditions are obtained in the dolomitic system, where bicarbonate acts as a natural pH buffering agent.

ORGANIC – RESULTS

The organic research component revealed that:

- Generally colder, *in-situ* temperatures of groundwater environments will tend to lower the microbial activity rates.
- Despite the influence of temperature, the type of solid support media plays a critical role in the degradation potential.
- Results indicate that all experimental columns were able to degrade all of the different compounds in the organic contaminant, and that no compounds were recalcitrant and accumulating.
- The relatively low degradation rate attained during the first part of the continuous culture growth experiment (up to day 36) was not likely a result of low microbial numbers or diversity and was most likely some form of growth factor, micro-element limitation ETC.
- it is clear that concentrations of many types of organic contaminants, including petroleum based contaminants, can be successfully reduced (degraded) by micro-organisms (at rates of 90% plus) in what could be called permeable bio-reactive barriers.
- One of the effective outputs of this section has been to highlight other areas that require investigation and the elucidation of which would serve to focus the results and assertions made here. These include investigating:

  - The effect of low contaminant concentrations and threshold values limits on biodegradation of the organic molecules;
  - The nature and dynamics of micro-nutrient, vitamin and other growth factor limitations in pine bark based solid media;
  - The use of other organic solid media investigated by other international studies, including saw dust, composted sewage sludge, chicken manure, wood chips and straw;

- The possible positive effects of bio-surfactants and other surface tension relieving agents in increasing a contaminant's susceptibility to degradation by microbes; and
- Increased retention times.

DISCUSSION & CONCLUSIONS

This study has provided a comprehensive review of PRBs, their functioning, characteristics and dynamics in the international arena. Building on this, it has then moved on to demonstrate, in a controlled laboratory setting, that columns acting as PRBs can and do work efficiently using, critically, local contaminants and firmly considering relevant (local) environmental parameters (e.g. dolomitic water).

It has, in addition, modelled the speciation of uranium in a detailed fashion, providing useful addition to the body of literature dealing with this pervasive South African contaminant. Furthermore, it has clearly illustrated the breakdown dynamics of a suite of organic contaminants, the customary treatment protocols of which may be enhanced by the preliminary assessments provided here.

CONSTRAINTS & LIMITATIONS

One of the constraints of this study, to a certain extent, is that due to its scope limitations it has not been able to properly assess the effect that the South African deep groundwater (>~10m) will have on PRB functioning. Notwithstanding this, some elements and dynamics of deep groundwater environments have been considered and assessed (the effect of lower temperatures on microbial activity for example), and the study has provided a thorough and comprehensive review of tools developed internationally that can potentially deal with deep groundwater environments.

This study has not aimed to provide a detailed and comprehensive demonstration of PRB technology to the extent that an unreserved endorsement and recommendation can be made regarding their potential use in the South African environment. Instead, the report has looked to defer to the wide body of international literature to achieve this aim, and has provided a limited analytical demonstration of their use and efficiencies. This to provide a solid platform for the envisaged future work and research areas identified below.

The organic and inorganic sections of this report particularly have gone to considerable length to highlight and discuss both the limitations and constraints that have emerged from the experimental runs and, developed from this, areas for further research. These are not repeated here and instead a more general recommendatory outline and summary is presented.

RECOMMENDATIONS

- While the research and the technology as it stands may seem more suited to sites that are characterised by surface or near surface groundwater pollution, the tools outlined in this report for dealing with deep groundwater environments, should be investigated in greater detail.
- A potential next step is the selection of a site for (i) the development of a detailed pilot design and installation plan where both shallow and deep groundwater areas can be targeted; (ii) the installation and operation of a pilot site, and (iii) the monitoring, analyses and reporting of the functioning of that site.
- Geohydrological characterisation and an understanding of the interplay between this and the optimal functioning of a PRB have emerged as critical elements, particularly as relates to any future work around PRBs in South Africa.
- One of the suggested outputs of this research has been the potential development of a decision tree to deal with site specific contamination (at, for instance, a stream or impoundment impacted on by material from a tailings dam). This decision tree would then effectively guide management action at the site, in terms of PRB treatment. This decision tree should be one of the products of the recommended next research phase outlined above.

GLOSSARY OF KEY TERMS

Aerobic	An environmental condition in which micro-organisms exist or are cultivated/developed in the presence of oxygen.
Anaerobic	An environmental condition in which micro-organisms exist or are cultivated/developed in the absence of both oxygen and nitrate/nitrite
Anoxic	An environmental condition in which micro-organisms exist or are cultivated/developed in the absence of oxygen, but in the presence of nitrate/nitrite
Authigenic	Produced from "outside"
Corrosion	To destroy a metal or alloy gradually, especially by oxidation or chemical action, also via moisture, acids and alkalis
Eutrophication	over enrichment of a water body with nutrients resulting in excessive growth of organisms and depletion of oxygen concentration
Environment	the external circumstances, conditions and objects that affect the existence and development of an individual, organism or group; these circumstances include biophysical, social, economic, historical, cultural and political aspects.
Environmental Impact Assessment (EIA)	a study of the environmental consequences of a proposed course of action.
Environmental impact	an environmental change caused by some human act
Geohydrology	the study of groundwater
Hydrology	the study of surface water and groundwater flow
Mineral Salts/Mineral salts medium	A culture medium containing only mineral nutrientsand no oxidizable carbon sources or necessary organic building blocks or cofactors.
Nutrients	Any chemicals, taken up by the cell from the environment, and of which the cell is built, by a process called biosynthesis, are called nutrients
Oxidation	Any process by which the proportion of the electronegative constituent in a compound is increased (e.g. Cu^{+}? Cu^{2+}+e)

Pore volume

Is equal to the total volume of liquid in a saturated column and is equal to the amount of space not occupied by soil particles in a bulk volume of soil.

Pregnant Solution

A solution laden with a compound/element that is the focus of a particular investigation/extraction process etc.

Xenophore

In many organic compounds resistance to biodegradation has been attributed to one, or more substituents which enhance the molecules recalcitrance. These substituents are often called xenophores and may include Cl, NO_2, SO_3H, Br, CN and sometimes CH_3, NH_2 and OCH_3 (ether). These xenophores are very seldom encountered in nature and, therefore, there are often not many organisms which have the enzyme compliments required for to degrade xenophores[27] and others

LIST OF ACRONYMS

ACVH	Azimuth Controlled Vertical Hydrofracturing
BTEX	The BTEX group of contaminants consist of benzene, ethyl benzene, toluene and three isomers of xylene. These organic chemicals make up a significant percentage of petroleum products.
COD	Chemical Oxygen Demand
DART	Deep Aquifer Remediation Tool
DWAF	Department of Water Affairs and Forestry
FWRWUA	Far West Rand Water Users Association
PRB	Permeable Reactive Barrier

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CHAPTER 1 INTRODUCTION

1.1 A CONTEXTUTAL INTRODUCTION

Significant financial resources have been directed toward (mine related) environmental restoration in South Africa, particularly as a result of the emerging importance of environmental protection in the collective public conscience and the formalisation of environmental management in legislation. With this allocation of resources has come limited progress in improving air quality, dumps and landfills, and surface & ground water quality.

Among the more difficult and expensive environmental problems, and often one of the primary factors impeding the legally prescribed closure of contaminated sites, is contaminated ground and surface water. Water issues share an even larger part of the environmental stage in southern Africa because of the paucity and value of these limited resources.

Generally, "pump-and-treat" technology has been used in remediation and is useful for certain scenarios, but the limitations of pump-and-treat technologies are well recognized[4]. Associated with this recognition is the need for innovative solutions to ground-water contamination. The use of PRBs may provide one potential solution. The concept of a PRB is relatively simple. Reactive material is placed in a subsurface structure to intercept a plume(s) of contaminated ground water which must move through it as it flows, typically under its natural gradient, thereby creating a type of passive treatment system[2]. As the contaminant moves through the material, reactions occur that transform it to less harmful (non-toxic) or immobile species.

Concerns have long been expressed within the mining industry in southern Africa regarding the radiological impacts of gold mining on the environment, given the particular nature and long history of the mining industry[58]. The contamination of adjacent water resources by slimes and tailings dams poses a health risk particularly to people in informal settlements where polluted streams or shallow ground water is consumed without adequate, or indeed any, treatment. This assertion is becoming more and more relevant in the Gauteng, NW and Free State Provinces of South Africa, as many informal settlements have established on land that contains residual mine wastes. Long term effects on livestock and crop farming and established drinking water supply schemes are also of concern[59, 60, 61].

1.2 THE PROBLEMS

The transport of dissolved uranium, amongst other contaminants, from slimes dams has been identified as a major mechanism of non-point source pollution[7] as the water borne transfer of slimes and tailings material often leads to the re-concentration of uranium in the environment, sometimes even exceeding uranium levels in the sources of the contamination.

Summarised analytical data from the old Western Areas gold mines[62] indicate that the dolomitic water entering the mines is often contaminated by radioactive uranium- it is fair to say that this picture replays itself in many South African mines . From an "affected environment" point of view, research has shown that water soluble uranium often occurs in rivers some 15-20km downstream of the mines' property[60].

Metallurgical plants present particularly significant problems. No less than 12 of the mines in the western areas of Gauteng province operated uranium recovery plants, (and in some case more broad based metallurgical plants that also focused on sulphuric acid production). It can reasonably be assumed[62] that radio-nuclide and trace element contamination is present in the surface water abstracted from the dolomites that the mines are situated in, as well as in mine water and in the discharges into surrounding streams and other water resources – discharges that originated from mine de-watering.

There is a clear need for alternatives to the traditional pump-and-treat technology - often ineffective in meeting discharge standards and costly to install and operate, particularly in situations where poorer communities are exposed to groundwater plumes (or plumes emanating from nearby tailing dams) containing radio-nuclides and organic contaminants.

The PRB technology under investigation may potentially have wide ranging applicability across a broad range of situations, from "active" mine and mining waste sites that border on residential areas, to abandoned mine sites that are utilized for housing or to which the population and biophysical environment are exposed. International research has shown that pilot scale studies (one of the recommendatory follow ups from this initial research work) could yield technology that may be a cost effective alternative to more traditional methods of contaminated water treatment and containment[2].

An additional output of the research will be the development of technology that would meet a number of South African regulatory requirements. The Department of Water Affairs & Forestry has developed "Best Practices Guidelines for Water Quality Management in the South African Mining Industry" which aims to pro-actively assist the industry manage environmental impacts from the outset to reduce risk[53]. According to this, water management strategies for mines will have to:

- Implement pollution prevention measures at the source;
- Implement reuse and minimization strategies for waste water or water containing waste
- Implement water treatment strategies; and
- Discharge to set standards.

The proposed research and the information and technology products that will flow from it dovetail neatly with these regulatory principles outlined for the industry.

1.3 AIMS OF THIS RESEARCH

The broad aims of this research have been:

1. To assess the application potential of permeable reactive barriers (PRBs) under local conditions, with specific reference to the applicability of the technique in the prevention or containment of groundwater contamination from mining (under conditions where ground water occurs in fractured aquifers relatively deep below surface), and in potentially controlling contaminated water from tailings and slimes dams.

2. To determine at a laboratory scale, the efficacy and efficiency of PRBs in the removal of inorganic and organic contaminants from groundwater contaminated by mining.

3. To identify those local conditions to which this technology is most applicable, and where it has the highest application potential.

4. To make recommendations concerning the usefulness of PRB technology, and the need for further research and development of the technology to facilitate its broad based application in the mining industry in southern Africa.

1.4 APPROACH

The laboratory and analytical investigation component of this study focused on the potential use of Permeable Reactive Barriers (PRBs) to treat inorganic and organic contaminants in water. The investigation focused (Sections 1 & 2) initially on:

(iii) a literature survey relating to organic and radionuclide contamination and treatment using PRBs.
(iv) assessing the feasibility and application potential of the technology under local conditions

Thereafter, two separate laboratory components (inorganic and organic, Chapters 3 &4) were undertaken wherein PRB situations were simulated in a laboratory – these components aimed to investigate:

(iii) the efficacy of specific reactive media to treat radionuclide contaminated water (uranium as the primary radionuclide); and
(iv) the efficacy of specific media (different innocula and bacteria) to treat (biodegrade) organic contaminants in water.

Material (a spilled solvent/crud/soil mixture) from a single site in the Free State province (central South Africa) goldfields was used in the laboratory investigation, as well as uranium similar to the type encountered in the Far West Rand dolomitic gold mining environment. This material constituted the "test contaminant".

A risk assessment philosophy was used to guide and inform aspects of this research, particularly as it related to the initial identification of sites and contaminants that may be of interest in the context of PRB technology and its application in South Africa.

1.5 SITE DETAILS

The Free State site forms part of a derelict metallurgical processing plant that was last active in the early 1990s. The specific contaminant that was used in the investigation is a complex organic solvent that was used in the uranium recovery process during the operation. It contains uranium as well as alamine-336 in kerosene with 4-5% isodecanol. Soil and groundwater from this site was also used in the laboratory to create a basic PRB model. This was undertaken to provide data to inform any recommendations regarding specific site and environmental conditions favouring PRB installation.

1.5.1 Future Pilot Test Site Suitability

The site itself is a prime candidate for the ultimate application of this type of technology because it has become significantly contaminated (soil and groundwater) from solvent spills during operational and closure stages. Laboratory data and the interrogation and assessment of these data will be used to provide guidance and recommendations for any future research that may have the ultimate design and implementation of PRBs as a focus.

1.6 RISK ASSESSMENT FRAMEWORK

A risk assessment philosophy was used, as one of research philosophies, to guide and inform aspects of this research, particularly as it related to the initial identification of sites and contaminants that may be of interest in the context of PRB technology and its application in South Africa.

While established risk assessment methodology, as defined for instance in the US Environmental Protection Agency's published risk assessment guidelines[9], was not specifically be followed, the methodology's four steps (summarised in the box below) did provide a guide of sorts to structuring and designing the research.

Box 4.1 Description of Typical Steps associated with a Risk Assessment

1. Data collection and evaluation

This phase involves gathering and analysing site data relevant to human and environmental health (at a relevant level) and identifying substances on site that pose an environmental risk.

2. Exposure Assessment

This involves assessing and understanding contaminant exposure frequency and pathways, as well as the dynamics and relationship(s) between a particular contaminant, its components (if applicable) and the ambient environment.

3. Toxicity Assessment

The focus of this component is the specific environmental and human health toxicity characteristics of contaminant(s) and considers (i) types of adverse health affects associated with chemical (contaminant) exposures, (ii) the relationship between the magnitude of exposure and any adverse effects, and (iii) any related uncertainties around the toxicity of the contaminant(s), for instance carcinogeneity.

4. Risk characterization

This phase involves a more specific characterization of the potential for adverse health and environmental effects to occur (for instance it would estimate cancer risk or lethal dose values). Furthermore it would evaluate uncertainty and summarise the risk information gathered.

1.7 THE TEST CONTAMINANT: SITE BACKGROUND AND COMPOSITION DETAILS

The contaminant that formed the focus of this investigation (in the sense of supplying the organic and inorganic fractions for testing within the (laboratory scaled) PRB set-ups) was obtained from the remnants of a metallurgical processing plant in the north-west Free State province of South Africa. The solvent contained residual uranium (the focus of the inorganic component of this research (Section 3)) and a number or organic constituents (the focus of the organic component of this research (Section 4)). Chemical information on the characteristics of the organic constituents is provided in Appendix 1.

The Metallurgical Processing Plant produced, from water monitored tailings from the surrounding goldfields, gold, uranium and sulphuric acid. The contaminant in question was utilised as a catalyst in the Uranium recovery process in the "Uranium Stage II" portion of the plant. A brief description of this process and the compound follows.

1.7.1 The Uranium Extraction and Recovery Process

The chief uranium bearing constituent in the slimes material that was processed at the metallurgical plant was uraninite, which varied in composition locally, but was most probably present in the form U_3O_8. Complete dissolution of uraninite, as was required for the production of uranium at the site, required oxidising conditions. Pyrolusite (MnO_2) was the most common and freely available oxidant and was utilised in the Uranium extraction process.

Acid leaching from the milled ore proceeded as:

$$UO_2 + MnO_2 + 2H_2SO_4 \rightarrow UO_2SO_4 + MnSO_4 + 2H_2O$$

Oxidative leaching (temperatures were elevated by steam injection to optimise the concentration of dissolved uranyl sulphate) took place in a series of flat bottomed pachucas. The pregnant solution was then separated from the barren slime by counter current decantation, followed by sand bed filtration.

After forward leaching (reverse leaching was discontinued in the mid 1980s and with it the use of manganese as an oxidant), the sulphuric acid (H_2SO_4) and pyrolusite were discharged to tailings dams (generally after neutralization with lime to a pH above 9.5).

Residual pyretic material (generally material with sulphide concentrations greater than 30%) was routed to the acid plant portion of the metallurgical processing plant for acid extraction.

1.7.1.1 Uranium Stage II – Recovery Specifics and the use of the Test Contaminant

Uranium was recovered after the oxidative leaching from the acid pregnant solution (containing approximately 5% free H_2SO_4) solvent extraction (PURLEX). Solvent extraction involved the following key (sequential) processes:

i. The pregnant solution from the oxidative acid leaching stage was clarified;

ii. Uranium was extracted from the pregnant solutions at approximately pH 1.3 – with a 5% solution of alamine 336 in kerosene with 4 to 5% iso-decanol used as the eluant. This extraction took place through a bank of 6 stages, with long residency times.

iii. Slimes were then re-pulped prior to the flotation of pyrite;

iv. Some volume of pyrite was generally reused in the cyanide leaching process at the old "gold plant" section of the works.

Filtration mechanisms were used at the Uranium Stage II plant to enhance the efficiency of uranium recovery and to limit solvent loss (high suspended solid concentrations affected the efficacy of this process). These filtration mechanisms/processes included:

- At the scrubbing stage, an aqueous 0.1M NH_4OH (ammonia hydroxide) was used to precipitate siliceous impurities. In order to achieve as complete as possible removal of iron (the main co-extracted element) and cobalt, H_2SO_4, was added at the third stage to maintain a pH of 1.5. In the final scrubbing stages, desalinated or softened water was used.
- During the next stage, stripping, the uranium was transferred from the scrubbed solvent into the water phase by counter current mixing with NH_4OH and $(NH_4)_2SO_4$ (ammonium sulphate), raising the pH gradually to approximately 5.
- Uranium was finally recovered by the addition of NH_3 and the subsequent precipitation as ammonium diuranate (ADU) or "yellow cake". Uranium oxide was then produced from the ADU by dewatering.

The solvent was then regenerated by washing with Na_2CO_3 – sodium carbonate - to remove thiocyanate, and the regenerated solvent was returned to the solvent tank for re-use. In the PURLEX solvent extraction process, large amounts of raffinate (a highly acidic saline crud with TDS values often between 20 000 & 60 000mg/l) was produced. This compound had no reuse value or potential, and as such was considered as waste material.

CHAPTER 2 LITERATURE SURVEY

2.1 INTRODUCTION AND CONTEXT

The aim of this literature survey is to provide a firm platform for the research project to move forward from, to inform the ongoing and future laboratory test-work for the organic and inorganic components (see descriptions in this report), and to understand any of the emerging limitations associated with the technology and their implications for future (recommended) research.

This literature survey has not elaborated on the "risk assessment framework" that will inform the final write-up and assessment as this approach (as a guiding approach employed during data assessment, synthesis and write up) is well established in the international literature. Instead, this survey has focused on collating the available information specific to PRB technology and its relevance in achieving the aims of this research project. This has been undertaken to understand more completely what is known about PRB technology, and to inform and fine tune the methodology and research approaches.

2.1.1 Similar Research in South Africa

The focus of more "passive" water treatment in the South African mining environment has been limited to the amelioration of acid mine drainage (AMD), in terms of addressing low pH levels and elevated concentrations of sulphate and dissolved metals[19]. The extent of the application in South Africa has been limited[19,20,21].

While some comprehensive work has been done on Passive Systems in the South African context[19] (comparatively similar to the PRB concept in that it relies on passive flow), that work has not focused on aspects that this research project aims to elucidate, *inter alia*,

- Applicability to (contaminated) groundwater at different levels
- Radionuclide contamination (U)
- Organic contamination (chlorinated solvents)

Similar or analogous (South African) work that may be compared to this PRB research work, specifically with respect to groundwater treatment, was not encountered during this literature survey.

2.1.2 *Objectives of the Research*

The overall objectives of the research (and the following literature survey that it is based upon) may be summarized as essentially two pronged. Firstly, to investigate and understand PRB technology in treating metal and radionuclide (specifically uranium) contamination in water contaminated by mine waste. Secondly, to investigate and understand the role of biological treatment (biodegradation) of particularly uranium and non halogenated organic compounds (such as the kerosene group), within a PRB context. The latter aim has particular local applicability due to the specific contamination present at one of the test sites used for this research.

Importantly, the nature of water contamination from mine wastes across South Africa is such that these aims also have much broader relevance in terms of providing potential solutions to (mining related) water contamination problems.

2.2 PERMEABLE REACTIVE BARRIERS – AN INTRODUCTION

A functional definition of a Permeable Reactive Barrier (PRB) is "an emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a preferential flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals at the discharge of the barrier."[1]

Figures 2.1 and 2.2 provide diagrammatic illustrations of typical PRB structures.

The concept of a PRB is relatively simple. Reactive material is placed in a subsurface structure to intercept a plume(s) of contaminated ground water which must move through it as it flows, typically under its natural gradient, thereby creating a type of passive treatment system. As the contaminant moves through the material, reactions occur that transform it to less harmful (non-toxic) or immobile species[2]. Table 2.1[57] highlights the range of compounds treatable via PRB systems.

It is critical to understand the driving factors in PRB technology for successful implementation of the systems. A basic understanding of the chemical basis of transformations of contaminant, both in lab and field, is essential[3].

The physical and technical detail and variations of PRBs are elaborated on in the report, specifically as regards their relative efficacies and the implications that the particular Southern African geohydrological environment, as well as the findings of the laboratory tests, have on them.

There are a number of advantages of PRB clean up methods over more traditional processes. The following attractive features are detailed in the literature.[3,4,5,6]

- Perceived (and demonstrated) favourable cost/benefit ratio relative to other treatment methodologies
- Implementation ease
- Inexpensive
- Low to zero maintenance costs
- No operational costs
- Mechanically simple
- Provision of effective long-term treatment
- Good efficacy of treatment
- No toxic end-products
- No energy consumption
- Conserves water
- Allows productive use of treatment area
- Can be combined with other treatment technologies for full in-situ remediation of a broad range of groundwater contaminants
- Minimal impact - may be completely removed at end of period of use
- May be left at short notice in the event of extreme meteorological events

2.2.1 PRB Treatment Scope

Full-scale applications of PRB's are being carried out to decontaminate groundwater streams contaminated with chlorinated hydrocarbons[1], chromate[1] and uranium[7]. Research is currently being carried out in laboratory and in the field on a variety of contaminants and reactants (see Table 2.1).

2.2.1.1 Reactive Media – Desirable Characteristics

The reactive media component of PRB technology is a critical constituent as it provides the very essence of the treatment technique. In a broad sense, there are a number of characteristics that reactive media should have. These include: [3,9]

- Reactive media should be effective in removing contaminants of concern

- Reactive media should be compatible with subsurface environments such that undesirable reaction products are not produced.

- Material properties should be well understood and characterised.
- The materials should persist for long periods, i.e. be not readily soluble in the emplacement setting, and should not be quickly depleted of reactivity.
- Operating and maintenance costs should be low.
- High permeability is required (greater than aquifer permeability), implying avoidance of small particle sizes for the reactive material[5]. Furthermore, particle size should be unimodal, since a broad range of particle sizes can lead to blocking of the intergranular spaces.
- The materials should be readily available, at low cost.
- The materials should be safe to handle.
- Transformation products should be stable, immobile, and non-toxic.
- Since transformation rates partly determine the total thickness of reactive material require, these should be high, to provide adequate residence times, and to ensure that barriers are not prohibitively thick.

Table 2.1 Range of chemicals treatable in PRBs[57] (using zero valent iron)

Aluminum	Al	Al bound as iron oxyhydroxides
Antimony	Sb	Sb reduced & bound as iron oxyhydroxides
Arsenic	As	As(V) and As(III) reduced & precipitated
Cadmium	Cd	Cd(II) reduced & bound as iron oxyhydroxides
Copper	Cu	Cu(II) reduced & bound as iron oxyhydroxides
Hexavalent Chromium		Cr(VI) Cr(VI) reduced & precipitated to Cr(III)
Lead	Pb	Pb(II) reduced & bound as iron oxyhydroxides
Magnesium	Mg	Mg(II) reduced & bound as iron oxyhydroxides
Manganese	Mn	Mn(VI) reduced & precipitated
Mercury	Hg	Hg(II) reduced & bound as iron oxyhydroxides
Nickel	Ni	Ni reduced & bound as iron oxyhydroxides
Selenium	Se	Se(VI) and Se(IV) reduced & precipitated
Technetium	Tc-99	pertechnetate Tc(VII) reduced & precipitated
Uranium	U	U(VI) reduced & precipitated
Vanadium	V	V reduced & precipitated
Zinc	Zn	Zn(II) reduced & bound as iron oxyhydroxides

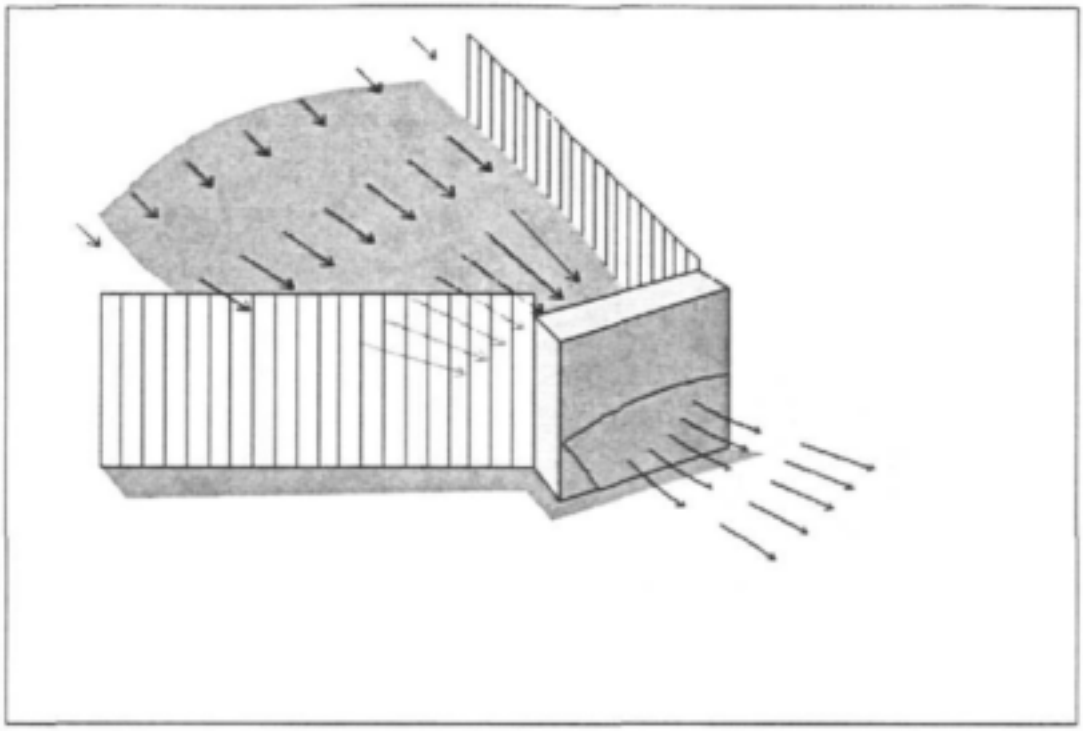

Figure 2.1 Typical conceptual PRB structure[57]

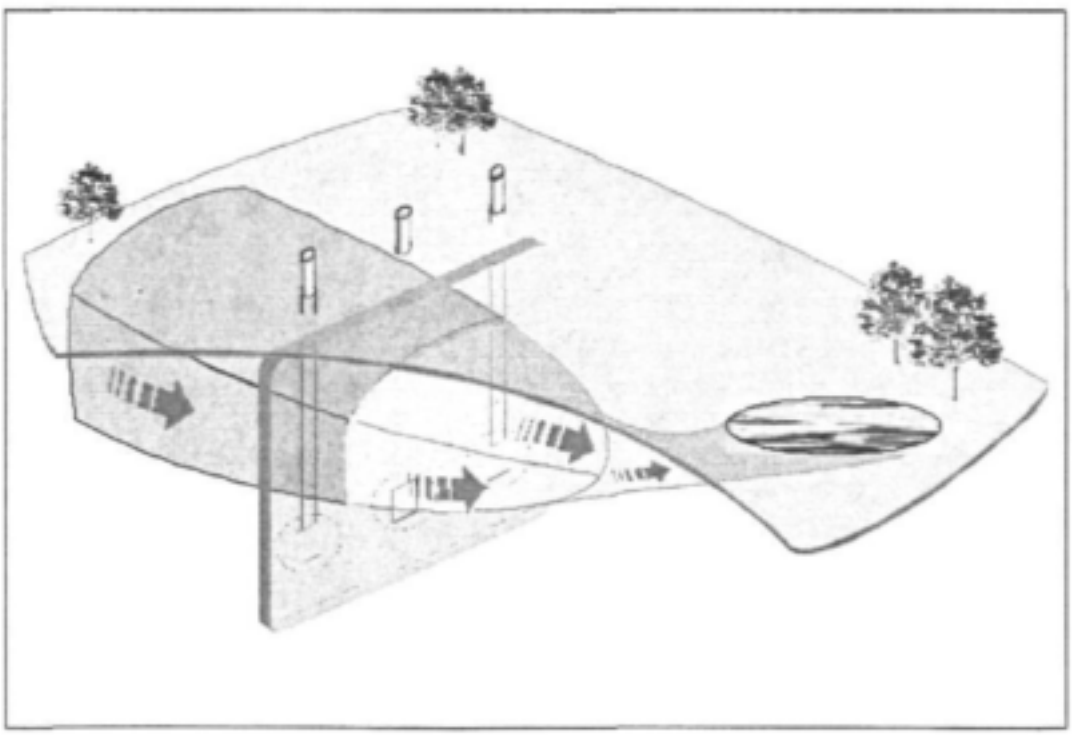

Figure 2.2 Three dimensional rendering of a PRB structure[57]

2.3 INORGANIC CONTAMINANT AND RADIONUCLIDE TREATMENT (URANIUM)

2.3.1 Introduction

Uranium removal is the main focus of the inorganic component of this research although there is some overlap with the organic component detailed in later sections of this survey. Metal removal by PRBs is not restricted to uranium (Table 2.1) but the focus of this particular element here is dictated by its importance in the South African mining environment, specifically as far as water pollution is concerned. With respect to other inorganic contaminant treatments, the following are known to be treatable by PRB technology[3]:

2.3.2 Mechanisms of Inorganic (heavy metal) decontamination

This section considers the mechanisms, processes and dynamics of decontamination applicable to heavy metal and radionuclide removal – particularly of uranium within the context of this study. Biological removal mechanisms (including biologically assisted removal of U in the presence of Fe) are considered in Section 4 which details "organic removal and treatment."

Chemical mechanisms postulated that decontaminate heavy metal-polluted groundwater (of direct importance to uranium decontamination) involve ion exchange, reductive precipitation and adsorption[10].

The use of thermodynamic chemical speciation calculations has been important in this research. For instnace MINTEQA2 was used to infer that the reduction half-reaction is the rate-limiting step, owing to the correlation between increased empirical rate of metal removal and the difference between the potential of the metal's redox half reaction and that of the Fe(II)/Fe(0) couple[10].

The mechanistic aspects of immobilisation of uranium onto zero valent iron barriers are still under discussion. Some workers[11] have proposed that reductive precipitation of hexavalent uranium or adsorption onto the corrosion products of Fe^0 takes place.

2.3.3 Treatment of anions

2.3.3.1 Adsorption and Precipitation of Inorganic Anions

Redox-sensitive inorganic anions (e.g. chromate) are possibly directly reduced to a more reactive lower oxidation state (e.g. tetravalent uranium), following which adsorption and surface complexation/precipitation occurs[3].

It proved difficult to locate literature references on explicit treatment of uranium as an anion, but treatment of uranium has been discussed in carbonate media where the dominant chemical form of uranium is the anionic carbonate species.

Biological treatment of anions is addressed in Section 3.

2.3.4 Treatment of cations

2.3.4.1 Reduction of Inorganic Cations

Laboratory experiments have shown there to be rapid immobilisation of uranium by elemental iron. It has been proposed[3] that the reactions removing uranium cations from groundwater involve reduction, followed by precipitation of the sparingly soluble UO_2 compound, or by co-precipitation with secondary precipitates, such as hydrous ferric oxides. The reaction proceeds with a nearly unitary stoichiometry between uranium and iron atoms, and under strongly reducing conditions.

It should be noted[3] that a return to oxidizing conditions would probably remobilise uranium.

Biological treatment of cations is addressed in Section 2.4.

2.3.5 Reactive Materials

Potentially suitable materials proposed for the reactive medium within construction barriers include[5]:

2.3.5.1 Granular activated carbon

This material is used for decontamination of petroleum and selected metals[5].

2.3.5.2 *Zeolites*

This material is used for treatment of cations. Disadvantages include small grain size, low porosity, and difficulty in containing contaminants due to entrainment and dispersal of zeolite particles[5].

2.3.5.3 *Iron*

Desirable characteristics of iron as a permeable reactive barrier material include[13]:

- Compatibility with subsurface media
- Effective in removing contaminants of concern
- Persistent over long time periods
- No adverse geochemical side-reactions or products
- Low operating and maintenance costs
- Readily available

Specifications for use of iron as a barrier material include[13]:

- Low carbon content
- Low levels of trace impurities
- No surface films

2.3.5.3.1 Zero valent iron in the form of "Foamed Fe(0)"

"Foamed Fe^{0}" is typically powdered, bound with aluminosilicate and moulded into plates[15]. Bricks were made of this material in a field experiment to remove uranium[14].

2.3.5.3.2 Iron barrier material

Iron has been used in a trench design, or injected into aquifers as a colloid[15].

2.3.5.3.3 Granular iron

Granular iron has been extensively used in metal remediation, including uranium contamination[15]. Typical granular iron characteristics include[13]:

- Grain size range: 2.0 to 0.25 mm (-8 to +50 mesh)
- Bulk density: 2.6 g/cm3 (160 lb/ft^3)
- Specific surface area: ~ 1.0 m^2/g
- Hydraulic conductivity: 5 x 10^{-2} cm/s (142 ft/day)
- Cost: ~ US$350-$400/ton + shipping[b]

2.3.5.3.4 Steel wool

Steel wool has been used in flow-through cells in a reactive material comparison experiment for the removal of vanadium and uranium[15], and a field experiment, in which it was placed in a "septic tank" – like design[14].

Advantages of steel wool include[5] greater manageability than, for example, iron filings, and less problems with dispersal. Steel wool bundles are sold commercially for use in woodwork and cleaning.

Steel wool has been found to experience progressive decrease in permeability due to the formation of gases and precipitation products within it (e.g. 95% efficiency versus 99.98% efficiency of granular Fe(0)[15]).

Reaction location on the iron surface

It has been proposed[9] that electrons are conducted through an oxide film on the iron surface, where reaction occurs with contaminants that have diffused through a "boundary layer", slightly chemically different from the bulk solution. Soluble reaction products (e.g. hydrogen, ferrous iron, etc) diffuse out of the boundary layer into the bulk solution.

b Information on local (SA) costs have not been determined

2.3.5.3.4.1 Changes in inorganic groundwater chemistry

The reactive zone has been graphically represented[9] as follows:

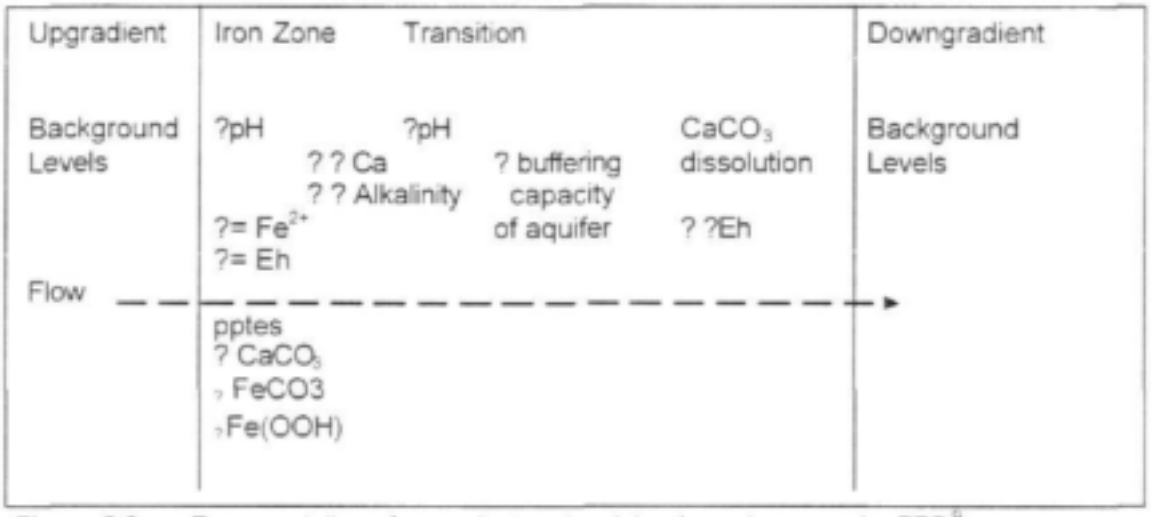

Figure 2.3 Representation of groundwater chemistry dynamics around a PRB[9]

2.3.5.4 Calcium carbonate

Calcium carbonate has been used with success in field trials in Antarctica[5] to treat contaminants flowing through a PRB.

2.3.5.5 Shredded polyethylene

Shredded polyethylene has also been used in field trials in Antarctica[5] to treat various contaminants, with relative degrees of success.

2.3.5.6 Animal chitin for U removal

Animal chitin has been tested in batch and continuously stirred reactors for the removal of uranium as a passive biosorbent[15]. The experiments were rationalised with chemical speciation modelling of surface complexation using the software programme FITEQL[c]. The general chemical framework included a two-site model, with analytical expressions for mass transfer and sorption over a range of pH values. The rate law expressions

c For more information see: Lenhart, J.J., L.A. Figuerca, B.D. Honeyman, D. Kaneko. *Modelling the adsorption of U (VI) onto animal chitin using coupled mass transfer and surface complexation*. Colloids and Surfaces 120 (1997) 243 – 254.

included Fick's law for hydraulic simulations, and reactor mass balance. Rate constants were calculated.

Perceived advantages of using animal chitin as a biosorbent include the fact that it is a non-living biomass with no toxicity problems, it is a byproduct of the seafood industry and can be obtained in flake form, a form that exhibits good mechanical strength and rigidity.

Results obtained[16] are 80% removal of 1 µM U(VI) with 3.9 g/l chitin at pH 6.5.

2.3.6 Empirical comparison of barrier materials for U treatment

Phosphate, zero-valent iron (ZVI) and amorphous ferric hydroxide (HFO) materials were compared in their ability to immobilise hexavalent uranium in groundwater[17].

The ZVI material reduced input U concentration by more than 99.9% after groundwater had travelled 1.5 ft into a PRB. There was no observable decrease in performance after the first year of operation[17].

Phosphate as hydroxyapatite (15 mg/L; 6.7 gram per litre) performed less well than the ZVI PRB.

The amorphous ferric hydroxide materials eliminated more than 90% of the soluble uranium after initiation, and less than 90% in the subsequent, later months. The efficiency was decreased with time and was also appeared to be inversely related to increases in pH[d] [17].

2.3.7 Enhancing Iron Reaction Rates

2.3.7.1 Aluminosilicates

It has been found that the reaction rates of iron in decontaminating heavy metals can be enhanced by contact with, for example, aluminosilicates. It is thought that the advantage of this modification is through the buffering of pH values at 7-8, as opposed to the higher (>9) values normally observed[3].

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d Poor performance of the HFO materials could indicate that U removal at an iron PRB does not proceed via the mechanism of U adsorption to "already formed" iron hydroxides (Peter Wade, pers. comm.)

An additional enhancement mechanism may proceed via the generation of protons by dissolution of the aluminosilicates, which then proceed to coordinate to cathodic regions of Fe^0. The Fe^0 accepts electrons, which then enhances the corrosion rate at the iron surface[8].

It is also possible that surface co-ordinated monoatomic hydrogen acts as an excited state reactant. This augmentation has been found to be effective for chromate reduction, where the half life of the reaction was enhanced by two orders of magnitude[8].

2.3.7.2 Metals

Bimetallic systems containing Fe/Cu, and Fe/Ni have been found to increase reaction rates by coupling a second, higher reduction potential metal. There are also possible catalytic effects of the introduced metal[3].

A potential drawback of using these systems is that sometimes quick passivity is observed[18].

2.3.7.3 Non-metallic reactive systems for promoting reactivity

Non-metallic reactive systems for promoting reactivity have been investigated[13], and potential mechanisms reviewed including:

- pH control
- Coprecipitation
- Sorption

2.4 ORGANIC CONTAMINANT TREATMENT/BIODEGRADATION (CHLORINATED SOLVENTS, PETROLEUM HYDROCARBONS)

2.4.1 Introduction

This section of the research (the literature survey) has focused on microbial degradation of petroleum for two key reasons. Firstly, the biologically mediated removal of heavy metals (U) by iron is well established in international literature and this information is summarized in the proceeding sections of this literature survey; and secondly the contaminant utilized in this research has specific petroleum hydrocarbons components for which microbial degradation has been suggested, and is deemed relevant, in the context of this research project, and future applications that may flow from it.

2.4.2 Abiotic degradation of organic contaminants by zero valent iron

Considerable research during the past several years has focussed on the degradation of chlorinated solvents, such as TCE and PCE, by reactions at the surfaces of zero valent iron.[30,31,32 and others]

Although met with initial scepticism, the degradation process is now widely accepted as abiotic reductive dehalogenation, involving corrosion of the Fe^0 by the chlorinated hydrocarbon. For more (supplementary) detail regarding iron corrosion, see Appendix 3.

Zero-valent iron is a mild reductant, and consequently the dehalogenation rates vary for the various chlorinated solvents of environmental interest. A number of studies have shown that the primary determinant of degradation rate is the specific surface area, or the surface area of iron per unit volume of pore water. Degradation rates are typically pseudo-first-order with respect to the halogenated hydrocarbon, with the rate constant relatively insensitive to the initial hydrocarbon concentration.

Published degradation rate data[31] and others for individual halogenated hydrocarbons show that transformation rates are proportional to iron surface area concentration and that observed rate constants can be normalized to iron surface area to yield a specific rate constant, or KSA, for the halocarbon. The reaction pathways by which Fe^0 reduces halogenated hydrocarbons have been determined for a few major classes of chlorinated hydrocarbons.

Such information is significant to the optimal design of a permeable reactive barrier, as incomplete dechlorination of a highly chlorinated ethene, for example, could produce an intermediate product, such as vinyl chloride, which is more hazardous and more persistent than the parent compounds. Even very low concentrations of undesirable by-products in the reactive barrier effluent should be avoided.

Researchers[31] have proposed that the reductive dechlorination of chlorinated organic compounds by iron metal corrosion may proceed as:

$$2Fe^0 \rightarrow 2Fe^{2+} + 4e^- \quad (2)$$

$$3H_2O \leftarrow 3H^+ + 3OH^- \quad (3)$$

$$2H^+ + 2e^- \leftarrow H_2\ (gas) \quad (4)$$

$$X\text{-}Cl + H^+ + 2e^- \leftarrow X\text{-}H + Cl^- \quad (5)$$

$$2Fe^0 + 3H_2O + XCl \leftarrow 2Fe^{2+} + 3OH^- + H_2\ (gas) + XH + Cl^- \quad (6)$$

Which of these reactions, or others, is dominant will depend on the conditions and contaminants present; for example, the presence or absence and the concentrations of other reactive species (including the partial pressures of gases such as O_2 and CO_2) and mineral surfaces, pH, etc. It should be noted that these reactions tend to increase the pH of the corrosion system. It is also important to note that although chromate is reduced and chlorinated hydrocarbons are reductively dechlorinated in the presence of Fe^0, current research[31] indicate that the mechanisms of the reactions are different.

The operational regime of a PRB will have a significant effect on subsequent treatment efficiencies. Research has indicated that magnetite forms as a result of anaerobic Fe^0, while ferrihydrite precipitation forms under aerobic corrosion as small (<0.1 µm), discrete clusters[33]. While magnetite passivates the Fe^0 surfaces of the PRB reactive media and decreases the effectiveness of this media, ferrihydrite, on the other hand, has a very high sorption capacity for many dissolved species including, Cd^{2+}, Pb^{2+}, Cr^{3+} as well as arsenic compounds. This adsorption capacity is significant enough to account for the effectiveness of zero valent iron PRBs treating arsenate contaminated water (previously reported due to reductive precipitation).

2.4.3 Non hydrocarbon biological degradation

2.4.3.1 Biologically Mediated Reduction and Precipitation of Cations

In experiments with microbes present, reduction of uranium was insignificant in the presence of organic carbon or hydrogen without the explicit introduction of microbes.

Bacteria have been found that sustain their metabolism through direct use of the U(VI)/U(IV) redox couple. Bacteria isolated from experiments, which use ancillary reactions to mediate the reduction of U include *G. metallireducens*, which reduces acetate, and *A. purefaciens*, which is known to oxidize hydrogen[8].

2.4.3.2 Biologically Mediated Reduction and Removal of Anions

As the biologically mediated reduction and removal of anions has more relevance with respect the research component dealing with organic contamination, it is highlighted to a greater extent in this section.

Biologically mediated decontamination of anions such as sulphate has been proposed to operate in wetlands[3]. There is a very clear effect of microbes in the reduction of nitrate on PRB's – it seems that *Paracoccus denitrificans* is instrumental in the reduced formation of ammonia (the elemental hydrogen produced by corrosion of iron is used by the bacteria, as opposed to reacting chemically with nitrate), to produce nitrogen products of lower toxicity. For biologically assisted remediation, a ready source of organic carbon is required.

Unlike the zero-valent iron, and other metal, reactive barriers which rely on adsorption and/or redox-promoted chemical reactions, processes for biological contaminant degradation rely on the metabolic activity of micro-organisms.

Biological processes (which are intrinsically tied to micro-organism functioning), affect the cycling of numerous other elements, including nitrogen, sulphur, iron and manganese. Treatment strategies employing these biologically mediated reactions have been proposed for direct treatment of nitrate[34] and sulfate[33,35].

To elaborate slightly on one of these elements, denitrification, a system for the removal of nitrate from ground water affected by discharge from site wastewater disposal systems has been developed[34]. This system intercepts a plume of nitrate bearing ground water with a reactive barrier containing solid phase organic carbon. In the presence of organic carbon, under anaerobic conditions maintained below a water cover in the subsurface, reduction of NO_3 - to N_2 gas is thermodynamically favoured. The proposed reaction is:

$$5CH_2O\ (s) + 4NO_3 \rightarrow 2N_2 + 5HCO_3^- + 2H_2O + H^+$$

CH_2O represents a simple form of organic carbon which is catalysed by bacteria of the *Pseudomonas* group. These bacteria use NO_3- as an electron acceptor in the oxidation of organic carbon. Results of these studies indicate that sufficient denitrification occurs

rapidly and reduces NO_3- from concentrations typically observed in the effluent of onsite wastewater disposal systems (5 - 90 mg/l NO_3^- - N) to below the World Health Organization drinking water standard (10 mg/l NO_3^- - N).

Indirect precipitation of inorganic cations results from the reduction of an anion-forming species, usually sulphate. Biologically mediated reduction of sulphate to sulphide, accompanied by the formation of metal sulphides occurs through the reaction sequence (below) where CH_2O represents organic carbon and Me^{2+} represents a divalent metal cation in solution.

$$2CH_2O\,(s) + SO_4^{2-} + 2H^+ \rightarrow H_2S\,(aq) + 2CO_2\,(aq) + 2H_2O$$
$$Me^{2+} + H_2S\,(aq) \rightarrow MeS\,(s) + 2H^+$$

Biologically mediated sulphate reduction has been proposed to treat metal cations derived from mine sites in wetlands[36] and in permeable reactive barriers.[33,37] Although these systems are designed to promote the removal of dissolved metals, metal removal is accompanied by removal of sulphate. In laboratory studies,[33] sulphate removal was observed at rates of 0.14 to 4.23 mg. $l.^{-1}$ day. $^{-1}$ g^{-1} of media.

2.4.4 Other related remediation techniques

PRB technology, *in sensu lato*, spans other established remediation techniques because of its specific (depending on the contaminants of concern or targeted) reliance on biological action. Although it should be noted that the processes described below are essentially *ex situ*. Fitting the technology into a single 'classificatory box" is therefore difficult because many of the technologies overlap and are not defined by unique remediation processes. With this in mind, it is relevant to consider a brief overview of other remediation techniques specific to (organic) contaminant treatment.

2.4.4.1 Biodegradation

Biodegradation is a technique to remediate contaminated soil and groundwater. Using this technique micro-organisms degrade the organic components to CO_2 and water. Oxygen and nutrients might be injected to promote the degradation rate. If nothing is being added the biodegradation is called intrinsic. The degradation may occur under the use of different electron acceptors other than oxygen. For instance, toluene may degrade via an anaerobic pathway using nitrate as an electron acceptor.

2.4.4.2 *Vapour phase extraction*

Vapour phase extraction is used for the removal of volatile organics from the unsaturated zone. By implementing vapour phase extraction, slotted pipes are placed in the soil and a vacuum is applied to volatilize the organic compounds. When volatilized, a pressure gradient will ensure that the organic compounds are transported to the extraction wells. As a side effect the increased air flow through the soil might be able to increase the natural biological degradation of the organics.

2.4.4.3 *Bioventing*

Bioventing is a microbiological degradation process. As in soil vapour phase extraction (SVE), both injection and extraction wells are installed, but in addition to the SVE technique air, moisture and nutrients may be added to stimulate a biological degradation of the organics. The process is able to remove both the volatile organics such as BTEX's, and the more heavy-end contaminants such as diesel and crude oil.

2.4.4.4 *Air sparging*

Air sparging is a physical and/or microbiological degradation process. By driving large quantities of air into the saturated zone this technique enables an aerobic degradation of organics. The injection of air to the saturated zone serves two purposes. First it drives the volatile organics into the unsaturated zone, from where they may be removed by vapour phase extraction. Secondly it increases the microbiological activity in the saturated zone.

2.4.4.5 *Activated carbon treatment*

This treatment is used after groundwater has been pumped out of the aquifer. The contaminated water is passed through the activated carbon unit where the organics are adsorbed and collected. This is accomplished through the adsorption of the chemical substance onto a carbon matrix. The effectiveness of this process is related to the amount of surface area on the activated carbon and the properties of the chemical substance. This process is often used to remove relatively low concentrations.

2.4.4.6 *Air stripping*

Air stripping is a pump and treat method that uses a counter current flow of upward air-solvent gas and downward water-solvent liquid to physically strip the contaminant out of the water. Often activated carbon systems are used as a secondary step to this procedure.

2.4.5 *The Effect of Physico-Chemical Properties on Biodegradation (specifically with respect to BTEX[e] compounds)[f]*

The effects of chemical structure and physico/chemical characteristics of various organics on their biodegradability has been comprehensively researched[23,24,25,26] and a selection of pertinent aspects are presented in this section.

2.4.5.1 *Molecular weight*

The molecular weight of compound is measured in g/mole. Generally, the higher the molecular weight the less soluble in water and, therefore, less available for biodegradation. Molecular weight also affects the density of a compound.

2.4.5.2 *Water solubility*

Solubility is the measurement of the maximum concentration of a chemical that will dissolve in pure water at a specific temperature, measured in mg/l. Water solubility plays a large role in a chemical's movement and distribution through soil and groundwater. Compared to the other main group of components in gasoline, such as the aliphatics, BTEX's are very soluble, and the solubility of the different BTEX components will have a great effect on the concentrations that may appear in the groundwater.

For alkanes, solubility decreases as the number of carbon atoms increases, for example, pentane (5-carbon) has a water solubility of 360 mg/l at 16°C, while hexane (6-carbon) and decane (10-carbon) have solubilities of 13 and 0.009mg/l, respectively. The organic fractions that are dissolved in the aqueous phase will be able to move with the

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e The BTEX group of contaminants consist of benzene, ethyl benzene, toluene, and three isomers of xylene. These organic chemicals make up a significant percentage of petroleum products.
f BTEX compounds are the main constituents of the test contaminant utilized for the organic section of this research.

groundwater, although, as mentioned, these will also be the compounds more bio-available for degradation.

2.4.5.3 Polarity

Polarity is associated with a compounds charge. The polarity arises from the existence of a slightly negative charge on one part of a compound and a slightly positive charge on the other, which will cause the formation of a dipole, such as water.

Non-polar compounds are hydrophobic, therefore, they will preferentially partition away from water molecules, and will be more likely to adsorb to the organic portion of a soil or they will volatilise.

Polar compounds, on the other hand, have an affinity for the water phase and are, thus, more mobile in this phase. Benzene is non-polar because of its almost neutral charge, although, it is not as non-polar as the other contaminants in the BTEX group and has the ability to dissolve in water.

2.4.5.4 Octanol-water partitioning coefficient (K_{ow})

This is a ratio of the concentration of a dissolved substance in a two-phase system at equilibrium. After a chemical has been mixed in an octanol and water solution, the system is allowed to reach equilibrium. The two phases will partition and a ratio of the chemicals concentration in the octanol phase and water phase is taken. This ratio is indicative of a chemicals accumulation in water and is, also, a measurement of the hydrophobicity of an organic compound.

More polar compounds will tend to have a low K_{ow} values. Furthermore, the more hydrophobic the compound the more the contaminant will adsorb to soil and have a low solubility. The BTEX compounds are not sorbed to the soil matrix as significantly as the aliphatic components (the different alkanes), and they are, therefore, more likely to contaminate larger water volumes. Sorption will be a factor in determining the movement of contaminants with the groundwater flow.

2.4.5.5 Vapour pressure

The vapour pressure of a liquid is the pressure of the gas in equilibrium with respect to the liquid at a given temperature. Vapour pressure represents a compound's tendency to evaporate and is essentially the solubility of an organic solvent in a gas. High vapour

pressures mean that the compound is more likely to volatilize out of solution. Vapour pressure of alkanes tends to decrease as carbon numbers increase. For example, pentane (5-carbon) has a vapour pressure of 430 mm Hg at 20°C, while hexane (6-carbon) and decane (10-carbon) have vapour pressures of 120 and 2.7mm Hg, respectively.

2.4.5.6 Henry's law constant

The Henry's Law constant is a property of a chemical that expresses its partition between the air and water phases. It helps to predict the behaviour of an organic compound in the environment and in remediation procedures such as air stripping processes (see Section 2.4.4.1 on bioremediation processes). These values also describe a chemicals movement from water to air and vice versa. High values mean that the chemical will move more toward the gas phase, whereas, low values will tend to stay in the aqueous phase.

2.4.6 The Effects of Chemical Structure on the Biodegradation of Selected Organics

Although the relative biodegradability has been determined for many organic compounds, including petroleum based hydrocarbons (the main components of the test contaminant from the Free State goldfields site), it remains a complex process that is further complicated by the characteristics of soil environment(s). One reason for this is that any petroleum based contamination will consist of numerous mixed compounds each with its own biodegradation potential which can vary significantly depending on the concentration of other organics, microbial factors, soil features, amount of time for acclimation etc[23].

Although generalisations may be made regarding the relative biodegradability of individual classes of compounds (in a particular soil environment), very few of these generalisations might be valid. The main reason for this lack of validity is due to:

- The microbial component differing significantly in different soils and even over short distances in the same soil. Also, different soils often have varying microbial environments which could favour the growth of certain organisms above others, for example, anaerobic soils are favoured in soils with a very high clay content compared with sandy soils.

- Structural features of different organic molecules could also alter their bioavailability.

- In many instances, a certain time period is required for adaptation of the micro-organisms to the contaminant to allow for the growth of unique populations to degrade the contaminants[g].

The highly variable nature of most environments together with the different physico/chemical factors may result in significantly different biodegradation rates even over short distances.

In many organic compounds resistance to biodegradation has been attributed to one, or more substituents which enhance the molecules recalcitrance. These substituents are often called xenophores and may include Cl, NO_2, SO_3H, Br, CN and sometimes CH_3, NH_2 and OCH_3 (ether). These xenophores are very seldom encountered in nature and, therefore, there are often not many organisms which have the enzyme compliments required for to degrade xenophores[27] and others.

The degradation of certain organics is, however, often stimulated by the addition of other substituents, such as, OH, COOH, an amide, ester or anhydride functional group. However, the impact of the substituents will vary depending on the rest of the structure of the different organic molecules as some compounds containing NO_2 (e.g. 4-nitrophenol) and SO_3H (e.g. some surfactants) and CN groups are rapidly degraded.

Furthermore, not only the type of xenophore but, also, number and position on a molecule will have an influence on the biodegradation of the molecule. In some compounds the position of the xenophore has a small impact and on others, a dramatic impact on biodegradation. For example, methyl branching leads to persistence of aliphatic hydrocarbons, aliphatic acids, alcohols and other chemicals.

Highly branched pristanes and phytanes, for instance, are significantly more resistant to biodegradation compared with non-branched alkanes. Further, short alkanes tend to degrade more rapidly than long chained compounds. The biodegradation potential for the aromatic and poly-aromatic hydrocarbons is more complex, although, to a large extent are dependent on the amount, type and position of substituents. Detailed metabolic pathways for the degradation of these molecules have been described in numerous sources[27,28,29] and are not repeated here due to scope limitations.

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g It could be theorised that this adaptation may actually allow a period for the synthesis/production/action of a surfactant. The development and utilization of a surfactant which increases the efficacy of microbial degradation is one of the key issues discussed under the organic results section of this report. Surfactant use, which effectively increases microbial degradation of the test contaminant significantly, will be a key consideration of the ultimate design, installation and use of a PRB.

2.4.7 Microbes & Reactive Media: Key considerations

There are a number of pertinent aspects with respect to reactive media that have particular influence on the optimisation of microbial activity. To be effective, support media should serve various functions:

- It should serve as a form of readily available carbon for the micro-organisms to use as a carbon source.
- It should, ideally, also provide other nutrients and large numbers of microbial innocula, as well as have a large surface area to maximise microbial attachment.
- Further, it should show minimal filter bed compaction over time to prevent pressure drops and have a high porosity to reduce back pressure.
- Lastly, these media should be readily available and are inexpensive.

Other non-halogenated organic molecules, such as petroleum hydrocarbons, on the other hand, serve as the carbon source *per se* and the media chosen for these PRBs does not primarily serve as a carbon source but should have all the above-mentioned attributes.

Further, the indirect precipitation of the metals mentioned above (sulphate reducing bacteria) requires anaerobic conditions, while hydrocarbon degradation requires an aerobic environment. Therefore, in theory, provided that all other microbial requirements have been met, the degradation of these compounds does not require an added reactive media as the actual soil could be used for this purpose in exactly the same manner as any bioremediation programme.

For example, researchers[22] have used a whey barrier in order to stimulate microbial activity which, in turn, reduced the oxygen concentrations and, thus, induced a negative redox potential upgradient from the pollution source (methyl tert-butyl ether) while the bioremediation was continued in the soil downgradient of the pollutant source. However, it must be pointed out that having the support medium in one place and, therefore, more accessible, especially in a funnel and gate design[h], would allow for far greater system optimisation.

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h A typically shaped PRB design, as illustrated in Section 2.1

2.4.7.1 *Biodegradation and microbial requirements (principally as related to BTEX components)*

Organic compounds, especially petroleum related hydrocarbons, are often a significant groundwater pollution problem. These non-halogenated organic compounds require a different method of treatment. For example, simple reductive processes used for the degradation of halogenated organics via the corrosion of zero-valent iron PRBs will not facilitate degradation of these compounds. The main reason for this is that hydrocarbons require oxidative, therefore, aerobic microbial metabolic processes. Aerobes thrive only in oxygenated environments using dissolved oxygen as an electron acceptor.

Middle distillates, including kerosene, may contain as many as five hundred individual compounds; however, these compounds tend to be more dense, less volatile, less mobile and less water soluble than the gasoline-range materials.

Kerosene (one of the principal constituents of the test contaminant used experimentally described: Section 4 of this report) applies to that portion of petroleum boiling between the approximate limits of 180° and 320°C. The chemical composition of kerosene depends upon its source and usually consists of a mixture of about 10 hydrocarbons containing 10 - 16 carbon atoms/molecule. The constituents include alkanes and cycloalkanes; benzene and substituted benzene and naphthalene and substituted naphthalene.

It has been shown that the average chemical composition by weight is 35% paraffin, 60% naphthenes, and 15% aromatics. Kerosene has a density of 0.839 (water 1.00) and a viscosity of 2.3 (water 1.14) at 150°C. Although the organic fraction of the solvent contaminated water is a highly complex mixture of different organic compounds (see previous report) for the purpose of this discussion and study the water soluble fraction of the solvent will be simplified and represented as BTEX compounds.

One of the more common sources for BTEX-contamination of soil and groundwater are spills involving the release of petroleum products such as gasoline, kerosene, diesel fuel and lubricating and heating oil from leaking oil tanks. Because of their polarity and very soluble characteristics, the organic chemicals (BTEX's) of petroleum products will be able to enter the soil and groundwater systems and cause serious pollution problems. These BTEX compounds may comprise more than 60% of the mass that goes into solution when gasoline is introduced to water. Due to their relatively high solubility, BTEX compounds are the hydrocarbons most frequently reported as groundwater contaminants.

The BTEX group of contaminants consist of benzene, ethyl benzene, toluene, and three isomers of xylene. These organic chemicals make up a significant percentage of

petroleum products – including, critically, the organic contaminant utilised in this research. One reason why BTEX compounds are considered a serious environmental and public health problem is that they all have some manner of acute and long term toxic effects. In addition, benzene is known to be carcinogenic[38]. The carcinogenity and toxicity of BTEX components and their prevalence in both the test contaminant site and in more general polluted locales in South Africa factored highly in the risk assessment framework used in his research. It was deemed prudent to focus on these components within this research and to prioritise investigation of their (potential) treatment within PRBs.

Fate and Transport

The environmental fate of a mixture of organic compounds is a complex phenomenon that depends on numerous factors, although, in general, there are two primary deterministic factors.

Firstly, the physico-chemical features of the compounds and, secondly, biodegradation potential and biological (microbial) requirements. For example, liquid petroleum hydrocarbons and solvents are present in several phases following release to the surface soil and subsurface environments. They may be present as:

(1) free-phase liquid, or Non-Aqueous Phase Liquids (NAPL)[i];
(2) vapour in the pore spaces of soils;
(3) adsorbed to vadose[j] or phreatic[k] zone soils; or
(4) dissolved in ground and soil water.

The amount and partitioning of the solvent between the phases is largely a function of it's chemical composition and characteristics. The water solubility, vapour pressure, octanol/water partition coefficient and organic carbon coefficient will, largely, determine the partitioning of the compound and, thus, its inherent biodegradability.

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i Liquids that remain insoluble when mixed in with water, these liquids also have relative densities, i.e. Dense Non Aqueous Phase Liquids refer to heavier insoluble liquids.
j Refers to the generally unweathered and unsaturated zone between groundwater and the land surface of soils.
k As opposed to the vadose zone which is unwetted, the phreatic zone is generally saturated and is characterised by capillary dynamics.

2.5 PRB'S – PRESENT STATUS QUO AND REVIEW OF LONG TERM PERFORMANCE DATA

2.5.1 Introduction

This subsection aims to provide a picture of the current (international) profile of PRB technology, and importantly, how PRBs have been developed, characterized and have functioned and performed over defined time ranges[1]. From a global point of view, The United States has designed, installed and monitored the largest number of PRBs and similar technologies. As such, the consequent database is most useful to use when analysing any potential of PRB technology in southern Africa.

Lessons learned from the United States and other countries in terms of the design, installation, monitoring and efficacy of PRBs are also critical to review. Although the consensus amongst the authors of this report is that South African conditions probably provide unique, although not insurmountable, challenges to the use of PRB technology (see the latter sections of this report), many of the potential problems related to PRBs have been highlighted by the relative wealth of international literature on the topic.

Recent advances in PRB technology and unique approaches to (particularly) installation and monitoring are also provided in this section and are important to discuss and consider against the backdrop of the data developing out of this research and potential innovations that may need to be made if PRBs are to be installed and uitlised in South Africa.

The two volumes of the Capstone Report[39,40] on the application, monitoring and performance of PRBs for groundwater remediation produced by the United States Environmental Protection Agency provide the most recent and relevant synthesis of the (long term) performance, monitoring and application data for PRBs. Relevant sections of these reports are summarized, and their potential implications for PRBS in a South African context discussed.

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1 It is by no means an exhaustive review, and aims only to provide information and analysis relevant to any potential use of PRB technology in a southern African context. There is a wide range of published (international) literature on PRBs and related technologies that is relatively easily accessible, particularly via the internet (some of these links are provided as references in this report). The majority of the material, review, critique and analyses presented in this section have their origin from conference proceedings, miscellaneous articles, studies, presentations and discussions obtained and undertaken during the annual RTDF Permeable Reactive Barriers (PRB) Team Meeting in Niagara Falls, USA, during October 2003. Where and as necessary, all material is referenced in Section 8 of this report.

As a potential analogue (notwithstanding the obvious environmental differences), performance data from two long term PRB sites in the United States are analysed and summarised. This has been undertaken with a view to understanding the longer term efficacy and longevity of PRBs, particularly as relates to their potential use in a South African situation.

2.5.2 The Elizabeth City Site

This site and the groundwater pollution plumes associated with it are relevant to this study because of the combination of contaminants (inorganic and organic) that characterise it. The heavy metal chromium and the organic TCE (trichloroethylene)[m] have resonances with the combination of metals and organic components in the test contaminant from the Free State site – not chemically but more principally in the sense that they illustrate, quantitatively the treatment of a multi-contaminant plume. A summary of relevant aspects and performance data from this site is provided in the context of the literature survey, as well as providing an idea of the efficacy of PRBs generally.

2.5.2.1 Site Description

The Elizabeth City site in North Carolina (USA) abuts the Pasquotank River and housed an old chrome plating shop which was used for 30 years until 1984[40]. Chromic and sulfuric wastes had discharged into the soils and groundwater beneath the site resulting in a diffuse chromium plume that migrated north from the shop toward the river[41]. The plume has high (>10mg/l) chromate concentrations, elevated sulphate (150mg/l) and minor amounts of chlorinated solvent compounds (TEC; cis-1,2-dichloroethylene, vinyl chloride). The width of the plume is some 35m and extends to 6.5m below ground surface. The lateral extension is approximately 60m towards the river[42].

(While the above does not emulate a generalized hypothetical groundwater scenario in South Africa (with typically deep groundwater levels), it does provide clear illustration of treatment principles. The following section illustrates (international) deep groundwater PRB developments that could well be applied to a South Africa context).

The groundwater table on this site ranges from 1.5 to 2.0m below ground surface and the average hydraulic gradient varies from 0.0011 to 0.0033. Slug tests indicated hydraulic conductivity values between 0.3 and 8.6m/day, and a multiple borehole tracer

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m $CHCl{:}CCl_2$ Most likely used as a metal degreaser in this instance.

test in wells screened between 3.9 to 5.9m below ground surface indicate groundwater velocities between 0.13 and 0.18m/day[42].

In June 1996, a 46m long, 7.3m deep and 0.6m wide PRB (continous wall configuration) PRB of zero-valent iron was established close to the river (~30m). The reactive wall was designed to remediate hexavalent chromium contaminated groundwater, in addition to treating portions of the larger overlapping plume of TEC. A detailed monitoring network of more than 130 subsurface sampling points was installed in November 1996 to provide detailed information on spatial and temporal changes in pore water geochemistry[42].

Summarised monitoring results[41,42] illustrate that the reactive barrier has effectively removed chlorinated solvents and Cr^{6+}, as well as, amongst other species, sulphate, calcium, magnesium and silica.

2.5.2.2 Groundwater chemistry

A comparison of groundwater chemistry between up- and downgradient wells at the Elizabeth City site under review indicate that the iron zones are long term sinks for carbon, sulphur, calcium, silicon, magnesium, nitrogen and manganese. (Concentrations of dissolved iron are somewhat elevated in downgradient monitoring wells).[42]

These elevated concentrations of dissolved iron in downgradient wells may be caused by the release of iron from the aquifer due to decreased redox potentials in the regions immediately downgradient from the reactive media. In the region immediately upgradient from the iron wall at the Elizabeth City site, increases in the levels (concentration) of ferrous iron have led to the development of a reducing zone where hexavalent chrome is removed from the groundwater plume[42].

Corrosion of zero valent iron at both sites have been shown to result in mildly alkaline (pH >9.5) and highly reducing conditions (Eh<-100mV) in the iron media. Over the four of operation and monitoring by the US EPA team[42], pH and Eh values within the reactive media have maintained consistent values. This observation suggests that granular iron will maintain reactivity and the capability to reductively degrade contaminants over several years of operation[42] – sound and integral projections put this time value at between 10 and 15 years.[41, 43]

Mineral Precipitates

Mineral precipitate(s) build up over the four year monitoring period have indicated mineral precipitate accumulations in the reactive media that are insoluble at high pH and low Eh[42]. This accumulation seems to be systemic and not necessarily significant. Solid

phase characterisation studies implementing XRD, SEM, TEM, reflected light microscopy, transmitted light microscopy and XPS indicate the formation of lepidocrocite, magnetite, carbonate minerals (aragonite, iron carbonate hydroxide and/or siderite), carbonate-green rust, and iron monosulfide as primary precipitates in the PRBs in a number of sites treating a range of contaminants[42, 44, 45, 46].

Microscopic observations indicate that mineral accumulation is occurring mainly on the surfaces of the iron particles where steep gradients in pH and redox potential result in mineral precipitation. After approximately four years of mineral accumulation,[42] a regular coverage of surface material ranging in thickness from 10-50µm is observed on iron grains collected near the upgradient interface.

Where mineral accumulation is the greatest, distinctive particle morphologies include aggregates of platy particles (characteristics of green rusts); homogenous crusts without euhedral morphologies (characteristics of iron oxyhydroxides); and thin coatings or aggregates of very fine grained particles (characteristic of iron monosulfides)[42].

Concentration distributions of inorganic carbon (IC) and sulphur from cores taken from the PRB and accumulation of IC and sulphur shown to be greatest near the upgradient aquifer-Fe^0 interface, with concentrations decreasing with increasing penetration into the iron[42].

Authigenic sulphur in the reactive barriers is mainly present as labile iron sulphides (mackinawite) rather than the more stable iron disuphides (pyrite, marcasite)[42]. This observation is important because the presence of mackinawite could potentially enhance the rate of degradation of halogenated aliphatic compounds in PRBs[47]. Furthermore, the high pH/low Eh geochemical signature in the iron media favours the chemical reduction of sulphate to sulphide. As rates of chemical sulphate reduction at low temperatures are extremely slow[48], it is expected that the low Eh environment supports metabolism by sulphate-reducing bacteria in the iron media[42].

Microbial Activity

A number of core samples were collected from the Elizabeth City site and were analysed for content and distribution of phospholipids fatty acids (PLFA). These organic compounds can be used as lipid biomarkers to provide a method to evaluate viable microbial biomass, community composition and nutritional status[40, 42].

At the site under consideration, the highest biomass levels were observed in upgradient core subsections that contained the aquifer-Fe^0 interface. These samples contained 600-900 pmoles of PLFA per gram of sediment and iron[42]. While total biomass peaked at the aquifer iron interface, the contribution of anaerobic biomarkers identified,[49, 42] (terminally branched saturate fatty acids, branched monenoics fatty acids, mid branched

saturate fatty acids) as a percent of total biomass peaked approximately 5cm into the iron matrix[42].

Microbial biomass correlates well with total sulphur, suggesting that the accumulated biomass around the PRB contains an aerobic sulphate reducing bacterial consortium[42]. The localisation of metal and sulphate reducing activity near the upgradient aquifer/PRB interface would seem to correlate reasonably well with the iron, sulphate and Eh results, in addition to the sulphur concentrations and porosity changes, highlighted by the site researchers[42, 40].

Evaluation of the microbial populations based on PLFA data from the downgradient PRB/aquifer interface indicates a 10-fold reduction in microbial biomass compared to the upgradient edge. The lower bacterial counts associated with the mid-barrier and downgradient region(s) suggest the environment at these locations is more challenging to bacterial growth and survival[42].

A parallel assessment of the geochemical conditions at these locales supports this assertion as it indicates a decrease in biologically available electron acceptors such as sulphate and cis-DCE and an increase in pH n the mid-wall and downgradient locations[42, 40].

Summary

In summary, groundwater chemistry, flow rate and microbial community structure are the principal factors that determine the amount of mineral precipitation and the spatial distribution of mineral precipitates in reactive iron media. After approximately four years of operation and monitoring, the PRB barrier under consideration developed consistent patterns of spatially variable mineral precipitation and microbial activity[42]. The average rates of IC and sulphur accumulation are 0.09 and 0.02kg/m^2/year respectively, where upgradient waters contain <400mg/l of TDS[42].

After four years of operation, the site is not showing the filling of available pore space needed to measurably impact hydraulic head distributions, suggesting that flow characteristics should not be affected by the accumulation of authigenic components. However, biofilm coverage and coatings of mineral precipitates on the reactive media may affect flow patterns,[50, 51] and they may adversely affect the reactivity of iron particles by decreasing the kinetics of contaminant degradation reactions[42].

At the Elizabeth City site, concentrations of chromium in excess of 0.01mg/l have not been observed in any of the downgradient monitoring wells since November 1996. Similarly, concentration of chlorinated organic compounds (TCE, cis-DCE, VC) are below (US) regulatory target levels in downgradient monitoring wells[42].

2.6 PRB DEVELOPMENTS AND REFINEMENTS: POTENTIAL TOOLS FOR APPLICATION IN THE SOUTH AFRICAN ENVIRONMENT.

2.6.1 Introduction

The literature survey, and concomitant discussions with key researchers and workers in the field, has revealed a number of areas of development that that may be applied to the South African situation. These relate specifically to the presence of (mining) related contamination in groundwater that occurs in aquifers relatively deep below the surface. Two of the technological advancements are highlighted here and are discussed in more detail, in addition to being framed in the context of the results of this research, in Sections 5 & 6 of this report.

Although the technologies are similar (in the sense of their potential applicability to the South African situation), specific aspects and nuances of the technology described are different structurally and, critically, in the amount of supportive data they have to illustrate their efficacy.

2.6.2 Deep Aquifer Remediation Tools (DARTs)

The US Geological Survey[53] has developed a groundwater treatment tool that is used in conjunction with non pumping wells and offers a low cost and virtually maintenance free alternative to (traditional) *ex situ* treatments.

Research[54] has shown that that water in subsurface environments will converge to arrays of unpumped wells (boreholes) in response to the difference in hydraulic conductivity between the well and aquifer. Numerical simulations conducted during DART development indicates that each well typically intercepts groundwater in the upgradient part of the aquifer that is approximately twice the inside diameter of the well.

2.6.2.1 DART Composition

DARTs are composed of three basic components and are designed to fit a variety of well dimensions and plume geometries[53]. These components typically comprise:

(i) A rigid PVC shell with high capacity flow channels to contain the reactive material;
(ii) flexible wings to direct the flow of groundwater into the permeable reactive material; and
(iii) Passive samplers to determine the quality of treated water.

Multiple DARTs can be joined together for the treatment of thicker contaminant plumes. DARTs also allow for "vertical stacking" of different reactive materials for the treatment of chemically segregated contaminant plumes[53]. Furthermore – and important potentially in the South African context – treatment of *in situ* deep plumes (~30m) is possible. These tools also allow for easy retrieval, replacement and disposal of reactive material after chemical breakthrough.

2.6.3 Azimuth Controlled Vertical Hydrofracturing[55]

An Atlanta (USA) based company, GeoSierra, has developed technology that may have potential applications in the South African deep groundwater environment. They have developed a method to induce fractures in (sandy) soils into which reactive material is injected in the path of a groundwater plume. Conventional boreholes are sunk in a string, perpendicular to a plumes leading edge. Shaft casings are expanded (using a propriety technique), sequentially inducing a fracture. Zero-valent iron is injected in an enzyme based gel solution which breaks down after a few hours, leaving an effective iron barrier to treat contaminants[55].

Figure 2.4 illustrates this technique.

The technique is capable of installation for treatment of contaminants at depths of ~80-100m, and can be applied to variety of geologies including clay tilts, sills and sands as well as flowing sands, gravels and cobbles. Critically though, design and installation should be preceded by hydraulic pulse testing and groundwater modelling to inform a probalistic design[56]. Typically the stages of installation and the associated pre and post installation testing are summarised below

- Pre-PRB construction
  (i) Groundwater Column Test
  (ii) Hydraulic Pulse Interference Test

(iii) Probabilistic Design

- During PRB Construction
  (i) Active Resistivity Imaging – visual verification of the fracture geometry and colalescence of different fracture segtments.
  (ii) Measured injection volumes of Iron
  (iii) Geometric verification of wall thickness & coalescence

- Post-PRB Construction
  (i) Hydraulic Pulse Interference Test to validate permeability of the reactive material to the influent contaminant
  (ii) Inclined Profile Resistivity Test verifies wall thickness and the maintenance thereof.
  (iii) Corrosion testing (longer term) to ascertain loss of integrity of reactive surface of reactive material.

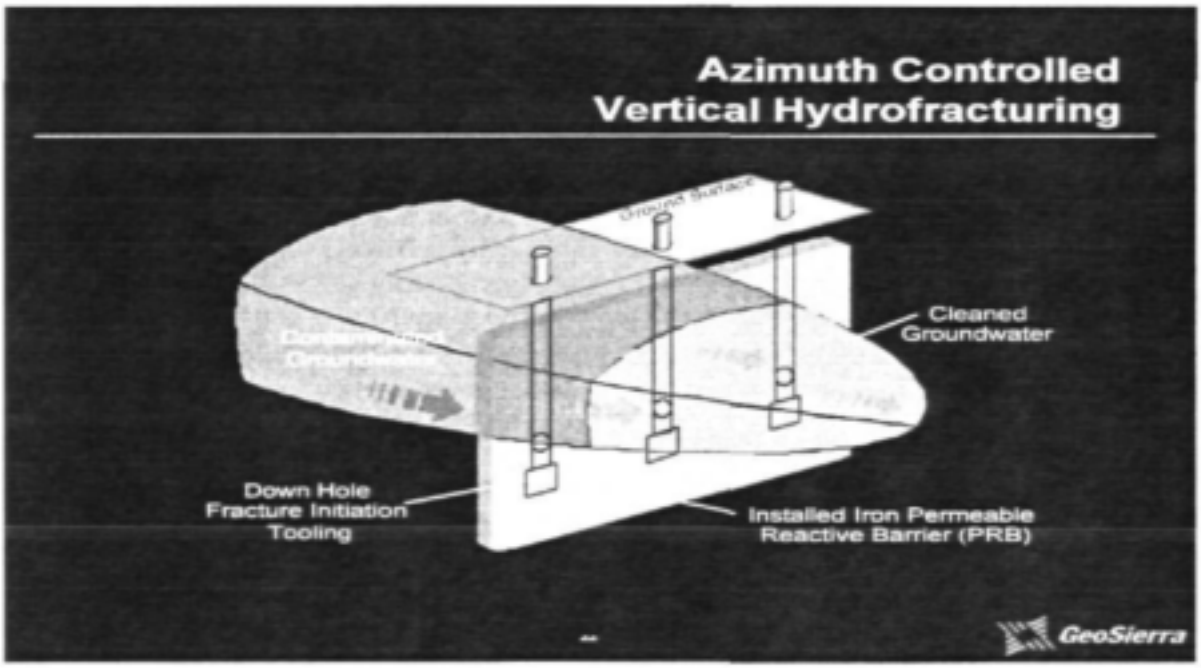

Figure 2.4 A diagrammatic illustration of Azimuth Controlled Vertical Hydrofracturing, a process that may have potential applications in the South African environment. (Source: GeoSierra 2003)

CHAPTER 3 INORGANIC RESEARCH COMPONENT

3.1 EXPERIMENTAL METHODOLOGY

3.1.1 Experimental Design Considerations

There is a significant body of information relating to the fact that many dolomitic aquifers in the Potchefstroom/Klerksdorp areas of the North Western Province (particularly) are polluted with uranium[64]. As uranium also formed a key component of the test contaminant from the metallurgical site, it was deemed particularly appropriate to focus this investigation on the applicability of PRB technology towards this contaminant. In doing this, further contextual validity has been added to the research as it can (potentially) be applied to other locales and contaminant complexes/dynamics in South Africa (one of the overall aims of the initial motivation for the research).

Uranium formed the contaminant (metal) under investigation for remediation by PRB technology for this component of the study[n]. Under conditions expected in aquifers known to be polluted with uranium, the form of the uranium is hexavalent, and the solution in which the uranium is transported is dolomitic water (simulating local conditions), containing high concentrations of calcium, magnesium and carbonate.

From the literature survey, zero-valent iron is known to very effectively remove uranium from contaminated waters, and thus it was the material of choice for this study.

From published batch reaction tests[10], it was assumed that chemical reaction rates at the iron surface would be such that the reactions would be over in less than two hours. An experiment was designed to proceed over three hours, to account for uncertainty and variability in reaction conditions.

Since the experiment dealt with a contaminant known to be immobilised in the barrier material proposed for testing, batch tests were deemed unnecessary, and the fundamental research question has been developed in Section 3.1.2 below.

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n Uranium was not obtained from the test contaminant from the Free State metallurgical site as separation from the other chemicals would prove too difficult (over time, it had bonded to the organic fraction of the complex). Instead, a sample of uranium nitrate was used to better imitate conditions in the field and in the interests of accurately discerning iron action on the uranium.

3.1.2 Primary Research Question

The primary research question that formed the basis of Section 3 may be stated as: "*To what extent, and at what rate, is the uranium in the contaminated water immobilised by iron?*" This research question formed the basis of further deliberations in this report and the assertions that are posited around its outcomes.

3.1.3 Reactive Material Sourcing

Iron grains were obtained from Saldhana Steel in the Western Cape, for use in the experiments. This material is also available locally at Kumba Resources steel plants in the Vaal triangle, southern Gauteng. The chemical composition of this material is provided in Annexure 2.

This material was chosen as one form of experimental reactive material as it is readily available and any efficient performance with respect to Uranium removal will bode well for future potential field trials and the availability of cheap, bulk sources of iron. Since steel wool is known to be extremely effective at immobilisation of uranium, it was chosen as a second test material, i.e. as a "positive blank". The "negative blank" was chosen to be swimming-pool filter sand, based on the fact that it had been used in a published study of a column test for PRB design[1].

From published batch reaction tests, it was assumed that chemical reaction rates at the iron surface would be such that the reactions would be over in less than two hours. An experiment was designed to proceed over three hours, to account for uncertainty and variability in reaction conditions.

3.1.4 Laboratory Column Tests

The Water Laboratory at the Council for Geoscience was utilised for the inorganic testwork. Lakefield Research handled the analytical and quantitative work. Two column tests were conducted to determine the capacity of elemental iron in two different forms to attenuate soluble uranium in dolomitic water. A "blank" column was run in parallel.

The columns contained mixtures of "pool filter" sand, granulated iron and iron in the form of shredded steel wool. The mass ratio of granulated iron to total was 7.9%, and the mass ratio of shredded steel wool was 7.8%

In the following sections, these columns are referred to as in the following table:

Table 3.1 Characteristics of columns used in the study

Column Number	Column Matrix
A	Swimming pool filter sand
B	8% granulated iron/sand mix
C	8% steel wool/sand mix

The columns were constructed of 50ml plastic measuring cylinders, with an approximate length of 15 cm and an internal diameter of 2.0 cm. Flow rate through the columns were adjusted by manually adjusting the pressure head between column outflow and the eluant reservoir. Flow rate was measured manually with a clock, and graduated collecting vessels.

Each column was carefully packed to ensure that the mixture was maximally homogeneously distributed. For columns containing the iron and sand mixtures, aliquots of the sand-iron mixtures were packed in lifts, taking care to reduce the probability of layering. All measurements were determined gravimetrically and are shown in Annexure 4. Porosity values were approximately 0.35.

Pore volume measurements were determined experimentally by weight and were of the order of 13.8ml. Several pore volumes of tap water were flushed through each column before the laboratory water was introduced. All column experiments were conducted at room temperature.

3.1.4.2 Column Sampling

The columns were sampled periodically over time until about 40 pore volumes had passed through. The set of column tests were run with an average flow velocity of 13 m/day and a standard deviation of 3 m/day. At all times attempts were made to keep the flow velocity constant and identical for all columns.

Eh and pH of the sample aliquots were immediately measured. Eh measurements are presented in this report with relatively low confidence levels as some instrumentation problems were encountered at times.

Samples were submitted to Lakefield Laboratories for analysis of major ions, uranium and iron (Appendix 4).

3.1.5 Chemical Composition of Column Test Solutions

Chemical composition statistics for DWAF monitoring data for the Wonderfoneinspruit Dolomitic Eye at DWAF sampling point C2H030 were kindly donated by Dr Frank Winde of the Far West Rand Dolomitic Water Users Association.

Based on these statistics, the following chemical composition of test stock solution was devised (Table 3.2).

Table 3.2 Composition of Stock Solution (simulated dolomitic water)

Salt	mg/l	Mr (g/mol)	mol/l
$NaHCO^3$	87.10	83.67	$1.04x10^{-3}$
$CaSO^4$	93.77	136.1	$6.89E^{-4}$
$CaCO^3$	85.50	100.1	$8.54E^{-4}$
$MgSO^4$	185.89	120.4	$1.54E^{-3}$
NaCl	47.35	58.44	$8.10E^{-4}$

Since the experiment was designed to simulate a real contamination situation, uranium concentration of the stock solution was devised to be similar to that obtained in the field (groundwater at the Koekemoerspruit, North West Province[65]).

A sample of uranium nitrate was kindly donated by the Council for GeoSciences, and this was added to the stock solution.

The stock solution was used immediately, i.e. maximum period of standing of the stock solution was one hour.

3.1.6 Determination of solution breakthrough point

The columns were initially flushed with approximately three pore volumes of tap water, after which the stock solution of simulated dolomitic water with uranium was siphoned into the column.

Since the stock solution had a higher salt content to the tap water, electrical conductivity was hypothesized to be an adequate "tracer" variable to distinguish the tap water from the eluant solution. Figure 3.1 features a plot of conductivity versus pore volume eluted, from which one may conclude that the eluant solutions broke through the columns after approximately 0.35 metres, or eight pore volumes of solution through-flow.

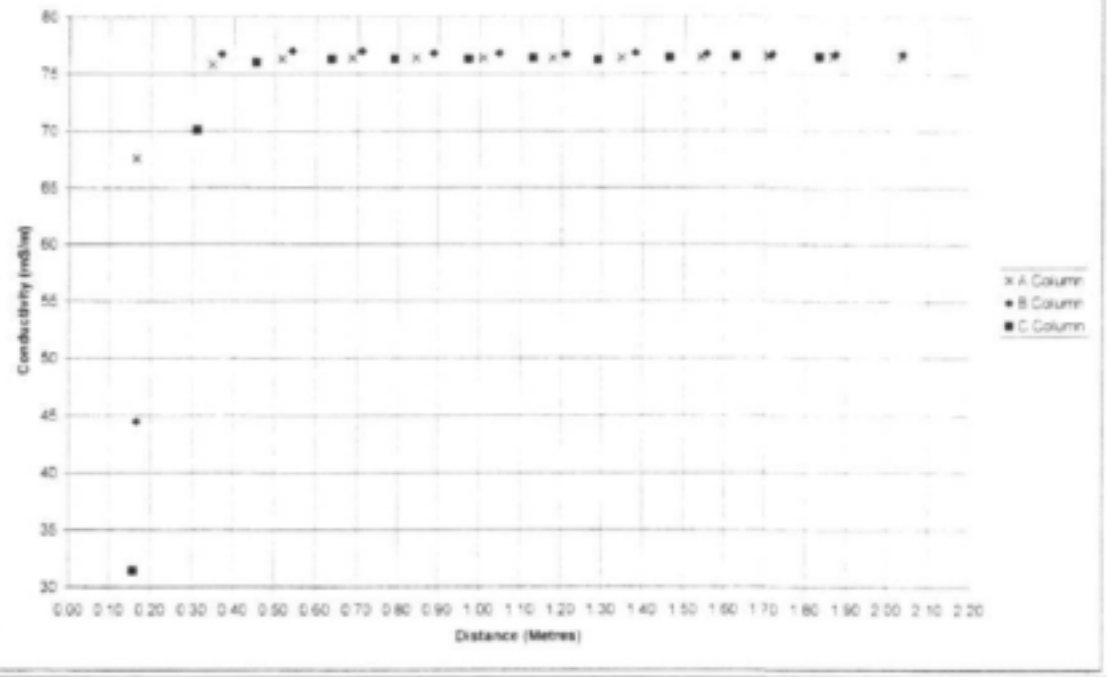

Figure 3.1 Use of electrical conductivity as a tracer to determine when eluant solution breaks through. The breakthrough for all three columns seems to be at 0.35 metres, or about 8 pore volumes.

3.2 RESULTS

3.2.1 Interpretation of "Distance travelled" in column experiments

There are a number of conventions that are used when representing the progress of materials through columns. Experimentalists are most familiar with the convention of using "pore volumes" as the measure for progress of reactants along a column. In this convention, the void space between the solid particles in the column is estimated, and the total void space in the column is referred to as one "pore volume". If an substance is carried by an inert liquid passing through a column such that the rate of progress of the substance is half that of the inert liquid, one may expect the substance to "break through" (i.e. manifest in the eluant) after two pore volumes.

In PRB studies, however, it is important to know how thick to make a barrier so that all contaminants of concern are safely disposed of. Thus, in this field, it is the *distance*

travelled by the average inert solution particle that is the measure of progress along the column.

As described in Section **Error! Reference source not found.**, the average porosity of the column matrices was determined to be 35%, making the average pore volumes of the columns 13.8 ml. The diameter of the columns was 2.0 cm, making the cross-sectional area 3.14 cm^2. Thus, in clearing one pore volume, the liquid flowing through the experimental columns would have travelled 4.4 cm.

The progress of reactants through the experimental columns is presented in the following figures in terms of metres of barrier material that would have been travelled through. The raw data is presented in **Error! Reference source not found.Error! Reference source not found.**, in terms of both pore volumes cleared, and distance travelled.

3.2.2 Profile of pH & Eh in the test columns

3.2.2.1 pH

The pH of aliquots of eluants of the three test columns are presented in Figure 3.2.

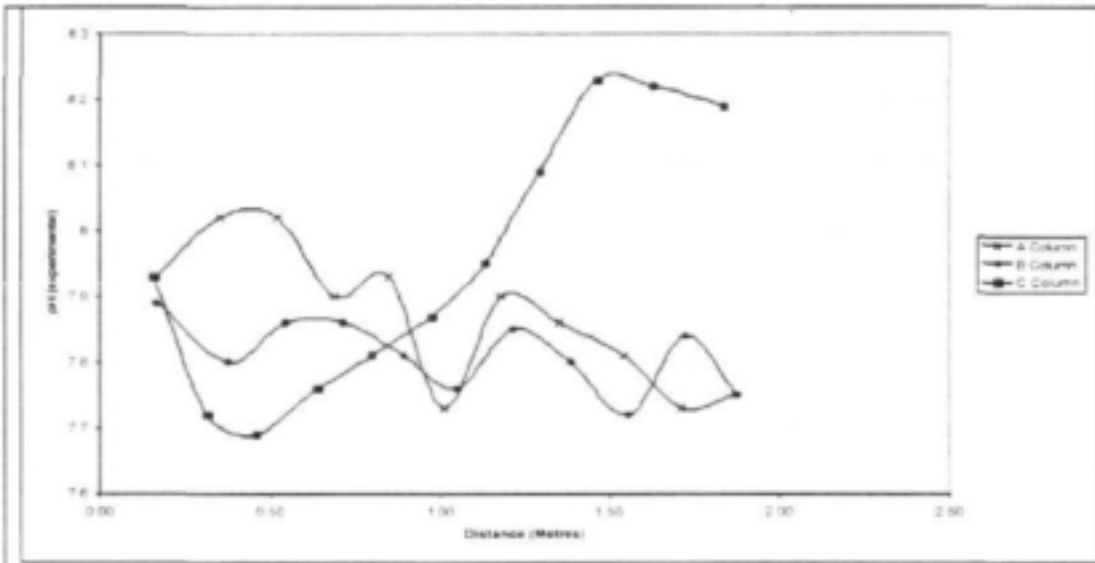

Figure 3.2 Profiles of pH as a function of distance travelled along the columns. Column A consists entirely of pool filter sand. Column B is a 8% granulated iron/sand mix, and Column C is a 8% steel wool/sand mix.

Three observations can be made regarding the pH of eluants:

- The pH readings of the A and B columns seem "chaotic". There does not seem to be a general trend in pH readings for these columns.
- The pH of the A column eluant seems to be generally higher than that of the B-column eluant. The B column contained granulated iron.
- The pH of the C column seems to gradually rise to about pH 8.2, in a very smooth, monotonic fashion. This was the column with steel wool in it.

3.2.2.2 Eh

The Eh profiles of eluates of the three columns are presented in Figure 3.3.

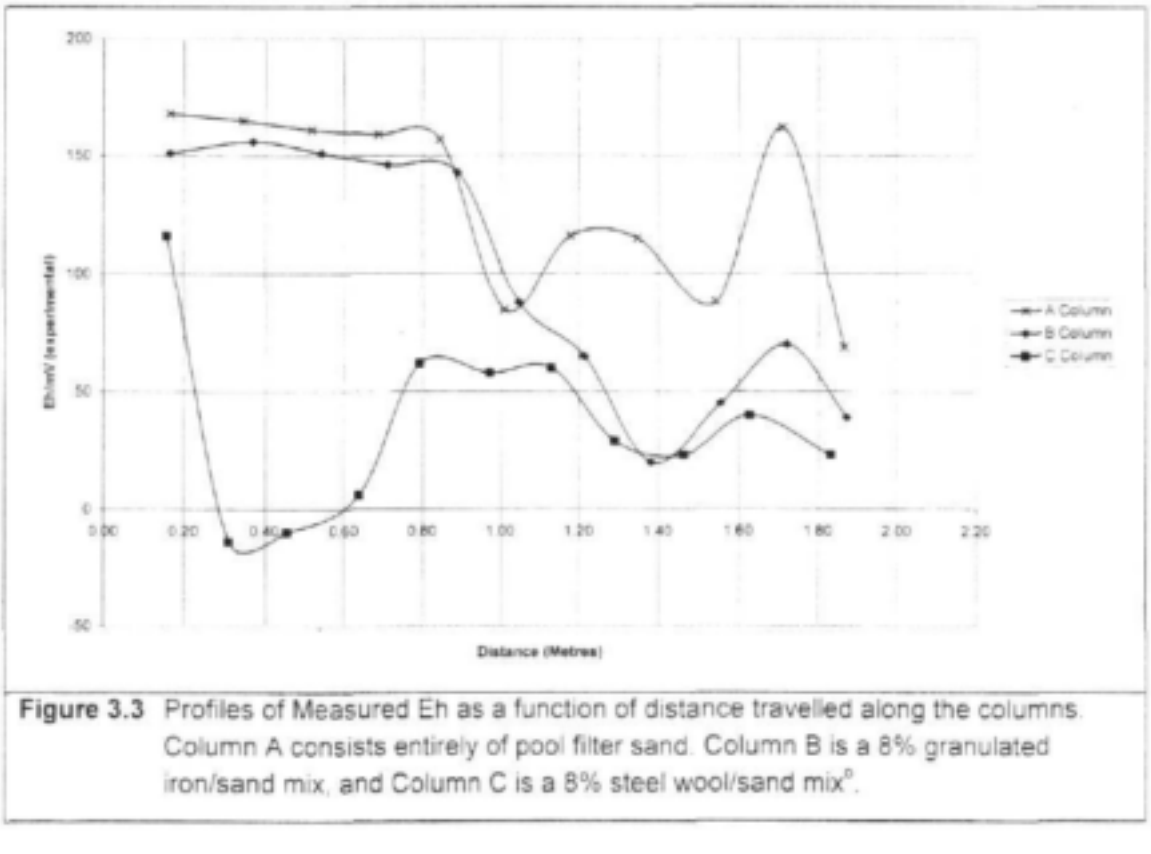

Figure 3.3 Profiles of Measured Eh as a function of distance travelled along the columns. Column A consists entirely of pool filter sand. Column B is a 8% granulated iron/sand mix, and Column C is a 8% steel wool/sand mix[o].

o There may be some degree of error associated with these readings due to a faulty electrode – ascertained after the experiment and too late for any experimental reruns.

There are three notable observations regarding Eh:

- The Eh readings of the columns are non-monotonic – they seem "chaotic" with respect to distance, or time.

- The Eh of the B column eluant seems to be generally lower than that of the A column eluant. The Eh of this column eluant seems to drop as a function of time. The B column contained granulated iron. This implies that there was some reaction of the iron with water to lower the Eh of the solution.

- The Eh of the C column, which contains steel wool, is almost always lower than that of the other two columns. The Eh of the C column seems to gradually rise, then lower, as a function of time.

3.2.2.3 *Eh and pH*

Usually, when a chemical influence directly causes a change in Eh, or in pH, there is a concomitant, and inverse, change in the other variable. In other words, if the pH of a system is lowered, the Eh rises, and *vice versa*. If the Eh of a system is lowered, the pH rises, and *vice versa*.

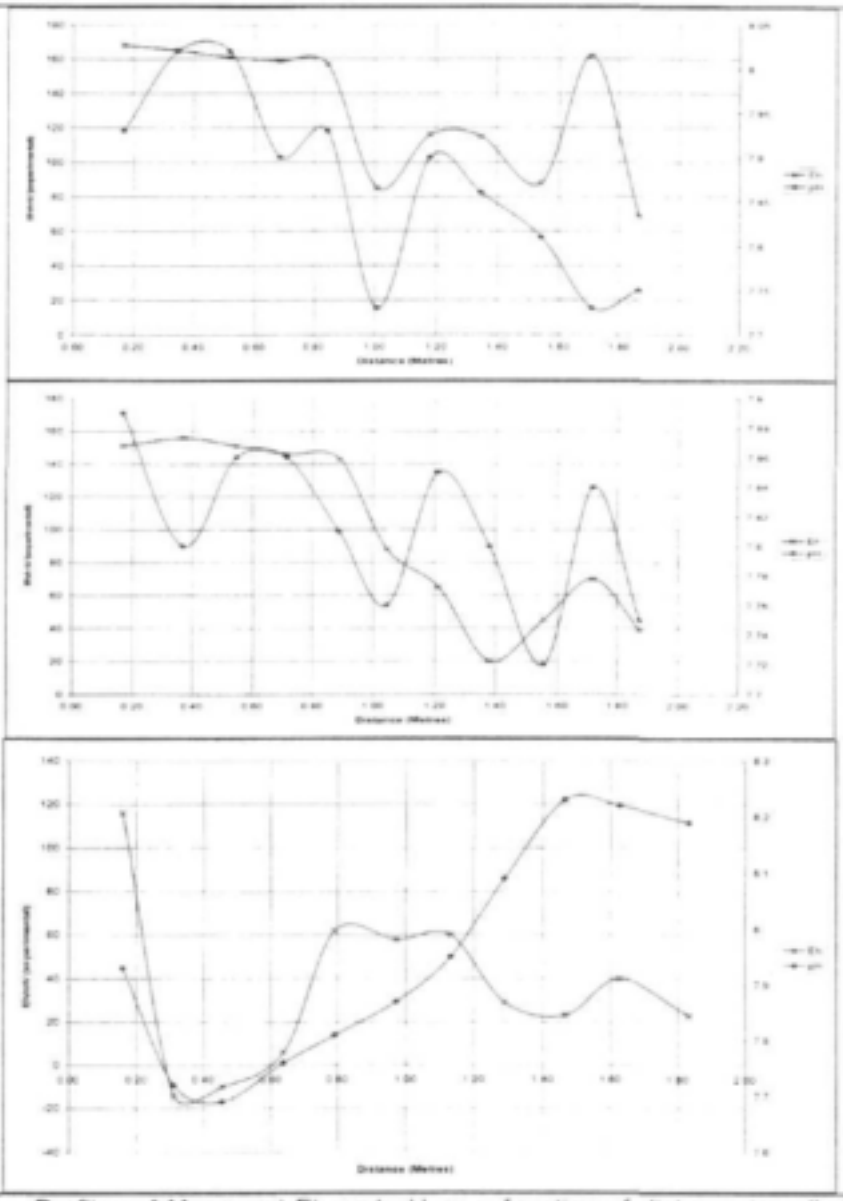

Figure 3.4 Profiles of Measured Eh and pH as a function of distance travelled along the columns. Column A (top) consists entirely of pool filter sand. Column B (middle) is an 8% granulated iron/sand mix, and Column C (bottom) is an 8% steel wool/sand mix.

The diagrams presented in Figure 3.4 show no such relationship between Eh and pH for the test columns. This could mean that there is a chemical process external to the process of interest that is buffering the Eh or the pH values, by coupling other reactions to either of these variables.

3.2.3 Profiles of soluble iron concentration in the columns

No iron was found in the eluant of the filter sand and 8% granulated iron/sand columns (Figure 3.5).

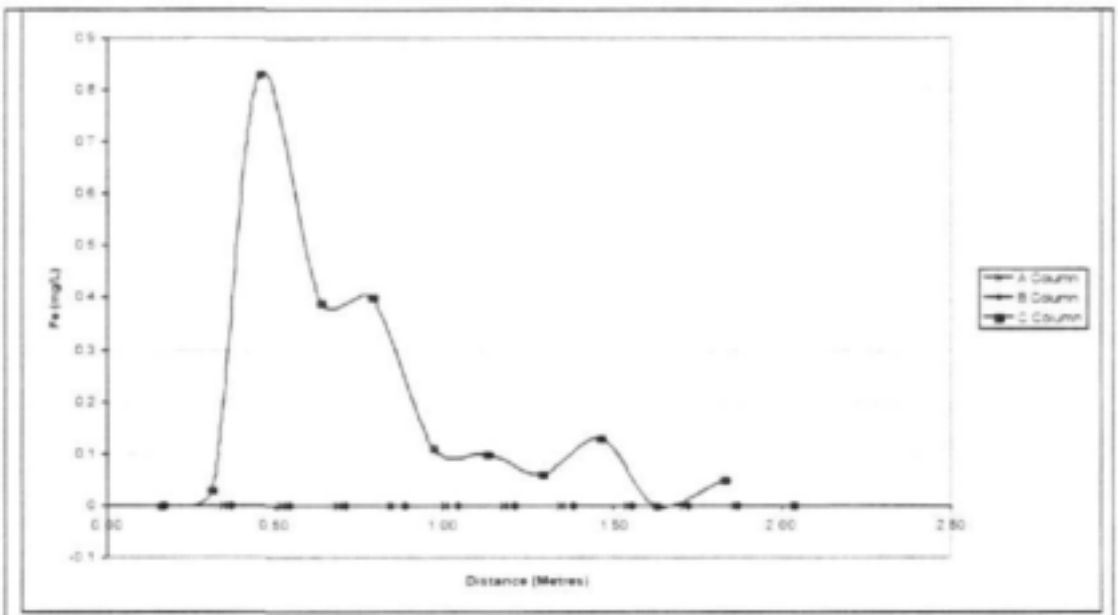

Figure 3.5 Profiles of eluted iron as a function of distance travelled along the columns. Column A consists entirely of pool filter sand. Column B is a 8% granulated iron/sand mix, and Column C is a 8% steel wool/sand mix.

The iron concentrations and pH of the eluant of the steel wool/sand column are presented in Figure 3.6.

The soluble iron concentration in column C is seen to appear almost immediately once the uranium-containing eluant breaks through the column (at 0.35 metres).

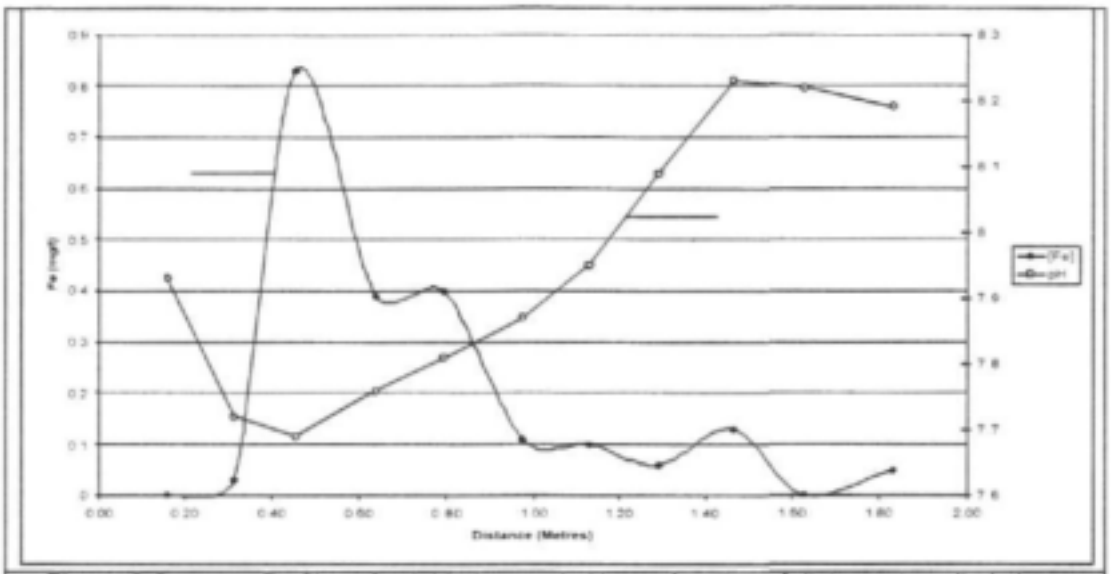

Figure 3.6 Profiles of soluble iron and pH as a function of distance travelled along Column C, which is a 8% steel wool/sand mix.

3.2.4 Uranium retention in the test columns

The eluant characteristics of the three test columns with respect to uranium concentration are presented in Figure 3.7.

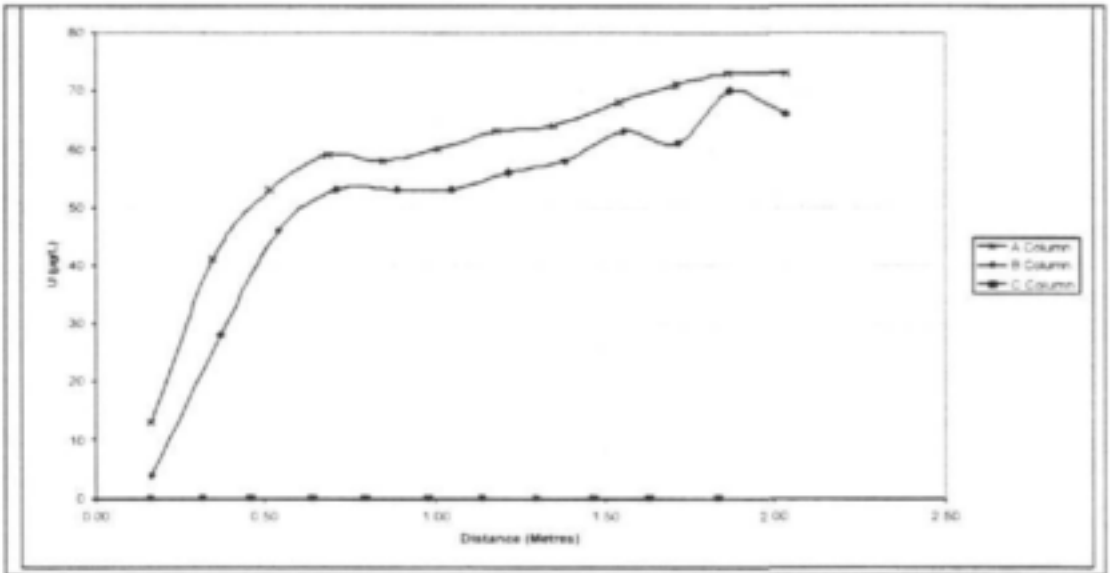

Figure 3.7 Uranium concentration as a function of distance travelled along the column. Column A consists entirely of pool filter sand. Column B is a 8% granulated iron/sand mix, and Column C is a 8% steel wool/sand mix.

Four important points may be made concerning the uranium concentration in the eluant.

- In column A, which consists entirely of filter sand, the "breakthrough" of uranium at 0.35 metres is not as clear as the breakthrough of electrical conductivity.
- The uranium concentration of the eluant of column A increases almost entirely monotonically, levelling off at about 2 metres, or about 40 pore volumes.
- The uranium concentration of the B-column, which contained 8% granulated iron, was lower than that of the A-column, although not as low as would be expected.
- The uranium concentration of the solution leaving the C-column, which contained 8% steel wool, was effectively zero (below instrumental detection limits of 2.1 µg/l).

The profiles of uranium concentration and pH in the B-column are presented in Figure 3.8

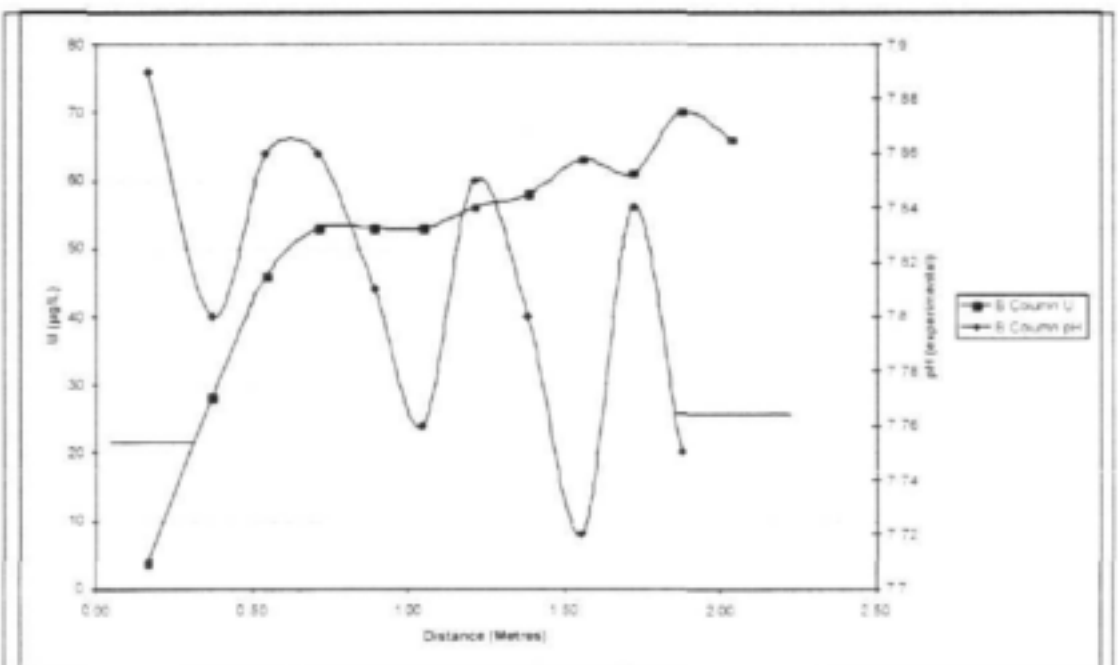

Figure 3.8 Profiles of uranium eluted and pH as a function of distance travelled along Column B, which is an 8% granulated iron/sand mix.

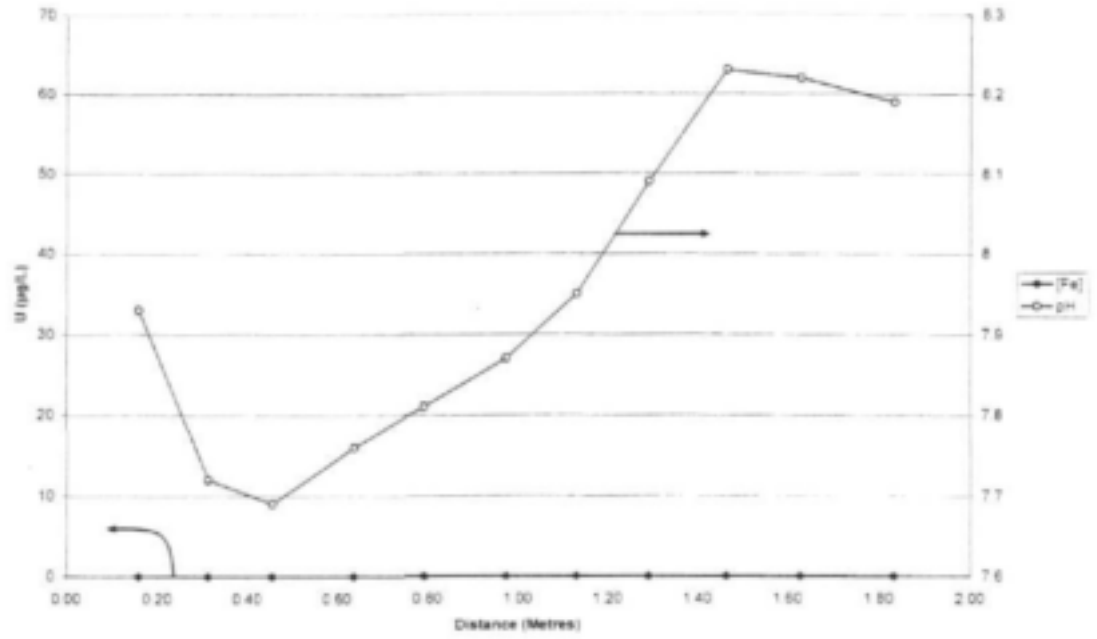

Figure 3.9 Profiles of uranium eluted and pH as a function of distance travelled along Column C, which is an 8% steel wool/sand mix.

3.3 SUMMARY OF OBSERVATIONS OF THE COLUMN EXPERIMENTS

3.3.1 Column containing sand only

Uranium concentrations in the eluant from the sand column rose steadily, accompanied by a possible slight decrease in pH readings. This is consistent with the hypothesis that uranium in the test solutions is binding with silica on the filter sand matrix of the columns. The silyl adsorption sites for attachment of uranyl ion are not sufficient in concentration to completely take up the influent concentration of uranium, and they saturate over time, becoming completely saturated at about 40 pore volumes of through-flow.

3.3.2 Column containing 8% steel wool in sand

Uranium was immobilised completely by the column bearing 8% shredded steel wool/sand mixture. The increase in pH during reaction of zero-valent iron with dissolved uranyl ion is probably due to concomitant release of zero-valent iron atoms, and oxidation of these atoms by dissolved oxygen. This hypothesis is corroborated by the

decrease in Eh over time, and the concomitant release of dissolved iron, undoubtedly in the form of ferrous ion.

3.3.3 Column containing 8% granulated iron in sand

The pH of the column seems to have decreased slightly during elution, and the oxidation potential seems to have decreased over time. There was greater uranium fixation by comparison with the sand column, though far less than the column with steel wool. There was no iron breakthrough. These observations are in accord with the hypothesis that uranium was displacing protons on silyl groups of the sand matrix, and was reacting with the zero-valent iron at a rate low enough for the precipitation of iron as siderite or ferric hydroxide to dominate, thus immobilizing iron in the column.

3.4 Reaction Progress - Modelling Studies

3.4.1 Introduction

Reaction progress modelling was undertaken for the inorganic component of the research to, principally, further understand the action on uranium by iron in a hypothetical PRB situation. Specifically, it was important to begin to critically understand the effect that a dolomitic water environment could have on the interaction and dynamics, specifically as regards, inter alia, the (i) immobilisation of the uranium; (ii) fate of the iron and the iron/uranium complexes; and (iii) leaching/movement of any compounds into "downgradient" sections of a hypothetical PRB in a dolomitic aqueous environment.

3.4.2 Modelling the Stock Solution

The chemical speciation of the stock solution should be understood before any experimental or further reaction progress modelling occurs.

3.4.2.1 Macro-ion description of the stock solution

Samples of solution were analysed, and the results are presented in Table 3.3. A chemical speciation calculation was performed on the analytical results using PHREEQC.

Table 3.3 Chemical analysis of stock solution, with charge imbalances from chemical speciation calculation

Parameter	Average Value	Error
U [µg/L]	63.22	10.3%
pH [unit]	7.86	0.7%
Cond [mS/m]	76.41	0.1%
T.Alk [mg/L $CaCO_3$]	33.11	1.0%
HCO3 [mg/L HCO_3]	20.00	0.0%
Cl [mg/L]	24.56	4.1%
SO_4 [mg/L]	251.89	3.4%
Ca [mg/L]	51.78	2.1%
Mg [mg/L]	39.67	1.8%
Na [mg/L]	43.89	1.8%

Simulation of this solution (using the alkalinity values) yields a charge imbalance of 10%, and if bicarbonate is used, charge imbalance is 12%. The quantity most out of balance is the chloride concentration. The chloride concentration was adjusted by chemical speciation calculation to yield an overall charge imbalance of zero (Table 3.4).

Table 3.4 Parameter values for stock solution used in modelling calculations

Parameter	Value
U [µg/l]	63.22
pH [unit]	7.86
Cond [mS/m]	76.41
HCO_3 [mg/L HCO_3]	20.00
Cl [mg/l]	77.75
SO_4 [mg/l]	251.89
Ca [mg/l]	51.78
Mg [mg/l]	39.67
Na [mg/l]	43.89

3.4.2.2 Chemical speciation of Uranium in the stock solution

The chemical speciation of uranium in the stock solution was calculated with PhreeqC, and the results of the calculations are presented in Table 3.5

Table 3.5 Chemical Speciation of Uranium in Stock Solution

Species[p]	moles/l	µg/l U	%
$UO_2(CO_3)_2^{-2}$	2.51	59.81	80%
$UO_2(CO_3)_3^{-4}$	3.38	8.04	11%
$UO_2(OH)_3^-$	1.58	3.75	5%
UO_2CO_3	1.43	3.40	5%
UO_2OH^+	1.04	0.02	0%
UO_2SO_4	1.75	0.00	0%
UO_2^{+2}	1.38	0.00	0%
$(UO_2)_3(OH)_7^-$	3.16	0.00	0%
$(UO_2)_3(OH)_5^+$	1.81	0.00	0%
$UO_2(SO_4)_2^{-2}$	3.67	0.00	0%
$UO_2(OH)_4^{-2}$	2.19	0.00	0%
$(UO_2)_2(OH)_2^{+2}$	1.16	0.00	0%
UO_2Cl^+	2.60	0.00	0%
$(UO_2)_4(OH)_7^+$	3.55	0.00	0%

p Charges on chemical species are in PhreeqC notation

Species[q]	moles/l	µg/l U	%
$(UO_2)_3(CO_3)_6^{-6}$	2.53	0.00	0%
$(UO_2)_3(OH)_4^{+2}$	2.19	0.00	0%
$(UO_2)_2OH^{+3}$	2.67	0.00	0%
UO_2Cl_2	2.21	0.00	0%
Total	3.15	75.03	100%

As anticipated, uranium is almost entirely in the form of anionic uranyl carbonates, with a trace of hydroxy species. This is the expected form of uranium in dolomitic waters.

The anionic uranium complexes are highly mobile in groundwater systems. The interaction of this simulated groundwater solution in a permeable reactive barrier system is therefore of great interest.

3.4.3 Modelling of Uranium fixation

The chemical reaction by which uranyl ion interacts with zero valent iron has been determined[6,10] as:

$$Fe^0 + UO_2^{2+}(aq) = Fe^{2+} + UO_2(s)$$

The rate equation is effectively unimolecular, i.e.

$$d(UO_2^{2+})/dt = -k\,(UO_2^{2+}).$$

The value of k = (1.1±0.09)x10^{-3} s^{-1} was chosen[6] to represent the reaction in the experimental columns.

As a test of the conceptual model, the reductive precipitation reaction of uranyl ion was simulated in isolation of coupled oxidation reactions at the iron surface (Figure 3.10).

q Charges on chemical species are in PhreeqC notation

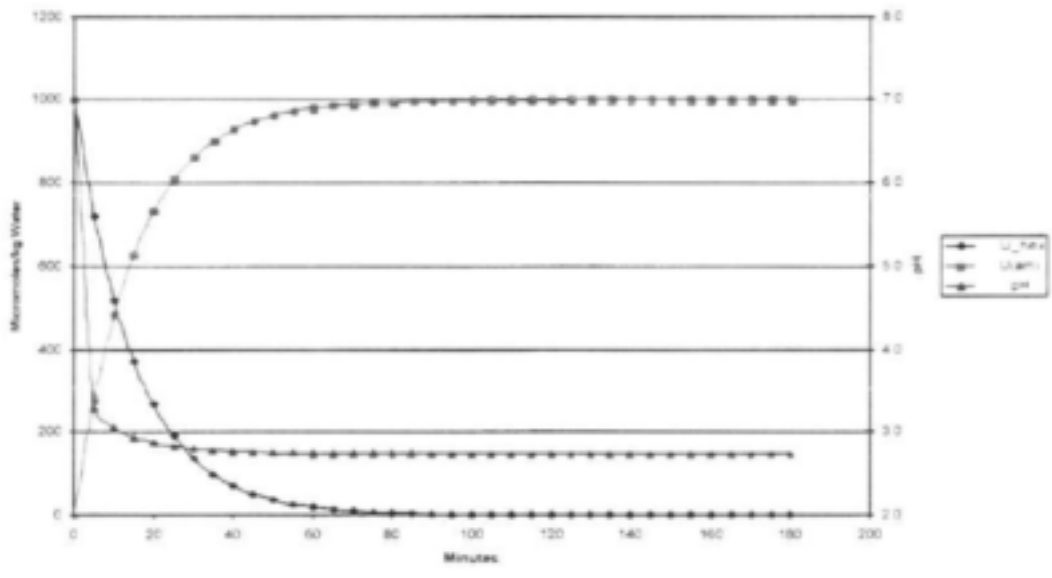

Figure 3.10 Modelling of reaction: $UO_2^{2+}(aq) = UO_2(s) - 2e^-$: $d(UO_2^{2+})/dt = -k\,(UO_2^{2+})$

The dramatic lowering of the pH, observed in Figure 3.10 is expected, and reproduction of this behaviour by the modelling program lends confidence to the chemical model under construction in this section.

The next step in the model construction was to include the coupled oxidative dissolution of zero-valent iron (Figure 3.11).

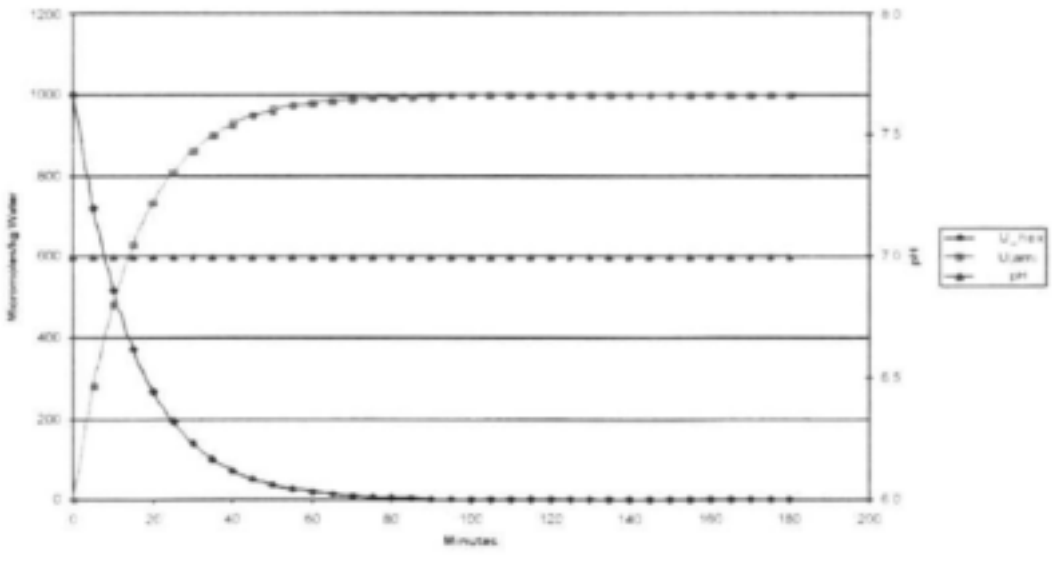

Figure 3.11 Modelling of reaction: $Fe^0 + UO_2^{2+}(aq) = Fe^{2+} + UO_2(s)$: $d(UO_2^{2+})/dt = -k(UO_2^{2+})$

As expected, the coupled dissolution of iron and precipitation of uraninite has no impact on pH. This lends further confidence to the model under construction.

3.4.4 Modelling the oxidation of ferrous to ferric ion

A model was developed to simulate the kinetic oxidation of Fe^{+2} to Fe^{+3} with dissolved O_2 in constant supply, according to the rate equation (Equation 1):

$$\frac{\partial[Fe^{2+}]}{\partial t} = -\left(2.91x10^{-9} + 1.33x10^{12} a_{OH}^{2} P_{O_2}\right)[Fe^{2+}] \qquad (1)$$

The model results (Figure 3.12) concur with the values established from the literature[52].

It is desirable not to have ferrous ion breaking through the column material, and contaminating the very water one is trying to remediate. Inspection of Equation (1) shows that as the pH rises, (resulting in an increase in a_{OH^-}), the rate of disappearance of ferrous ion increases as the square of the OH^- concentration. It is also seen to be necessary to have oxygenated water present, for a non-zero rate of precipitation of ferrous ion.

On the other hand, it is not desirable to have ferrous ion convert too quickly to ferric ion, causing great supersaturation of ferric hydroxide species, with catastrophic generation of gel-like precipitates, which may clog the "permeable" reactive barrier.

A pH of approximately 8.0 would satisfy the requirements for a high rate of removal of ferrous ion, without resulting in impaired flow of remediation water through the permeable reactive barrier.

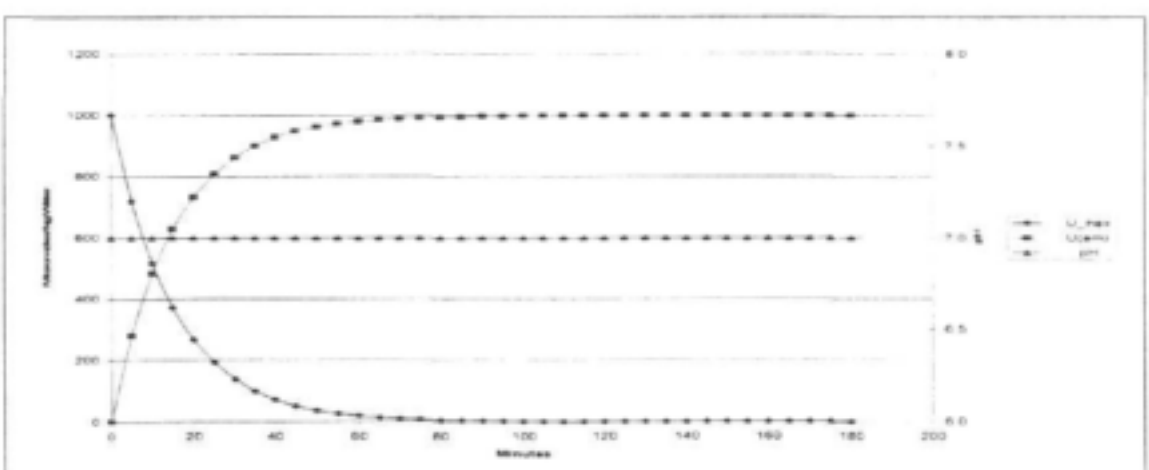

Figure 3.12 Modelling of reaction: $Fe^{0} + UO_2^{2+}(aq) = Fe^{2+} + UO_2(s)$: $d(UO_2^{2+})/dt = -k(UO_2^{2+})$

3.4.5 *Modelling the oxidation of zero valent iron to ferrous ion (corrosion reaction)*

The simulation was performed using a unimolecular rate constant for oxidative dissolution of Fe^0 = $1x10^{-3}$ moles/second, derived from data encountered in the literature review[67], with the rate constants for conversion of ferrous to ferric ion, as developed in the previous section.

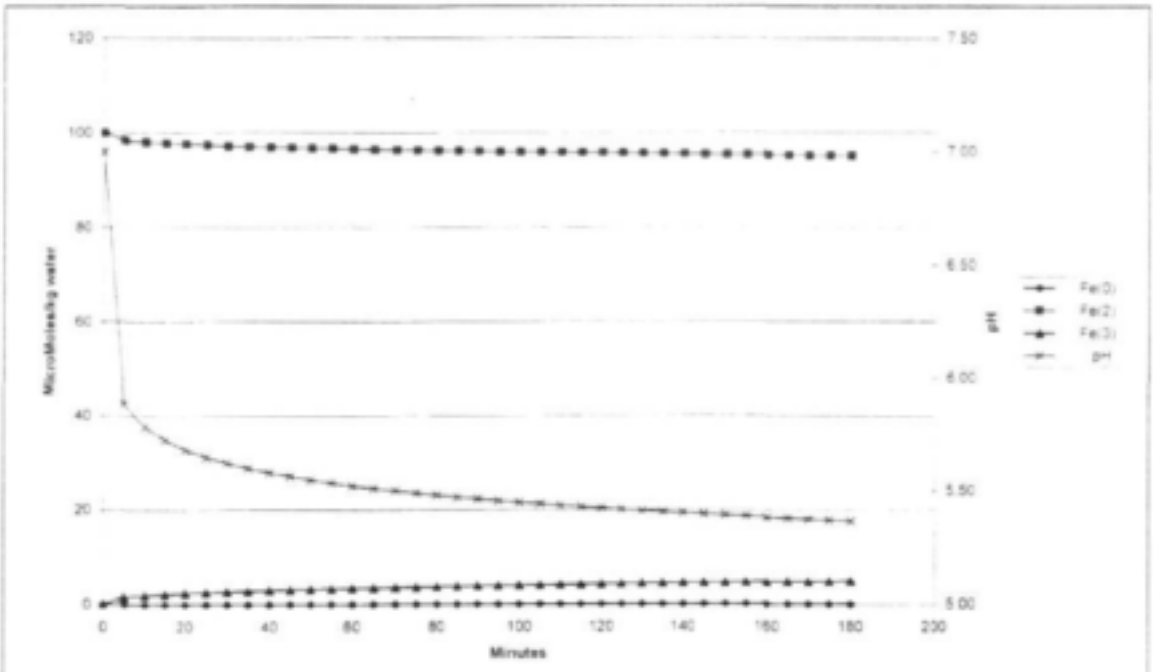

Figure 3.13 Modelling of reaction: $Fe^{2+}(aq) = Fe^{3+}(aq) + e^-$, with formation of aqueous ferric hydroxides

The pH of the solutions is much higher than in the previous simulation, and thus the oxidation reaction to form ferric from ferrous ion is very fast – hence the low concentrations of Fe^{2+}.

3.4.6 *Modelling major ion chemistry in the steel wool column:*

After 18h (64,800 s) of standing, the steel wool column delivered:

- Fe (probably Fe^{2+}) at a concentration of about 0.8 mg/ℓ (14.86 µmol/ℓ),

- at a pH of about 7.7 (from an initial pH of about 7.9 – change in pH probably due to complete consumption of oxygen to form ferric).

The following reasoning was used to derive the rate coefficients:

- Mass of iron = 4.1 grams.
- Density of iron = 7.86 g/cm^3.
- Volume of iron = 0.522 cm^3.

It is assumed that the particles can be approximated as cylinders, with shape formula: volume = p r^2 h, where r = radius of cylinder, h = length of cylinder. The surface area of this cylinder would be 2 x (p r^2) + (2 p r) x h = 2 p r (r + h). The number of such cylinders in the mass of iron available would be $N_{cylinders} = V_{iron} / (p\ r^2\ h)$. The total surface area is $N_{cylinders}$ x 2 p r (r + h).

For the steel wool, we assume a radius of 0.05 mm = 0.005 cm.

Mass of iron = 7.34x10^{-2} moles.

Simulation of reaction for 18h was performed, with Fe^0 reaction constant = 1.0e-8 moles/m^2/s (Figure 3.14):

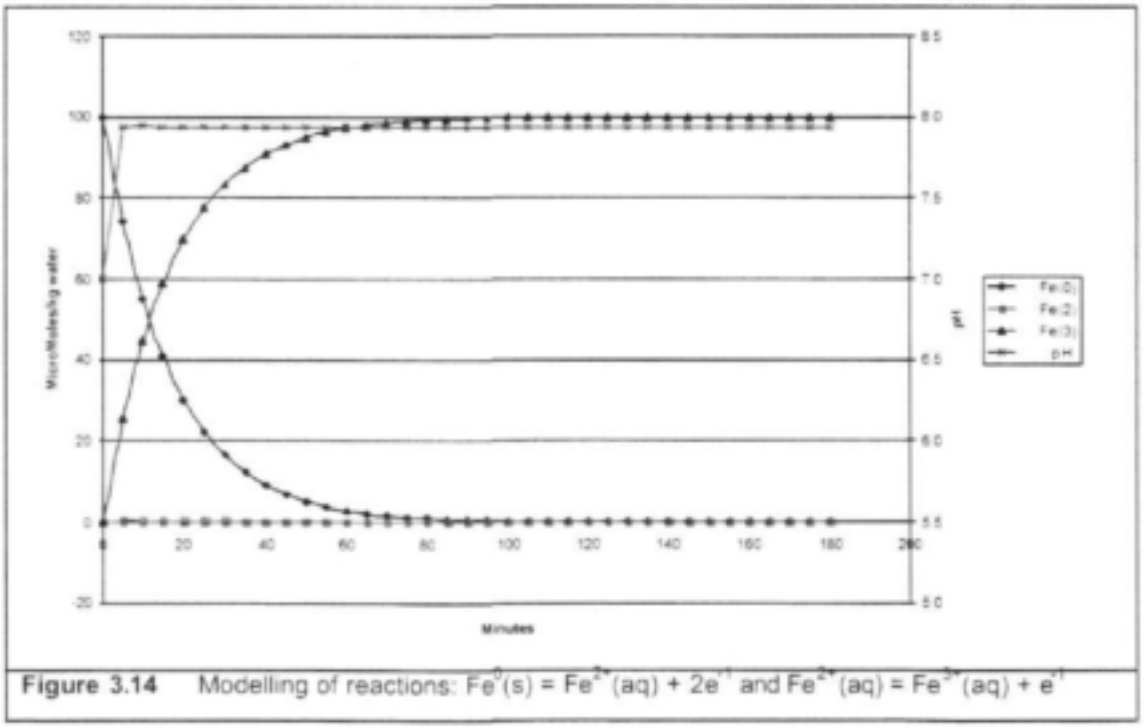

Figure 3.14 Modelling of reactions: $Fe^0(s) = Fe^{2+}(aq) + 2e^{-1}$ and $Fe^{2+}(aq) = Fe^{3+}(aq) + e^{-1}$

It may be observed in the above figure that the pH predictions are inconsistent with observed pH upon beginning of column elution.

The parameters driving the pH change in the column are:

- Dissolution of Fe^0: Increase in pH
- Precipitation of Fe^{3+}: Decrease in pH.

The column initially contained Fe^0 and oxygenated water. After 18 hours, the pH has decreased and the concentration of Fe^{2+} is high. Thus, some Fe^0 has reacted to form Fe^{2+}, with an increase in pH, after which Fe^{3+} precipitated, decreasing the pH.

Rates of dissolution of Fe^0 and formation of Fe^{3+} were subjected to a manual Simplex optimization. The conditions of dissolved iron at 0.8 mg/l, and pH lowered to 7.7 are mutually exclusive (Table 3.6).

Table 3.6 **Exploration of the values of Fe^0 dissolution and Fe^{3+} precipitation reactions**

k(Fe(0))	logk(Fe(0))	si_O2	Fe(2)	Fe(3)	pH	Fe(2+3)	SSE
	Opt	Opt	14.9		7.7		
$1x10^{-9}$	-9	-3.09E+00	0.5	1.0	7.9	1.5	55
$1x10^{-8}$	-8	-2	0.7	14.0	7.9	14.7	54
$1x10^{-7}$	-7	-1	3.1	144.2	8.0	147.2	38
$1x10^{-6}$	-6	0.0859	0.1	0.0	7.9	0.1	58
$1x10^{-7}$	-6.75	-0.70705	0.3	0.0	7.9	0.3	57
$5x10^{-9}$	-8.25	-2.29295	1.3	0.0	8.0	1.3	55
$5x10^{-10}$	-9.25	-3.37885	0.4	0.0	7.9	0.4	57
$1x10^{-8}$	-8	-1	0.0	0.0	7.9	0.0	59
$1x10^{-8}$	-8	-10	14.7	0.0	8.7	14.7	4
$1x10^{-8}$	-8	-2	0.7	14.0	7.9	14.7	54
$1x10^{-7}$	-7	-2	134.3	13.0	9.8	147.2	3845
$1x10^{-7}$	-7	0	0.0	147.2	7.9	147.2	60
$1x10^{-5}$	-5	0	13221.0	1444.9	12.1	14665.9	46826997
$1x10^{-6}$	-6	0	19.1	1452.9	8.0	1472.0	5
$1x10^{-5}$	-5	-0.67	14365.0	301.3	12.2	14666.3	55291287
$1x10^{-6}$	-6	-0.67	1164.8	307.1	10.9	1471.9	355093
$1x10^{-7}$	-7	-0.67	0.0	147.2	7.9	147.2	59
$1x10^{-8}$	-8	-0.67	0.0	14.7	7.9	14.7	59

The only way that the conditions can be satisfied is if there are additional protons in the system. This could happen if Fe^{2+} adsorbed to column material to release protons, thereby dropping the pH to the observed level.

The note on the Eh readings and the low confidence levels associated with them made in the early parts of this section needs to be reiterated. If there were higher confidence levels associated with this portion of the methodology, and concomitantly more accurate Eh readings, input to the chemical model would have provided additional information on the possible ratios of oxidation states of iron in the columns. This would have, in turn, assisted with identifying the mechanism whereby the pH is lowered to 7.7 in the column after standing for 18 hours.

3.4.7 Modelling of Slow Hydroxide Formation in the steel wool column:

The assumption is that the rate of generation of Fe^{2+} is slow by comparison to the conversion of Fe^{2+} to Fe^{3+}. If this is the case, then the rate may be obtained from the experimental data.

A unimolecular curve was fitted through the analytical data, and the results are presented in Figure 3.15.

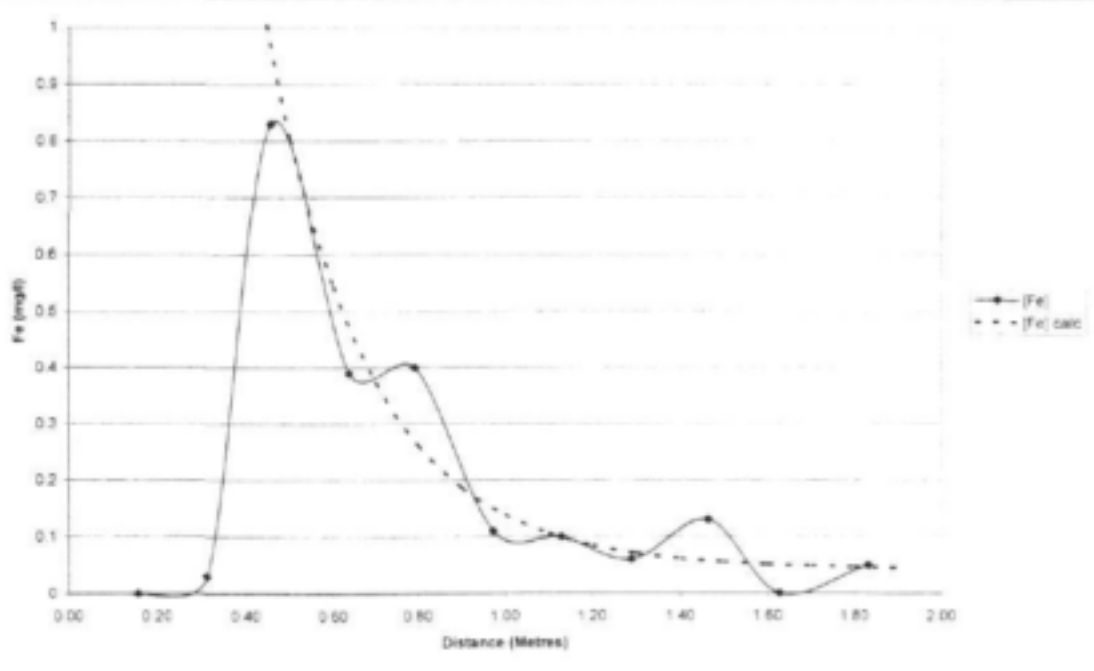

Figure 3.15 Profiles of soluble Fe as a function of distance travelled along the columns, and [Fe] calculated as the function: [Fe(II)] = a + bexp (-t/c) where a = 0.04, b = 0.78 and c = 1608, and t = time in seconds. The rate constant for the decay reaction is $k = 1/c = 6.219 \times 10^{-4}\ s^{-1}$.

The next step in assembling the model of the steel wool column is simulation of conversion of ferrous to ferric ion (Figure 3.16).

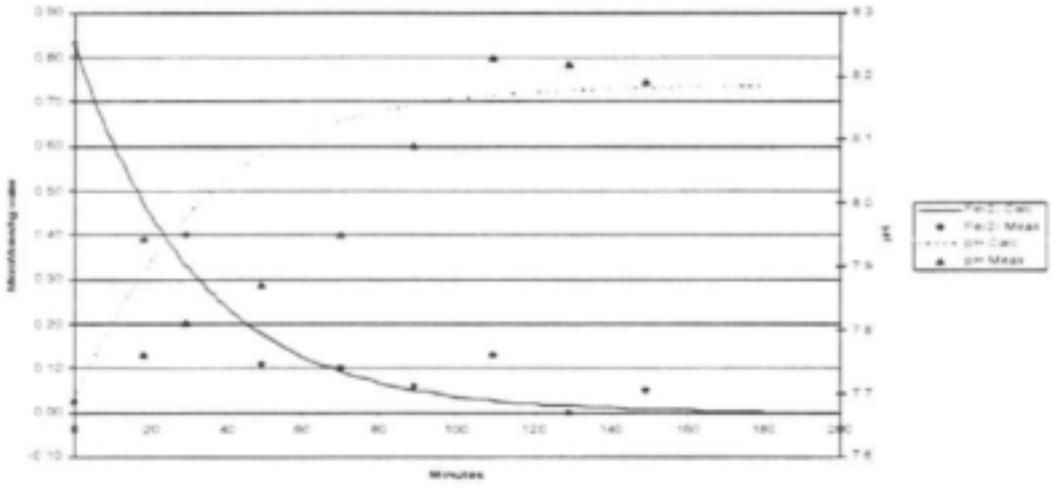

Figure 3.16 Modelling of Ferrous conversion to Ferric, without formation of Ferric Hydroxides

It is observed that a steeper ascent of pH is required at the beginning of the simulation to approximate reality. This is achieved by allowing ferric ion to precipitate as ferric hydroxide, thus inducing a more realistic modification of pH (Figure 3.17).

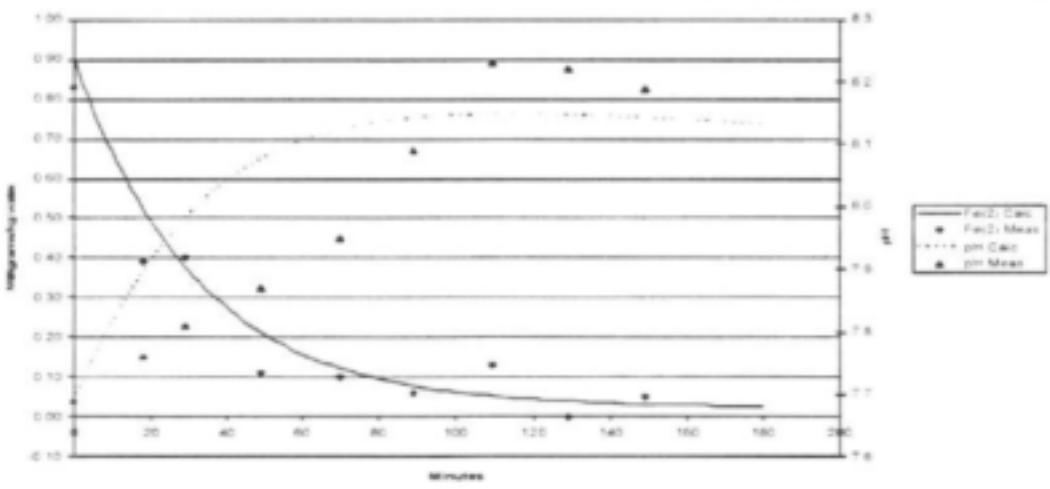

Figure 3.17 Modelling the conversion of Ferrous to Ferric, with the generation of ferric hydroxides at a rate $k=2x10^{-5}$, and generation of ferrous ion from Fe(0) at a reaction constant = $1.0X10^{-8}$ moles/m^2/s.

3.4.8 Modelling of Uranium removal in the steel wool column:

Finally, in combination, uranium as uranyl carbonates is allowed to react with zero valent iron, zero valent iron corrodes to form ferrous ion, ferrous ion oxidizes to ferric ion, and ferric ion is allowed to precipitate as ferric hydroxide (Figure 3.18).

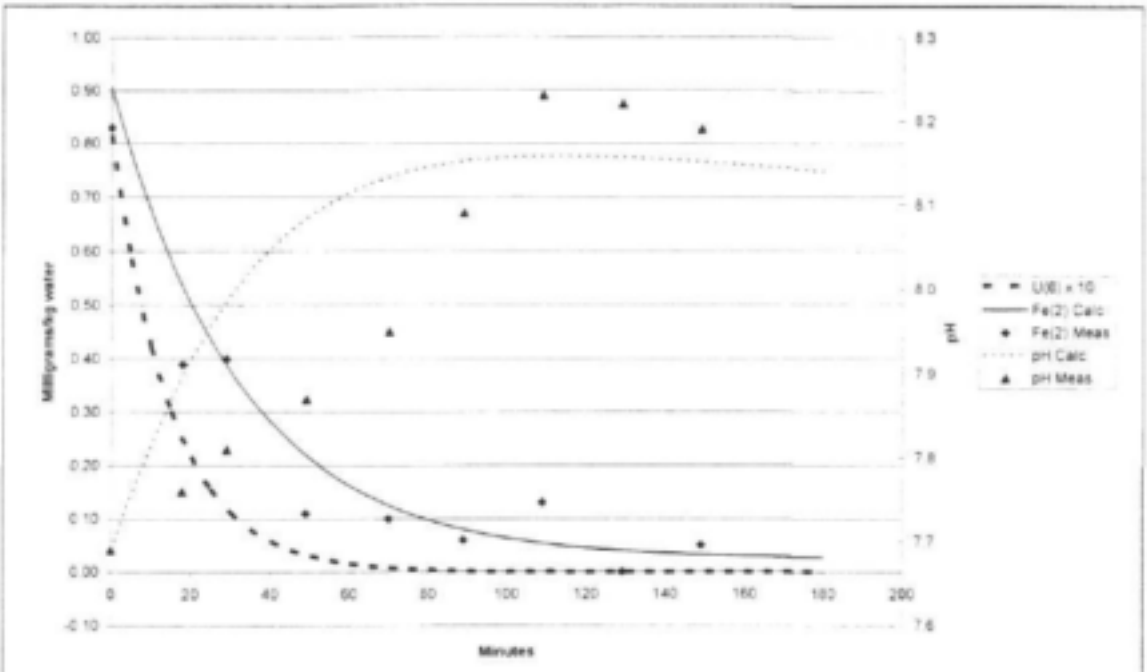

Figure 3.18 Modelling the reaction of UO_2^{2+} with zero valent iron in dolomitic water. The reaction rate constant for $Fe^0 + UO_2^{2+}(aq) = Fe^{2+} + UO_2(s)$ is $1.1x10^{-3}s^{-1}$. Fe(0) dissolves to form ferrous ion with a rate constant = $1.0x10^{-8}$ moles/m^2/s. Ferrous ion oxidizes to Ferric, with the generation of ferric hydroxides at a rate $k=2x10^{-5}$ s^{-1}.

As seen in Figure 3.18, the simulated pH differs somewhat from the observed pH. While this deviation is acceptable by comparison with other modelling studies, it may indicate hydraulic processes not accounted for, such as the heterogeneous nature of the pores in the column.

3.4.9 *Modelling the chemical reactions in the granulated iron column*

The kinetic rate constants obtained from literature, and derived to describe the reactions in the steel wool column, are conditional constants, dependent on the reactive surface *area* present in the test columns.

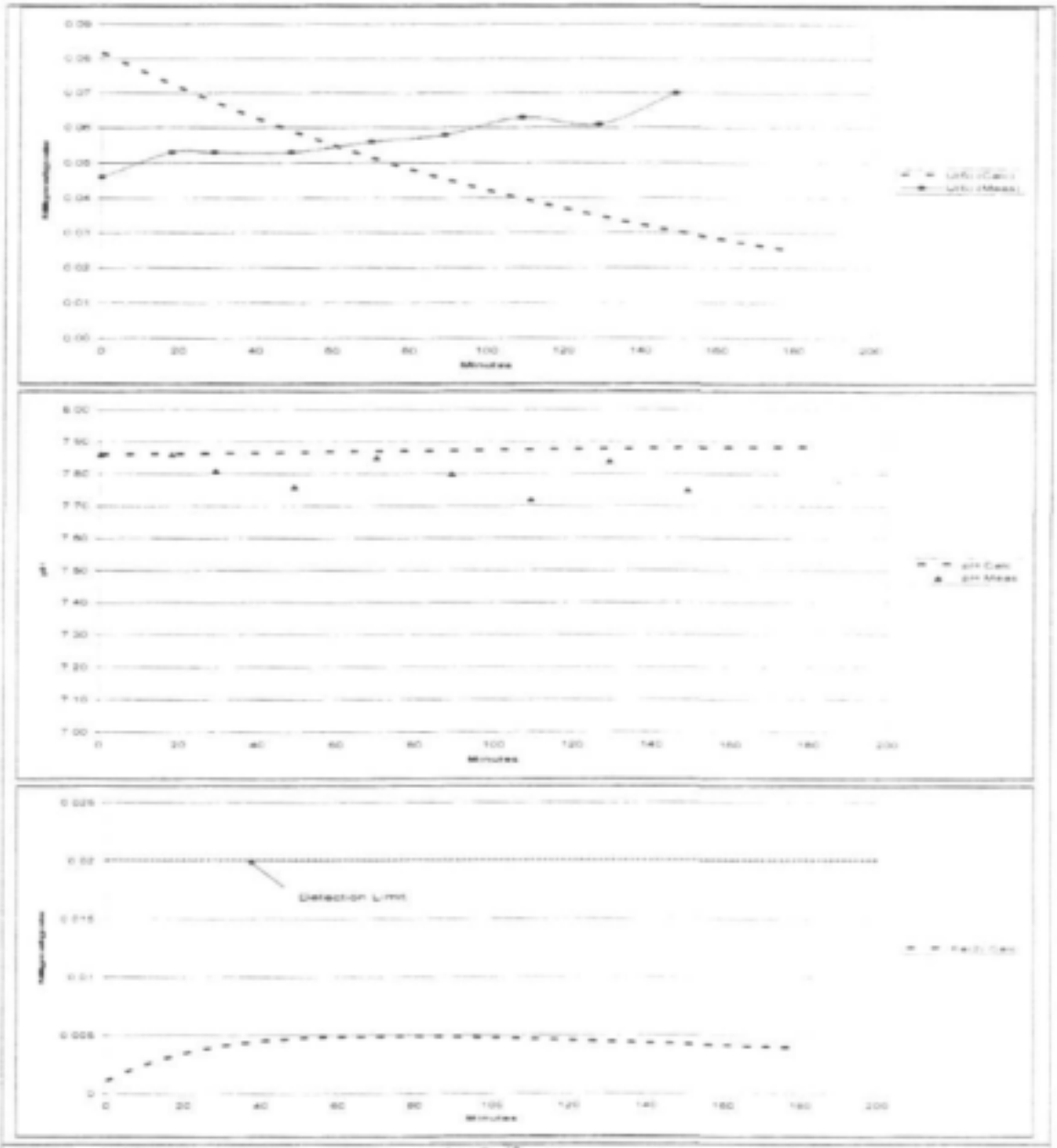

Figure 3.19 Modelling the reaction of UO_2^{2+} with zero valent iron in dolomitic water. Reaction rate constants are as in Figure 18, but the reactive surface area of the zero-valent iron is assumed to be $1/10^{th}$ of that illustrated in Figure 3.18.

If we assume the average granulated iron particle to have a diameter of 0.5 cm, and a height of about 0.05 cm, then the difference in surface area between the steel wool and the granulated iron is about an order of magnitude (or ten times).

The chemistry of the B-column was simulated, with the rate constants adjusted for a ten-fold reduction in reactive surface area. The results are presented in Figure 3.19.

As seen in Figure 3.19, the simulated iron concentrations emitted from the column are below the threshold detection limit, which is according to observation. The pH values projected by the simulation are similar to those observed.

The projected profile of uranium emitted by the granulated iron column does not conform well to observation. There is an overprediction of uranium emission in the early stages of the column elution. This may result from neglect of adsorption of uranyl ion to binding sites on the silica matrix in the column.

The underprediction of uranium concentration in emissions from the experimental column at later stages of the elution may suggest that the reactive surface area of the zero valent iron was overestimated (a possibility that is corroborated by the slight upward deviation in projected pH profile as a function of time). It is also possible that the form of the zero-valent iron in this column is easily passivated by the formation of secondary minerals near the reactive surface, such as siderite ($[Fe^{2+}CO_3]_{(s)}$).

3.4.10 Influence of dolomitic water on the chemical reactions

In order to test the influence of the dolomitic water on the chemical reactions, the above simulation was performed, with a sodium chloride solution replacing the simulated dolomitic water (Figure 3.20).

While the projected uranium removal is fast and complete, the pH of the emanating solution is higher than when dolomitic water is simulated. This means that the dolomitic water is buffering pH changes in the system, resulting in water of a more acceptable nature for domestic use.

The pH buffering that is observed here may be responsible for uncoupling of the pH and Eh profiles of the column eluants, as alluded to in Section 3.2.1.

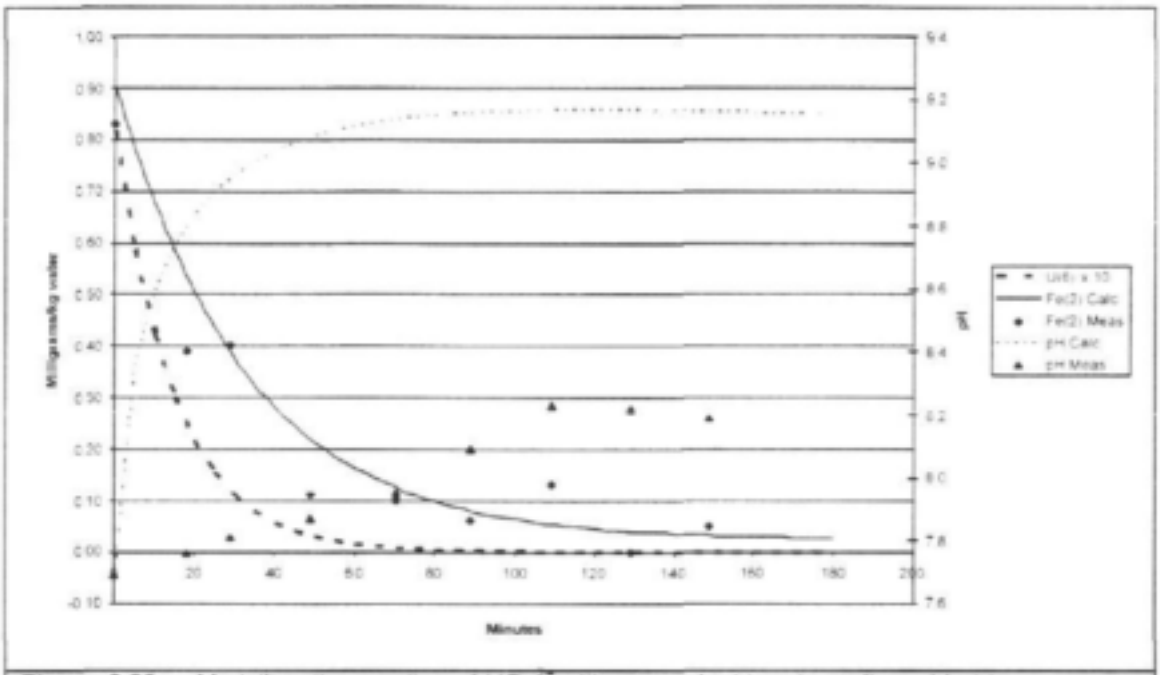

Figure 3.20 Modelling the reaction of UO_2^{2+} with zero valent iron in sodium chloride.

It was mentioned previously (Section 3.4.1) that it was possible that siderite is forming in the columns, due to the presence of dolomitic water. The saturation ratio of siderite was calculated for the simulation involving the granulated iron column (Figure 3.21).

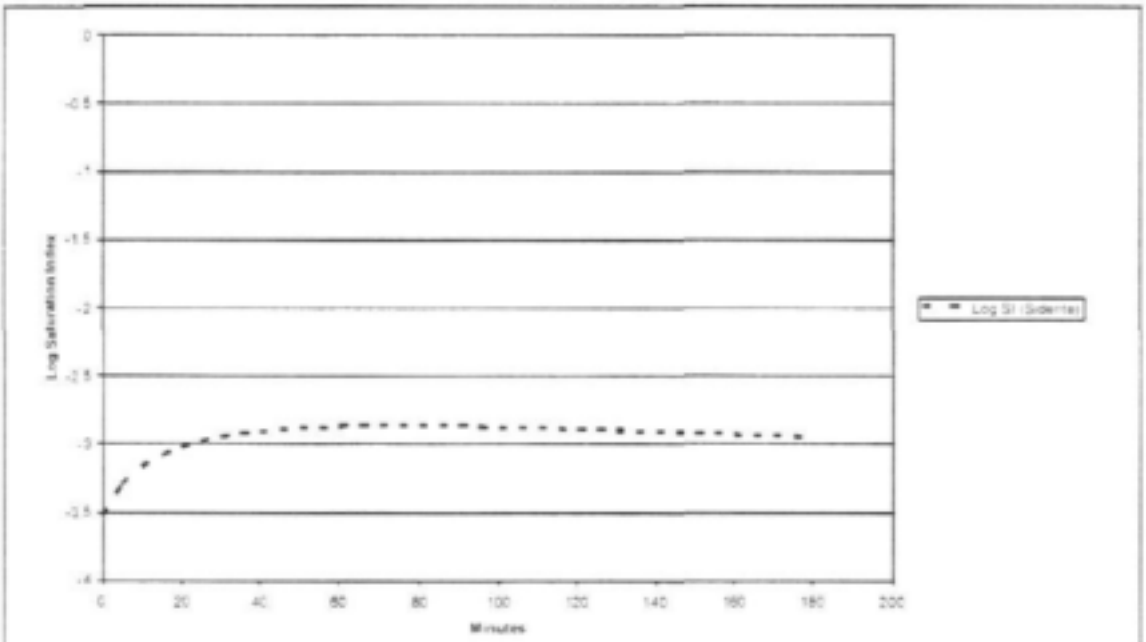

Figure 3.21 Modelling the saturation index of Siderite in the granulated iron column.

As seen in Figure 3.21, the logarithm of the saturation index of siderite remains resolutely negative, meaning that the mineral is projected to remain dissolved throughout the progress of the reactions with zero-valent iron.

It should be mentioned, however, that this simulation refers to the saturation index of siderite in the *bulk* solution, and not at the reactive surface, where the concentration of ferrous iron may be much higher, resulting in precipitation of this mineral, and passivation of the reactive surface. The uncertainty in the potential of the mineral to form, or if, indeed, the reactive surface of the zero-valent iron is being passivated at all, cannot be resolved with the current data, and further experimentation is necessary to clear up the questions.

3.4.11 Summary of modelling conclusions

The observed behaviour of the experimental column with steel wool was reproduced tolerably by reaction progress modelling. Reaction constants comprising the models were taken from literature and developed from laboratory data.

Differences between simulated and observed pH elution profiles in the steel wool column suggest hydraulic processes not accounted for, such as the heterogeneous nature of the pores in the column. The literature survey develops this point further, with considerable attention paid to the phenomena of pore clogging, pore deposition and through flow efficiencies, etc.

The observed behaviour of the experimental column with granulated iron was reproduced well by reaction progress modelling, with the assumption of a ten-fold lower reactive surface area as in the steel wool column. Lower ultimate removal of uranium from the test solution may be due to erroneous estimates of reactive surface area, or due to passivation reactions, such as the possible precipitation of secondary minerals such as Siderite.

The close fit between modelled and observed behaviour suggests that the chemical processes in the column may be well understood.

The dolomitic water that was used as test remediation solution buffered potentially undesirable pH changes in the permeable reactive barrier.

Based on the simulations, zero valent iron is a good material for use in a permeable reactive barrier for the remediation of uranium-contaminated dolomitic water.

3.5 Discussion

3.5.1 Uranium retention in the test columns

3.5.1.1 Uranium adsorption to silica

In the "blank" column, which had filter sand only (column A), uranium broke through at 0.35 metres, and the uranium concentration in the eluant increased as a function of time until possibly levelling off close to 40 pore volumes (Figure 3.7). The same phenomenon is visible with the B-column, which had 8% granulated iron, or 92% sand.

The only material capable of adsorbing uranium in the sand column was the sand itself. It is hypothesised that the following reaction (2) occurred between surface silyl groups on the filter sand and dissolved uranyl species:

$$\}-Si-O-H+UO_2^{2+} \rightarrow \quad \}-Si-O-UO_2^{2+}+H^+ \qquad (2)$$

where "}-Si" represents silicon bound to the sand particle – i.e. silicon on the surface of the particle.

This would potentially account for:

- the low initial concentration of uranium leaving the column, implying that some uranium had been retained by the column; and
- the increase in uranium concentration as a function of time, implying that the uncomplexed surface silyl groups were being saturated by uranium adsorption.

This mechanism was probably also acting in the 8% granulated iron/sand column (column B).

Since the mechanism of uranium immobilisation by silica is adsorption, or more specifically, surface complex formation by displacement of a proton (represented as equation (2)), the reaction is reversible. The tendency of a system composed of silica, through which low concentrations of uranium percolate, is to *concentrate* the uranium as an adsorbate.

A pulse of acidic water through a zone in which uranyl had been immobilised in this way will certainly displace the uranyl ions attached to silyl groups, and remobilise the

uranium, usually in a much higher concentration than the original percolating waters contained.

3.5.1.2 Uranium retention by reaction with iron

The 8% steel wool/sand column (column C) exhibited no breakthrough of uranium species throughout 40 pore volumes of eluant (Figure 3.7). This implies that the following reaction (3) was occurring to completion:

$$Fe^{0} + UO_2^{2+} \rightarrow Fe^{2+} + UO_{2(s)} \qquad (3)$$

In the B-column (8% granulated iron/sand), uranium broke through the column immediately at 0.35 metres of flow-through. This means that uranium was not completely immobilized by the 8% granulated iron/sand in the B-column.

The concentration of uranium in the eluant of the B-column was, however, systematically lower than that of the sand-only column (A-column) (Figure 3.7). This implies that there was some retention mechanism operating in the B-column that was not happening in the A-column. The only difference in the column material was that the B-column was 8% by mass of granulated iron. Thus, it is likely that the reaction expressed as (3) is operating to some extent in the B-column. If this is happening, it remains to be seen what the fate is of the soluble ferrous iron released by this chemical reaction.

Uranium was completely immobilised in column C, and partially immobilised in column B, although the bulk concentration of iron was the same in both columns. The major differences between the two columns are:

- Being packed with shredded steel wool, column C had a significantly greater reactive surface area than column B; and

- The difference in size and shape of the iron particles in the two columns must have led to a difference in porosity, and in distribution of porosities, thus influencing the tendency for "channelling" to occur in the columns.

Thus, it is likely that column B was much less effective at immobilising uranium because of much lower reactive surface area by comparison to column C, and because channelling might have occurred in channel B that reduced the probability of test solution contacting the reactive metal surfaces.

3.5.2 Profile of soluble iron in the test columns

The only column that emitted iron in the eluates was column C, the column with 8% steel wool/sand as the packing material (Figure 3.5). If the chemical oxidation of iron was causing reductive immobilisation of uranium as $UO_{2(s)}$, then one would expect generation of soluble ferrous iron, as in Equation (3).

There are two points of interest, indicated by the following questions:

- If uranium immobilisation releases soluble iron, and uranium is partially immobilised in column B by granulated iron, why don't we witness a breakthrough of soluble iron in this column?

- If uranium is constantly being removed from column C by a process that yields soluble ferrous iron, why is the concentration of ferrous iron not constant in the eluate, instead of dropping sharply, as it does, over 40 pore volumes of eluant?

These questions aspects raised are dealt with in more detail in the following sections and sub-sections.

3.5.3 Profile of pH in the test columns

3.5.3.1 Irregularity of pH curves in A and B column

There was observed variability in the pH readings of the eluants of the A and B columns (Figure 3.2), although these deviations were between two pH units (close to neutral) and there was the suspicion that the pH electrode may have had a slight malfunction.

Assuming the electrode was functioning optimally, the following two considerations have relevance with respect to the observed pH variabilites:,

- The eluant from all three columns was initially tap water, and the pH reading for all three columns is similar at this point.

- There is no irregularity in the pH readings of the C-column.

If the observed pH variance was real, the non-monotonicity of the pH readings for these columns may indicate low buffer capacity of the solutions, although there was a large amount of carbonate deliberately added to simulate dolomitic water[r].

r The simulation of dolomitic water conditions is an important experimental design aspect. Dolomitic groundwater environments are common in South Africa, particularly in the majority of gold mining areas

A potential explanation for the observed pH variance is channelling in the columns - the fluctuations in pH are perhaps indicative of mixing of eluant water with tap water which was trapped in "dead" zones in the columns. This is not, however, considered a very likely scenario, given the high porosity of the filter sand (~30%).

The pH fluctuations in the A-column may be explained by asserting that as there were fluctuations in uranium concentration then, by Equation (2), it follows that there should be fluctuations in the pH readings.

3.5.3.2 Reduction of pH by reactions of iron

The pH of the B column eluant seems to be generally lower than that of the A column eluant. The B column contained granulated iron, and, since there was an apparent decrease in uranium concentration emitted by this column, it is likely that zero-valent iron was being oxidized to ferrous iron (Equation (3)), as the uranium that came into contact with the Fe^0 was reductively immobilised. If this is the case, ferrous iron would break through the column if there was no mechanism for immobilising it.

There is a significant concentration of bicarbonate ion, and the following reaction may be occurring (4):

$$Fe^{2+} + 2HCO_3^- \rightarrow [FeCO_3]^0_{(s)} + 2H^+ \qquad (4)$$

Precipitation of ferrous carbonate, or siderite, would tend to decrease pH, which is observed in column B. There would be a concomitant consumption of bicarbonate ion, though, which is not seen in the analytical results (Table 9.4).

It is also likely that, in the presence of dissolved oxygen, the following pair of reactions were occurring ((5) & (6)):

$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}H_2O \qquad (5)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \qquad (6)$$

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where Uranium and other radionuclide contamination is likely. The anticipation of, and adaptation to, these conditions are important considerations with respect to potential field applications of PRBs in South Africa. Importantly however, this dolomitic consideration does not apply as particularly in the surface water

When these reactions progress to form ferric hydroxide, there is a net generation of protons, which could explain the (possibly) lower pH of the column containing granulated iron. If iron is being immobilised as ferric hydroxide, then this would explain why soluble iron is not emitted by column B.

This mechanism would also account for the initial drop in pH of the solution generated by the column containing steel wool (column C) (Figure 3.2). It would also account for the gradual decline in concentrations of soluble iron eluted from the column (Figure 3.6).

This mechanism does not explain, however, the rise in pH of the eluant of column C (see next section).

3.5.3.3 Increase in pH by reactions of iron

An increase in pH is observed in the eluant of column C. It is possible that the following reaction is occurring (Figure 3.7):

$$Fe^{0} + \tfrac{1}{2}O_2 + 2H^{+} \rightarrow Fe^{2+} + H_2O \qquad (7)$$

Because the oxidation reaction (7) consumes protons, the pH would rise if the hydroxy-complexes that lower the pH form comparatively slowly (6). This phenomenon is observed in practice[52].

As time goes on, the reaction producing hydroxy-complexes begin to dominate[52], which might explain the "levelling off" of the pH curve in column C, as the soluble iron emitted decreases to near-zero (Equation 6).

The soluble uranium concentration and the pH in column B seem to be inversely related (Figure 3.8). If immobilisation of uranium is yielding ferrous iron, which is being oxidized to ferric iron hydroxide, with concomitant production of protons, then a dip in uranium concentration would be expected to decrease the pH of the solution, as opposed to increasing the pH, as is observed.

If the action of uranium reductively adsorbing at the surface of the iron particles causes concomitant release of zero-valent iron atoms (as the adjacent surface sites are disrupted by the chemical activity), these atoms can then react with water to consume protons. In this scenario, reductive immobilisation of uranium can result in an increase of pH, observed in column C (Figure 3.2). This may be occurring in column B.

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environment. Results from the experimental components of this project must be understood in this context as the experimental design has taken, albeit broadly, dolomitic (groundwater) environments into account.

3.6 SUMMARY & PRELIMINARY CONCULSIONS

3.6.1 Uranium retention in the test columns

3.6.1.1 Uranium retention by reaction with silica

Uranium in the test solutions is binding with silica on the filter sand matrix of the columns. The silyl adsorption sites for attachment of uranyl ion are not sufficient in concentration to completely take up the influent concentration of uranium, and they saturate quickly over time, apparently becoming completely saturated at about 40 pore volumes of through-flow.

Uranium bound to silica is potentially very easily displaced by a pulse of moderately acidic water, often resulting in a plume many orders of magnitude more concentrated in uranium than the original waters. In the field, it is desirable to immobilise uranium in a different chemical form to that bound to silica.

3.6.1.2 Uranium retention by reaction with iron

Uranium was immobilised completely by the column bearing 8% shredded steel wool/sand mixture. This was determined to be the most optimal mixture of reactive material with respect to U removal. The increase in pH during reaction of zero-valent iron with dissolved uranyl ion is probably due to concomitant release of zero-valent iron atoms, and oxidation of these atoms by dissolved oxygen. The pH changes were reasonably accurately reproduced in the reaction progress modelling, suggesting that the latter process is, in fact, occurring.

As discussed in section 5.4.3, with reference to Equation (1), the optimum pH for operation of a zero-valent-iron PRB is around 8.0, to simultaneously ensure high rate of ferrous (dissolved) iron removal and to reduce clogging of the PRB by gelatinous ferric precipitates. These conditions are obtained in the dolomitic system, where bicarbonate acts as a natural pH buffering agent.

3.6.1.3 Relative performances of the iron/sand columns

While the 8% shredded steel wool/sand mixture completely immobilised the uranyl ion, the 8% granulated iron/sand mixture seems to have only partially immobilised the uranyl

ion. This difference in immobilisation potential could be due to the vast difference in reactive surface area of the two forms of iron, and perhaps differences in porosity distribution of the columns, caused by differences in shape and size of the two forms of iron particles, which induced channelling in the column with granulated iron. It is difficult to determine which of these factors dominate, i.e. if surface area is the limiting factor, or if channelling is occurring in the granulated iron column. Further testing is needed to distinguish between these effects.

3.6.2 Iron emission from the test columns

Soluble iron broke through the 8% shredded steel wool/sand column in appreciable concentrations, whereas there was no breakthrough in the 8% granulated iron/sand column.

The breakthrough of soluble iron is not expected to be a problem in field applications of the PRB technology, since (as dealt with in section 3.4.6 – "Modelling of slow hydroxide formation in the steel wool column"), the effect is kinetic, and a consequence of the very short length of the column (less than 5 cm in length).

Ferrous iron can be immobilised by complexation with bicarbonate to produce solid siderite, or it can be immobilised by oxidative precipitation as ferric hydroxides. The pH profiles of the columns suggest that one of these mechanisms is occurring. The lack of concomitant consumption of bicarbonate ion implies that the latter reaction dominates.

The columns were not at steady state, even after a flow-through of 40 pore volumes of test solution, over 3 hours. This is a comment on experimental design, and not on the feasibility of a PRB to remove uranium. Steady state would probably be achieved in less than 24 hours, and the typical PRB operates with a lifespan of many years.

CHAPTER 4 ORGANIC RESEARCH COMPONENT

4.1 INTRODUCTION

4.2 MATERIALS & METHODS

4.2.1 Influent Working Solutions

As the solvent phase of the test contaminant consisted of many different organic compounds ranging from hydrocarbons with 10 carbons (decane) to pentadecane (15 carbon compound) and others, as well as numerous benzene and substituted benzene and naphthalene based molecules which all have different water solubilities, the water soluble fraction had to be determined.

Ascertaining the water soluble fraction of the test contaminant is additionally important given the fact that this is the fraction that will potentially move into and disperse in groundwater, and as such constitute that portion of a (groundwater) pollution plume that will be most difficult to treat.

The water soluble fraction of the solvent portion of the test contaminant was obtained by mixing and shaking 2l of the solvent, which has a lower density than water, with 18l of glass distilled water. Following separation, the newly contaminated water was decanted and used as the influent for all further experimentation.

4.2.2 Mineral Salts Medium

The mineral nutrient media stock solutions, used as a nutrient feed stock for the microbial fauna present in the pine bark, comprised the following: Solution A: 3.64 $CaCl_2.2H_2O$; 2.25 g $MgSO_4.7H_2O$; 0.02 g $FeCl_3.6H_2O$ and 0.04 g Na_2 EDTA in 100ml & Solution B - 8.5 g KH_2PO_4; 21.75 g K_2HPO_4; 50.3 g $Na_2HPO_4.7H_2O$ and .5g NH_4Cl in 1000ml was prepared in a separate vessel and stored in the dark.

The final mineral salts working solutions, for all further experiments, were made by diluting 1ml of solution A and 10 ml of solution B in 1 L of liquid which gave final nutrient concentrations (mg/l) of:

$CaCl_2.2H_2O$	36.4	KH_2PO_4	85.0
$MgSO_4.7H2O$	22.5	K_2HPO_4	217.5
$FeCl_3.6H2O$	0.2	$Na_2HPO_4.7H_2O$	503
Na_2 EDTA	0.4	NH_4Cl	5.0

4.2.3 Primary Research Question

The primary research question that formed the basis of Section 4 may be stated as: *"To what extent, and at what rate and dynamic(s), do microbial communities inherent in substrate degrade the organic constituents in the test contaminant and how might this be applied in a hypothetical PRB scenario?"*

4.2.4 Chemical Characterisation

Following a solvent (n-hexane) extraction of a sample of the free phase solvent in the test contaminant, the extract was analysed by gas chromatography mass spectrophotometer (GCMS) and the results shown in Appendix 6.

Another sample was extracted from the influent working solution to determine the solubilised fraction and, especially, BTEX compounds, these results are shown in Appendix 7. Lastly, organic compounds were solvent extracted (n-hexane) from a half a litre of the effluent, after passage through the PRB, and influent working solution and analysed by GC and the results shown in Appendix 8.

4.2.5 Biodegradability Testing

The biodegradability of the liquid sample was determined by US EPA recognised methods (OPPTS 835.3120) and is based on the modified Sturm-Test. This method details the tests required to determine, ready and ultimate, aerobic biodegradability of organic chemicals by monitoring CO_2 production in sealed vessels containing the test compound and a dilute activated sewage sludge inoculum.

The method involves incubation, at 20°C, of the test and control compounds (25 mg C/L) with the diluted inoculum and a mineral salts medium (see section 2.2) in small sealed vessels for 28 days. The biodegradation is determined by monitoring the sum of gaseous CO_2 produced in the headspace of the test vessels (30 vessels per series), compared with a control series containing no added carbon compounds, as well as, a

control series with added phthalic acid. The produced CO_2 was monitored with a Series 225 gas analyser. Because of the stringency of the test conditions, it can be assumed that a compound that is degraded to the extent of 60%, or more, in this test will also degrade extensively in most aerobic environments.

4.2.6 Adsorption Breakthrough Curves

The breakthrough of the water soluble fraction was determined by placing 300 grams (w/w) pine bark (16 - 20 mm) in a glass column (15cm), and determining the amount of retardation due to adsorption relative to time. The relative retardation was also compared to the Cl-1 tracer anion (NaCl, 350 mg/l). The pore volume of the pine bark was 145 ml (approximately 48%). The flow rate of the liquid phase was set (using rate variable flow metering equipment) at 2.4 ml/min - equivalent to a pore volume change every two hours.

All leachable components were allowed to exit the system, prior to any experimentation, by perfusion of pure water for 7 days. Chlorine was monitored by ion selective probe while the organic carbon was monitored by the TOC analyser (Shimadzu TOC 5000A).

4.2.7 Batch Studies

Two sets of batch growth studies were conducted, in triplicate, in 200 ml medical flat bottles. The first, or control, series was made by inoculating a mineral salts media (150 ml) with 5g of composted pine bark and allowed to stand at room temperature for 4-5 days after which the CO_2 concentrations were determined.

The second series was made by inoculating a contaminated water sample, which had identical mineral nutrients added, with 5g of composted pine bark and, also, monitored for CO_2 production. Following the growth period (4-5 days) and after CO_2 determinations the respective vessels were cross-inoculated into their respective fresh growth media and stored for an additional 4-5 days after which the relative growth, as indicated by CO_2 generation, was again determined.

The second set of batch experiments set-up in duplicate and operated in an identical manner to those described above but at two different temperatures; 18° and 27° C were made to determine the relative effect of temperature on the biodegradation of the solvent. The different support media added and operational modes for each of the batch experiments are shown below (Table 4.1).

Table 4.1 Operating Variables For Batch Growth Cultures at Two temperatures

Batch Number	Support Media	Liquid Media
Low Temperature (C)		
Sample 1	Pine Bark	Contaminated water
Sample 2	Composted Bark	Contaminated water
Control 1	Pine Bark	Water
Control 2	Composted Bark	Water
High Temperature (27°C)		
Sample 3	Pine Bark	Contaminated Water
Sample 4	Composted Bark	Contaminated Water
Control 3	Pine Bark	Water
Control 4	Composted Bark	Water

4.2.8 Continuous Culture Column Studies

The glass columns used for this phase of the experimentation were 50 cm long with a 2.5cm inside diameter and equipped with sampling ports at the influent and effluent ends and aerated by means of fish tank pumps. Two sets of two columns each were constructed (Table 4.2), the first set being, the control columns, which consisted of one glass column with 100 g of composted pine bark and the other packed with 100 g of fresh pine bark (16 - 20 mm).

These control columns were perfused by an up-flow of glass distilled water only. The second set of columns also had one composted and one fresh pine bark column with the only difference being that these columns were perfused with the contaminated influent water. See Plates 4.1 & 4.2 for photographs of the experimental set up and pine bark used as substrate.

The volume of 100g of fresh pine bark was approximately 500ml and had a pore space of 295 ml which is equivalent to a porosity of approximately 59%, while the composted

pine bark had a volume of 400 ml and a pore volume of 248 (porosity 62%). The influent flow rates for the respective columns were set at 20 ml/ h which was equivalent to an approximate pore volume change every 12 hours. The columns were all covered with tin foil to exclude sun light. Initially (7-8 days), the columns were operated in batch mode to allow for microbial adaptation and the microbial activity monitored by carbon dioxide generation.

Table 4.2 Operational Modes for Continuous Column Operation

Column No.	Packing Material	Influent
Column 1	Pine Bark	Water
Column 2	Composted Pine Bark	Water
Column 3	Pine Bark	Contaminated Water
Column 4	Composted Pine Bark	Contaminated Water

After passage through the column samples were firstly filtered (0.22 µm), and then stored at 40°C until needed. For the GC analyses, 0.5l samples were extracted with 50ml of n-hexane which was evaporated down to 1 ml by overgassing with oxygen-free nitrogen before injection into the GC.

After 33 days of operation, nutrient supplementations were made by adding nutrients, with a Watson-Marlow peristaltic pump, at concentrations similar to the batch growth cultures at 2 ml/h. After day 63, the supplement was switched over to the commercially available Bioactivator X256 which is produced and marketed by FranberFran. This technology (Bioactivator X256) does not involve the continuous addition of bacteria or enzymes to the treatment process. It is based on the generation of natural effector molecules by a bacterial process in a reactor. The effector molecules are entrained by a small continuous water flow and introduced at an appropriate stage of the process to be enhanced.

The chemistry of the effector molecular compounds generated during the bacterial breakdown of bio-activator feed materials and the fundamental mechanisms involved in receptor processes are, to the best knowledge of Franberfran, still unknown. The conventional wisdom in the current scientific literature suggests that the effector molecules generated by the bacterial activity are a form of bio-surfactants. Various scientific attempts have been made to explain their chemistry and their biological effects but these still form part of the core of the scientific debate. The bio-activator supplied by Franberfran does not infringe any patent rights.

4.3 RESULTS AND DISCUSSION

4.3.1 Chemical Characterization and Biodegradability

Middle distillates, including kerosene, may contain as many as five hundred individual compounds; however, these compounds tend to be more dense, less volatile, less mobile and less water soluble than the gasoline-range materials.

Kerosene applies to that portion of petroleum boiling between the approximate limits of 180° and 320°C. The chemical composition of kerosene depends upon its source and usually consists of a mixture of about 10 hydrocarbons containing 10 - 16 carbon atoms/molecule. The constituents include alkanes and cycloalkanes; benzene and substituted benzene and naphthalene and substituted naphthalene. It has been shown that the average chemical composition by weight is 35% paraffins, 60% naphthenes, and 15% aromatics. *Kerosene has a density of 0.839 (water 1.00) and a viscosity of 2.3* (water 1.14) at 150°C.

These characteristics are clearly shown in the GCMS scan (Appendix 6) of the liquid sample taken on-site (pure free- phase). In this scan, the typical hydrocarbon "hump" is visible and extends from decane (10 carbon compound) until pentadecane (15 carbon compound). The remainder of compounds listed comprise different alkanes, as well as, numerous benzene and substituted benzene and naphthalene based molecules, as well as, other long chain alcohol molecules such as 1-octadecanol.

An extraction and GCMS scan of the water soluble fraction used in the influent working solutions (Appendix 7) showed that far fewer of the compounds had dissolved in the water, compared with the parent material (Appendix 8).

Although original assessments of the test contaminant some 2 years prior t this research had revealed significant proportions of BTEX compounds, only negligible proportions were revealed after analyses for the purposes of this research. This was believed to relate to high rates of volatilisation and actual sampling location. Nonetheless, this was not deemed significant in the context of this research as BTEX compounds are known to be present in the in situ location of the contaminant spill and, conceivably, in other contaminant sources in South Africa, that may be a target for PRB technology.

The implication then is that all the more water soluble compounds had already been leached out of the working solution. This does, in no way, imply that the risk from BTEX

can be discarded, in the case of the site if the contamination, as original analyses of the contaminant under consideration, showed relatively high concentrations of BTEX.

In addition, other circumstantial evidence related to this experiment (such as qualitative GC analysis) showed concentrations of BTEX compounds between 2-6mg/l.

4.3.1.1 Alkanes

The alkanes are the most biodegradable of the hydrocarbons, however, normal alkanes in the C5 to C10 range are inhibitory to many microorganisms in high concentrations. Alkanes in the C20 to C40 range (waxes) are hydrophobic compounds and their very low solubilities interfere with their degradation. The alkanes determined in the liquid sample from the test contaminant thus, fortunately form the more biodegradable fraction of alkanes.

It must be pointed out that alkane degradation relies on microbially produced monooxygenase enzymatic activity which, in turn, is only active in fully aerobic environments. The complexity of the scan, also, indicates that there are many compounds which are classified as volatile (benzenes) and others which could be classified as semi-volatile (naphthalene) while others are relatively non-volatile (pentadecane).

4.3.1.2 Aromatic molecules

Aromatic molecules are also, as expected, present in the sample which all have chemical structures based on the benzene molecule. In this sample, different substituted benzene molecules are present. These different substitutions can, significantly, affect their biodegradation potential. Regarding these compounds, it is important to point out that some aromatics are very soluble (i.e. benzene) and often the most mobile compounds of conventional petroleum based products. These volatile organic compounds are also some of the most potentially hazardous, especially benzene, being a carcinogen.

4.3.1.3 Polycyclic Aromatic Hydrocarbons

The last group of compounds present are the polycyclic aromatic hydrocarbons (PAHs) which are characterised by 2 or more benzene rings and include compounds such as naphthalene. As the biodegradability of the PAHs decreases with amount of rings, it is fortunate that the sample of test contaminant appears to only contain two-ring PAH molecules. This could, under certain circumstances, be beneficial as the smaller PAH

molecules are more soluble and more volatile than the many ringed compounds. This could facilitate biological clean-up of the soil and, especially, if any air stripping is to be used for soil decontamination.

4.3.1.4 Environmental Toxicity

Despite these encouraging facts, it must be pointed out that the solvent phase of the test contaminant does contain numerous compounds which have relatively low LC_{50} values and, therefore, may pose a significant threat to the environment as indicated. These values, *inter alia*, are presented in Table 4.3 below.

Table 4.3 Chemical Characteristics for some Compounds found in Kerosene and1-Decanol

Compound	Molecular mass	Acute Toxicity* (LC_{50}) mg/L	Solubility mg/L	Vapour Pressure mmHg	Henry's Constant H (250C)	Log Kow (250C)
1-Decanol	158.3	23	37	1		4.11
Benzene	78	2.2	1800	75	0.224	2.13
Toluene	92	13	515	22	0.276	2.69
Xylene	106.2	11	575	37139	0.21	3.26
Naphthalene	128	3.8	30	0.05	0.0174	3.36

* Source Minimum Requirements DWAF (1998)

Liquid petroleum hydrocarbons and solvents (as predominant in the test contaminant sample), are present in several phases following release to the surface soil and subsurface environments. They can be present as (1) free-phase liquid, or Non-Aqueous Phase Liquids (NAPL); (2) vapour in the pore spaces of soils; (3) adsorbed to vadose or phreatic zone soils; or (4) dissolved in ground and soil water.

The amount and partitioning of the solvent between the phases is largely a function of chemical composition and characteristics. The water solubility, vapour pressure, octanol/water partition coefficient and organic carbon coefficient will, largely, determine the partitioning of the compound and, thus, its biodegradability.

4.3.2 Biodegradability detail

The relative biodegradability of the solvent sample from the test contaminant is shown in Figure 4.1. From this figure it can be seen that the sample was significantly more biodegradable than the phthalic acid reference compound.

According to the method, in order to be regarded as readily biodegradable, the test compound (solvent) must be degraded to the extent of at least 60% of theoretical CO_2 production within 28 days, and this level must be attained within 10 days of the time that CO_2 production exceeds 10% of theoretical (10-day window). From the results it can be seen that after day 8 the sample reached a theoretical CO2 production of 22.5 and nearly 200% by day 13.

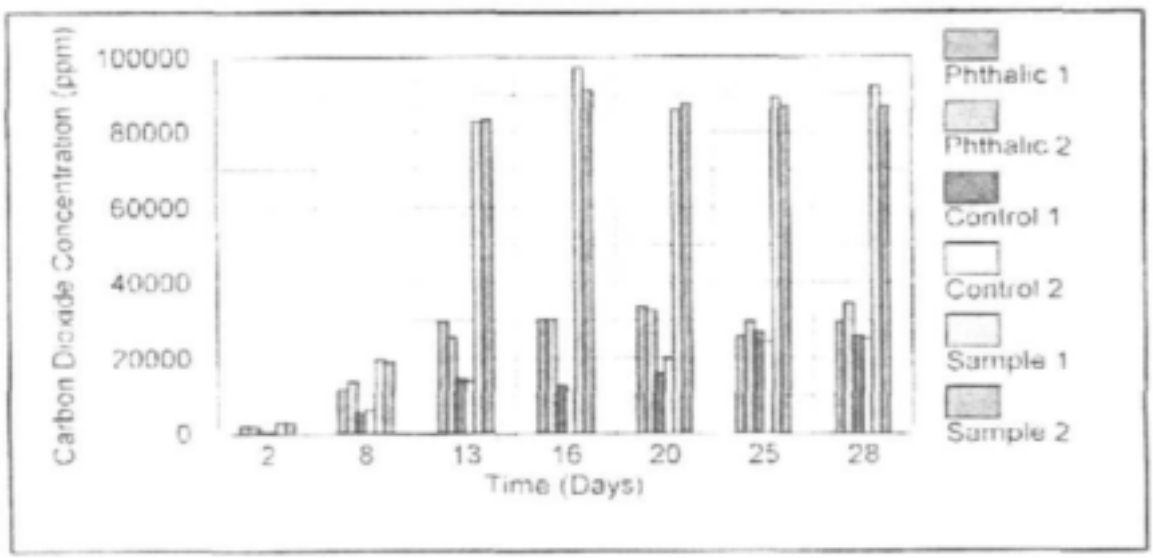

Figure 4.1 Relative Biodegradabilities of Phthalic Acid, and a Solvent Sample Compared with a Control Sample.

Therefore, the contaminant, according to the method, can be described as readily biodegradable under aerobic conditions. It must be pointed out that the degradation rates achieved during this study may never be achieved in full-scale or on-site situations. This is due to distribution limitations of nutrients, air and inoculums.

Further, this method does not directly indicate which compounds are being degraded and which are recalcitrant. To ascertain these unknowns, additional quantitative assessments will have to be undertaken.

4.3.3 Breakthrough Curves

The movement of a chemical through soil or compost is often a complex phenomenon which is controlled by numerous factors such as the hydrophobicity of the chemical, electrical charge, chemical and physical characteristics of both the matrix and the contaminant.

However, the retardation and more specifically the adsorption, of a compound or mixture of compounds to the matrix is of significant concern as it will affect the amount and rate of movement. A breakthrough curve can show the relative amounts of a chemical that will adsorb to a matrix and, thus, the amount of retardation due to abiotic adsorption.

In breakthrough experiments the concentration is plotted as a relative concentration, C/Co rather than the measured effluent concentration. The relative concentration is obtained by dividing the effluent concentration C by the concentration of the influent Co.

When relative concentrations are plotted, all the data is on the same scale, so results can be compared more easily. For the same reasons, relative pore volumes are often used for the horizontal scale rather than time. One pore volume is equal to the total volume of fluid in the column. The results for the breakthrough curves are given in Figure 4.2.

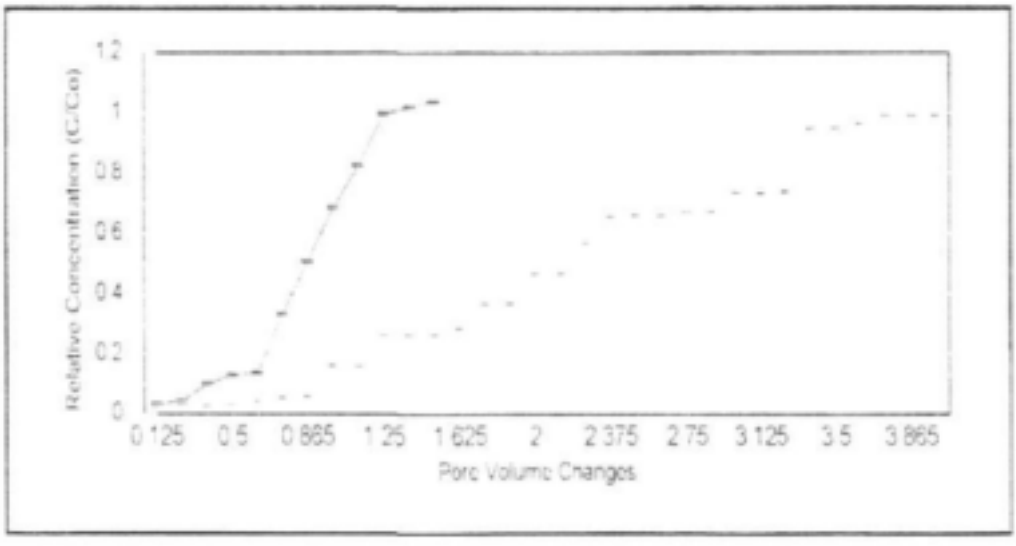

Figure 4.2 Breakthrough Curves for the Chloride Tracer (solid line) and the Solvent Contaminant (dashed line) in Fresh Pine Bark (16 - 20 mm)

In this figure the chloride tracer is given in blue, and it can be seen that there was a significant amount of elution before one pore volume. In any matrix a tracer (Cl^-1) compound, which is used because it does not adsorb to the matrix in any significant amount, should elute approximately after one pore volume in a near vertical curve.

In reality, however, the shape is more often than not, in the shape of a shallow "S" due to mainly dispersion and diffusion. These processes cause the tracer to start breaking through before one pore volume and to flatten out the nearer the relative concentration comes to one. Further it is generally accepted that the relative tracer concentration should be about half (0.5) when one pore volume has passed through the column.

Clearly the relatively fast flow rate (0.5 pore volumes per hour) resulted in higher rates of dispersion and diffusion which, in turn, resulted in the tracer prematurely breaking through, so that the relative concentration of 0.5 occurred at approximately 0.87 pore volumes.

The solvent contaminated water, as expected, showed greater adsorption with a relative concentration of 0.5 occurring at 2.25 pore volumes. It is also, worth noting the significantly flatter angle of the breakthrough curve which also indicates higher adsorption rates. In effect what the graph is showing is that in a fuller-scale PRB, more than two pore volumes will have to pass through the matrix before significant concentrations breakthrough without the intervention of microbial activity. Given the much slower hydraulic conductivity of average soils, compared with the pore volume changes of two hours for the experiment column, this could be a significant time depending on the thickness of the PRB support matrix.

4.3.4 Batch Studies

The first series of batch studies were made to evaluate whether the composted pine bark has inherently sufficient microbial numbers and associations to degrade the solvent contaminated water. The main aim of these, initial, batch experiments was to determine the relative biodegradability and/or the relative toxicity of the solvent to the indigenous micro-organisms.

During the first inoculations both the control and the test samples had all the required nutrients for growth (nutrients, carbon source and electron acceptors) and all the experimental vessels during this stage produced significant concentrations of carbon dioxide. For example, the average recorded concentration, of the three control samples, was 7200 ppmv, while the contaminated water samples recorded an average of over 8000 ppmv.

Following these batch cultures, an inoculum (2 ml) was taken from each vessel and cross inoculated into fresh media. Therefore, the control sample was cross inoculated into fresh media which contained distilled water and mineral nutrient solutions but no added compost.

Likewise, the test samples were cross inoculated into fresh contaminated water and mineral nutrients, thus, these samples had a carbon source. After 4 days the amount of microbial activity was measured and, as expected, the control vessels showed no carbon dioxide generation while the test vessels recorded CO_2 concentrations of over 8000 ppmv. This indicates that the micro-organisms are indeed able to utilise the solvent contamination as a carbon source. This does, however, not indicate which fractions of the solvent are biodegradable or to what extent – this assessment would require relatively extensive additional study.

The second series of batch cultures were made to determine the effect of temperature on growth rates, and are graphically illustrated below (Figure 4.3).

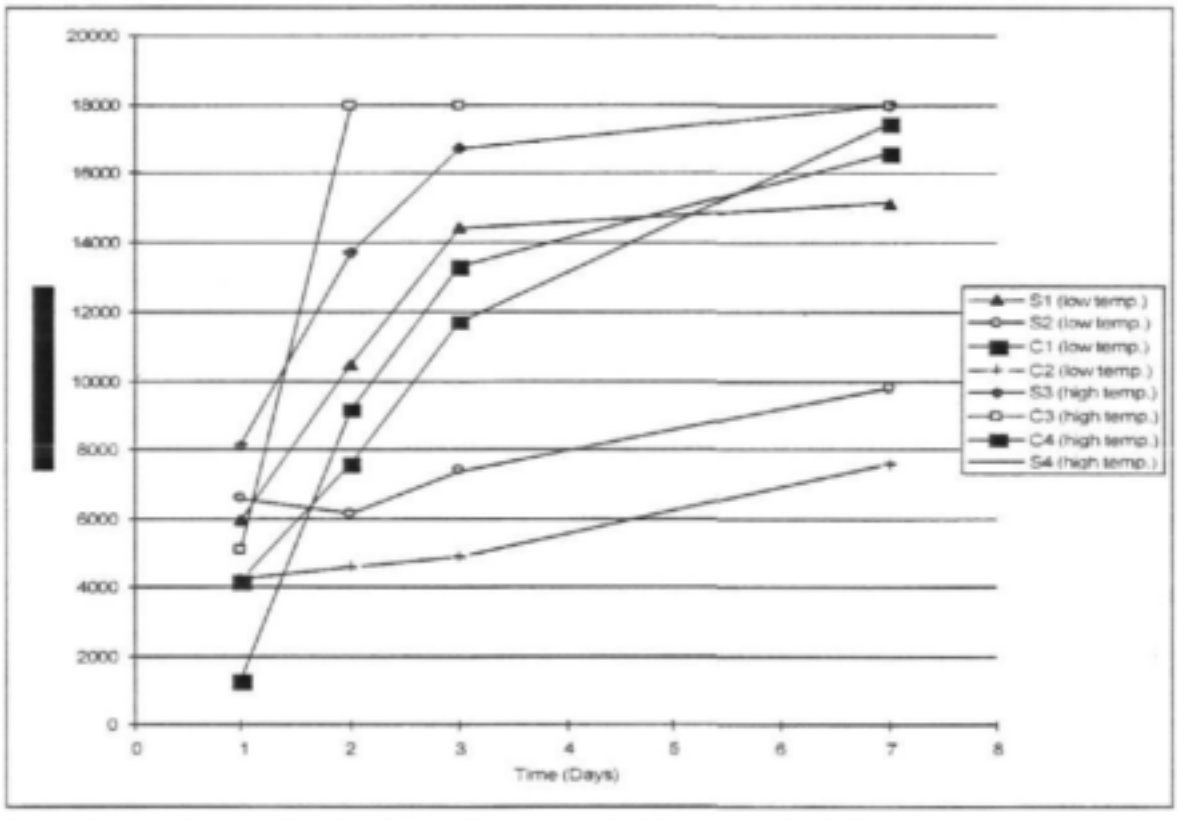

Figure 4.3 Carbon Dioxide Generation in Batch Cultures Under Different Temperatures. S=sample; C=Control. Numeric descriptors 1 & 3 = non-composted pine bark media; 2 & 4= composted pine bark media. "Low temp." = 18°C; "High temp." = 27°C.

4.3.4.2 *Temperature effect on degradation*

From the results it can be seen that for the lower temperature the non-composted pine bark sample and control (S1 and C1) both recorded significantly higher CO_2 generation rates than the experiments with composted pine bark (S2 and C2). This is unexpected, as composted materials often contain not only higher numbers of micro-organisms, but also, greater diversity.

This phenomenon was, also observed for the experiments run at the higher temperature, with S3 and C3 recording greater CO2 generation than S4 and C4. As expected, however, the experiments poised at the higher temperatures, with the exception of the early results for C4, recorded higher generation rates compared with the similar experiments at the lower temperatures. The major reason for this is that microbiological processes are enzymatic in nature and most enzymes, up to an optimum, function at greater rates with increasing temperature.

These results indicate that colder, in-situ temperatures of groundwater environments will tend to lower the microbial activity rates. For example, the experiments at higher temperatures recorded maximum carbon dioxide generation after 2-3 days, while the composted pine bark experiments required more than seven days. In full-scale set-ups, it is very likely that this factor will have to be recognised and perhaps further explored before any PRB design can be finalised.

From the above results it is clear that, despite the influence of temperature, the type of solid support media plays a critical role in the degradation potential. However, it must be born in mind, that this experiment was conducted over only seven days and that the period required for microbial acclimation was, as shown in the continuous cultures, longer.

4.3.5 *Continuous Culture PRB Configuration*

The results for the continuous culture experiments are shown below (Figure 4.4). From these results it can be seen that, during the initial two weeks, all the columns were characterised by a considerable amount of leaching of various organic compounds and recorded total organic concentrations (TOC) greater then the influent concentrations During this stage the composted pine bark (Column 2 and Column 4) showed less leaching than the non-composted columns. This is to be expected, as the composting process will eliminate many of the more labile and biodegradable compounds.

4.3.5.1 *Total Organic Carbon decrease*

After about 10 days both the control columns (Column 1 and Column 2) showed rapidly decreasing TOC concentrations to approximately 15mg/l, while the two experimental column required an additional 7 days. This increased time to attain concentrations below the influent concentrations can be ascribed to microbial adaptation to the contaminant and other factors.

Unlike the batch cultures the composted pine bark experimental column (Column 4) showed, prior to the addition of nutrients, greater contamination degradability compared with the equivalent pine bark column (Column 3). Following the period of adaptation and until the addition of nutrients (day 17 - day 36) the experimental columns recorded values around 20-25mg/l while the influent concentration fluctuated around 50mg/l

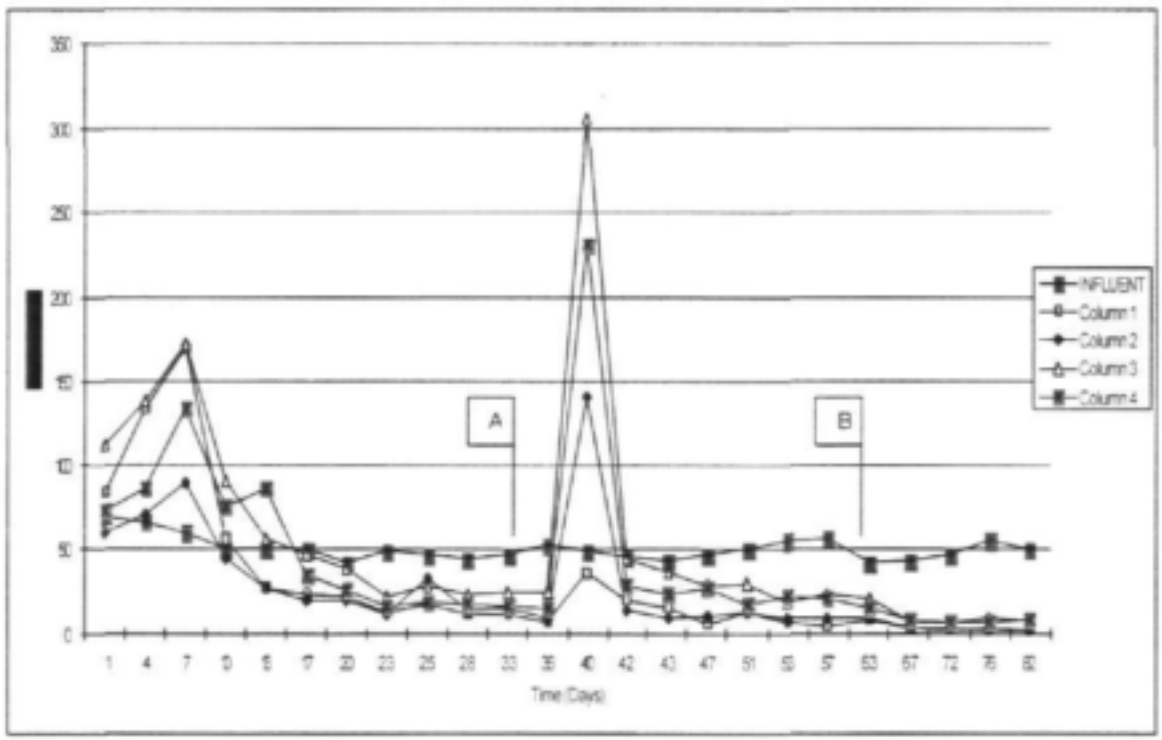

Figure 4.4 Total Organic Compounds Concentrations Recorded for the Continuous Culture Column Studies. Point A: Nutrient Addition; Point B: Bioactivator Addition

The essential feature of the continuous culture regime is that microbial growth takes place under steady-state conditions - that is, growth occurs at a constant rate and in a constant environment. The more or less constant attenuation rate of the contaminant from day 23 seems to indicate that steady-state had been reached. Presuming that

steady-state had been reached the actual rate of contaminant degradation would not be environmentally sufficient and would represent only about 50% removal (without the addition of the surfactant – see later sections).

4.3.6 Microbial activity: influencing factors

Bioremediation techniques are destruction techniques directed toward stimulating the micro organisms to grow and use the contaminants as a food and energy source by creating a favourable environment for the micro organisms. Generally, this means providing some combination of oxygen, nutrients, and moisture, and controlling the temperature and pH. . The rate at which micro organisms degrade contaminants is influenced by the complex interactions between the specific contaminants present and their concentrations, oxygen supply, moisture, temperature, pH, nutrient supply, bioaugmentation, and co-metabolism.

Nutrients required for cell growth are nitrogen, phosphorous, potassium, sulphur (macro-nutrients) and magnesium, calcium, manganese, iron, zinc, copper (micro-nutrients) as well as trace elements. If nutrients are not available in sufficient amounts, microbial activity will become limited.

Nitrogen and phosphorous are the nutrients most likely to be deficient in the contaminated environment. These are usually added to the bioremediation system in a useable form (e.g., as ammonium for nitrogen and as phosphate for phosphorous). The concentration of N and P required for mineralization of the organic contaminants can be calculated as there is a direct relationship between the concentration of organic C and the N and P needs for microbial growth. For example, it is known that a ratio of C:N of approximately 10:1 and C:P of 50:1 is needed for growth and to be incorporated into new biomass.

4.3.6.1 Nutrient additions

Therefore, a basic nutrient supplement was added which did not appear to increase the rate of degradation significantly. This was unexpected as the addition of N and P has shown, in most instances, to stimulate the biodegradation of organic contaminants in most soils and other polluted environments.

Circumstantial evidence for nutrient limitations (N and P) before the nutrient additions was provided by the conspicuous lack of algal growth, while, following the additions algal growth flourished (algal growth was limited inside the columns by encasing the columns with tin foil, the prolific growth was seen in the effluent tubes only). Many bacteria, and

fungi, however, also require low concentrations of one or more amino acids, B vitamins, fat-soluble vitamins or other organic molecules - these trace organic nutrients are termed growth factors.

In most soil environments, the supply of the micro-nutrients K, S, Mg, Ca, Fe and other micro-elements, is greater than the demand. From the above, it would appear that neither the basic nutrient media used as a supplement nor the support media (pine bark) provided for all the nutrient requirements. It is possible, however, that in-situ experiments, in soils, could have all their micro-nutrient requirements provided for by the soils which were not provided for by the pine bark, although, this would have to be confirmed experimentally. The concluding section of this report elaborates on rate limiting factors associated with micro and macro nutrients as potential secondary research areas.

4.3.6.2 Hydrophobicity

It is well known that the hydrophobicity of a compound has a direct influence on it's biodegradability due to it's relative willingness to partition into the water or non-aqueous phase (Alexander, 1999). The relative partitioning is determined by the amounts present in an organic solvent (n-octanol) and in water at equilibrium and is known as the octanol-water partition coefficient (Kow).

A compound with a high value is relatively hydrophobic and little of this compound is present in the water phase. The biodegradability of this compound will tend to be much lower than a chemically similar compound with a lower value as microorganisms, in general, consume only soluble or solubilised organic molecules.

4.3.6.3 Microbial utilisation of compounds in NAPLs

Three mechanisms appear to explain how microorganisms utilize compounds in non-aqueous- phase liquids (NAPLs) or metabolize organic solvents that have low solubilities in water. These mechanisms focus on how the chemical is transferred from the environment surrounding the organism to the cell surface, from which point it is transported through the membrane and to intracellular sites of enzymatic activity. Mechanisms include:

- Only the chemical in the water phase is used. Once the supply is assimilated into the cell, the organism can only use molecules that enter the aqueous phase by spontaneous partitioning, and hence further degradation would depend on the rate of spontaneous partitioning into the water phase.

- The microorganism excretes products that convert the substrate into droplets with sizes less than 1 μm, and these are then assimilated by the organism. Because of the small size of the droplets or particles, this process is sometimes called pseudosolubilization. The process commonly involves the excretion by the microorganism of surfactants that facilitate pseudosolubilization.

- The cells come into direct contact with the NAPL, on the surface of which the population develops, and the chemical at or near the point of contact with the organism passes through the cell surface into the cytoplasm.

4.3.7 Surfactant Use

Further, as it is known that many surfactants not only increase the partitioning of the hydrophobic compound into the water phase but, also, assist in the rapid assimilation of hydrocarbons by the indigenous micro-organisms (via mechanism (b) above), bioactivator X256 (as described in this report) was added to the columns. Although the active ingredients of this supplement have not been identified yet, it is thought to act as a bio-surfactant.

The effect of the addition of this compound is clear from the results recorded after day 63 (Figure 4.4), where it can be seen that the bio-surfactant increased the degradation rate significantly and effluent concentrations were below approximately 4ppm until the end of the experimental run. Although, the hydrocarbons were already dissolved in the water phase, it is likely that this surfactant played a dual role. Firstly, by decreasing the surface tension of the hydrophobic compounds, and, secondly, by facilitating the movement of the compounds from the external environment across the cell membrane.

Although not in all cases, most reactions involved in the degradation of sparingly soluble organic compounds probably take place within the cell. This enhanced transport into the cell by surfactants, and especially biosurfactants, which affect the microbial cell wall and increase it's permeability to hydrophobic compounds, thereby increasing the rate of degradation has been noted before[23]. These factors seem to have increased the bioavailability, and hence, the biodegradation of the organic compounds and resulted in approximately 90% removal of these compounds.

On day 63, just prior to the bioactivator addition, samples were taken for GC analyses with the results shown in Appendix V. The first GC trace shows that during batch growth the micro-organisms were able to use all the different compounds to varying degrees. The bio-availability and biodegradation rates are influenced by various factors which have been described in Section 1.3, however, in short, they include:

- Physical/chemical properties of contaminants (substrates);
- Interactions of substrates with support surfaces;
- Environmental parameters, e.g. nutrients, electron acceptors etc;
- Lack of enzymes (microbial consortia); and
- Mass transfer phenomena.

4.3.8 Summary of experimental results

Despite the different degradation factors described above, the results from Appendix 8 show that all of the experimental columns were able to degrade all of the different compounds in the organic contaminant and that no compounds were recalcitrant and accumulating. This is very clearly seen in the batch operated experiment where the size of all the peaks decreased irrespective of carbon chain length. The main reason for the relatively large amounts of contaminants still recorded in this analysis is that the batch growth cultures would have utilised the nutrients supplied and as soon as any nutrient became limiting, growth would have ceased before degradation of all the organic contaminants.

The GC traces also show very clearly that the relatively low degradation rate attained during the first part of the continuous culture growth experiment (up to day 36) was not likely to be as a result of low microbial numbers or diversity and highlights the need for further study to investigate this limitation – most likely some form of growth factor, micro-element limitation.

Another factor that could have limited the degradation of the compounds was the relatively fast flow rate (20 ml/h) which resulted in a residence time of 12 hours. In a full-scale PRB set-up, the flow rate would, depending on soil type and width of PRB media, be orders of magnitude lower, resulting in significantly increases residence times of days to weeks which would, in all likelihood, have significantly increased the removal rate. This is another area that clearly requires further study and is highlighted in the concluding sections of this report.

Lastly, as microbial growth and, thus, degradation is directly related to substrate concentration there is a substrate threshold limit, below which microorganisms are not able to sustain growth. This phenomenon could allow for low concentrations to remain in the environment. Further, due to the low solubility, tendency for adsorption and, especially, due to dilution in the groundwater, it is possible that many of the compounds used in this study will be present at much lower concentrations in-situ. Therefore, it is important to determine these threshold limits under field conditions by further studies.

4.4 ORGANIC COMPONENT: PRELIMINARY CONCULSIONS

From the results of this component of the study (in addition to numerous research and full-scale studies), it is clear that concentrations of many types of organic contaminants, including petroleum based contaminants, can be successfully reduced (degraded) by micro-organisms (at rates of 90% plus) in what could be called permeable bio-reactive barriers. In effect, these results mean that, as long as microbial requirements are met, most organic contamination plumes originating from sectors (mining, industrial, agricultural and domestic) may be treated to very low effluent concentrations.

Although, hydrophobic compounds, as used in this study, appeared to require the addition of surfactants to enhance degradation, other more ionic and hydrophilic molecules (i.e. phenol and halogenated organic compounds) will, in all likelihood, not require any additional supplements. This may make the use of PRB technologies, for organic treatment, additionally favourable.

These "bio-barriers" could have all of the benefits of conventional PRB configurations and could be incorporated into the design of units that would deal with inorganic pollution (provided design prerogatives eluded to in this report, such as the use and separation of aerobic and anaerobic environments, are adhered to). Although there are various methods of emplacing iron slurries to greater depths (> 30 m) there are, presently, no such methods of emplacing biobarriers. It is doubtful if using biobarriers at greater depths would have any economical benefits over more conventional bioremediation techniques.

However, this phase of the study, as framed in the introductory sections of this report, is preliminary and should be viewed with necessary qualification. One of the effective outputs of this section has been to highlight other areas that require investigation and the elucidation of which would serve to focus the results and assertions made here. These include investigating:

- The effect of low contaminant concentrations and threshold values limits on biodegradation of the organic molecules that characterised this study and that typify many organic contamination sites in South Africa;
- The nature and dynamics of micro-nutrient, vitamin and other growth factor limitations in pine bark based solid media;

- The use of other organic solid media investigated by other international studies, including saw dust, composted sewage sludge, chicken manure, wood chips and straw;

- The possible positive effects of bio-surfactants and other surface tension relieving agents in increasing a contaminant's susceptibility to degradation by microbes; and

- Increasing retention times which, in turn, would provide a greater period for micro-organism degradation of the contaminants in question.

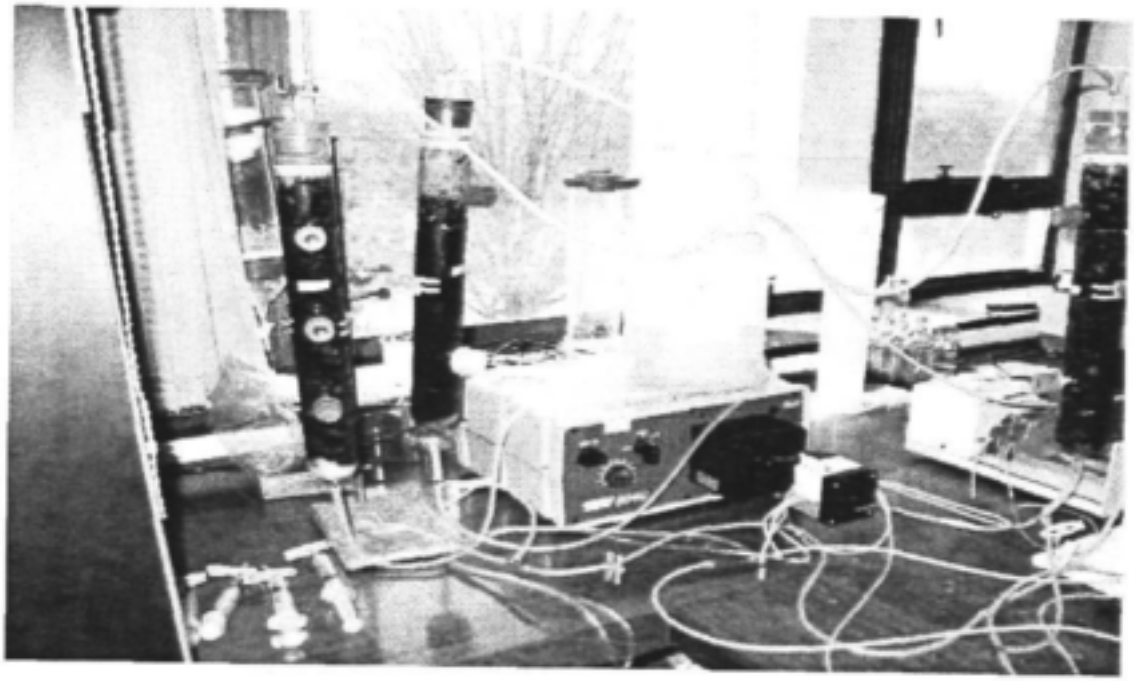

Plate 4.1 General view of experimental set up showing columns and flow meter

Plate 4.2 Pine bark material used as substrate media

CHAPTER 5 CONCLUSIONS

5.1 SUMMING UP THE RESEARCH OUTPUTS

5.1.1 Introductory comment

This final chapter provides a broad and general review, in terms of concluding commentary, of the research project. It relies on the approach of the preceding organic and inorganic section wherein "preliminary" conclusions and recommendations are enlarged upon and discussed and does not repeat them here.

It is important to contextualise the nature and intention of the "preliminary" conclusions and assertions made more specifically in Chapters 3 and 4, but also more generally through the entire report. "Preliminary" does not infer an incomplete or "draft" status of the study and its conclusions, recommendations, data, discussion etc. Rather it refers to a wider reporting/research philosophy that has become important to embrace when concluding the reporting of this study. The report has undertaken to look only generally and *preliminarily* at PRBs and asserts that the findings and data that have flown from it should be tested, verified and enlarged upon in the field in research projects with wider scope. It is in this sense that preceding sections, in conjunction with this conclusion, should be read and assessed.

This study has provided a comprehensive review of PRBs, their functioning, characteristics and dynamics in the international arena. Building on this, it has then moved on to demonstrate, in a controlled laboratory setting, that columns acting as PRBs can and do work efficiently using, critically, local contaminants and firmly considering relevant (local) environmental parameters (e.g. dolomitic water).

It has, in addition, modelled the speciation of uranium in a detailed fashion providing useful addition to the body of literature dealing with this pervasive South African contaminant. Furthermore, it has clearly illustrated the breakdown dynamics of a suite of organic contaminants, the customary treatment protocols of which may be enhanced by the preliminary assessments provided here.

5.1.2 Assessing the attainment of research aims

It is relevant in the context of the final section on this research report to assess the relative degrees of attainment of the original aims of the proposal, as discussed and enlarged upon in the introductory section. These aims were stated originally as:

> *1. To assess the application potential of Permeable Reactive Barriers (PRBs) under local conditions*

While there is a wide range and scope of international literature and descriptive, experimental and field description of PRB's and their usefulness, there is a marked paucity of South African scientific commentary on the subject. It was therefore important to emulate the well established performance of PRBs using local conditions.

This research achieved this using three local "conditions". These were (i) the use of the radionuclide U as a focused contaminant of the research (it is a particularly pervasive contaminant associated with, in particular, the gold mining areas of the country); (ii) a suite of organic contaminants from the site of a demolished metallurgical processing plant was used as "test contaminant" in the organic focus of the study and (iii) the dolomitic groundwater environment of key mining areas was recreated in a laboratory setting to understand any effect on PRB functioning.

The respective inorganic and organic sections of this report detail the relative data outputs of the experiments run under/using "local conditions". In general, the research team believe that there has been a good assessment of PRBs under local conditions. Importantly, local conditions have also emerged as a theoretical constraint in the form of deeper groundwater systems' applicability and suitability for the application of PRB technology (discussed the succeeding paragraphs).

> *2. To determine at a laboratory scale, the efficacy and efficiency of PRBs in the removal of inorganic and organic contaminants from groundwater contaminated by mining.*

Using established experimental protocols and the wide range of international literature available, the organic and inorganic research components both demonstrated, albeit on a restricted size and time scale, the efficacy and efficiency of PRBs in "the removal of inorganic and organic contaminants from groundwater contaminated from mining".

Potential performance has been adequately and positively demonstrated, with the associated caveats and assumptions. It has further provided a firm framework for moving forward with pilot field studies that will increase, as appropriate, the technical investigative aspects of the technology.

3. To identify those local conditions to which this technology is most applicable, and where it has the highest application potential.

It has emerged, both implicitly and explicitly through this research, that the local conditions for which this research is the most suited (given the level and degree of investigation (scope limitation) undertaken for the purposes of this research study) are shallower groundwater systems. The specific reasons for this are elaborated elsewhere in this report and are not repeated here.

Additionally, situations in the South African polluted (mine) water milieu where there may be particular application potential have been identified. Areas of tailings dam/water interfaces where movement of polluted water via formal (anthropogenic) or natural drainage routes to the surface/shallow groundwater zone are of environmental concern are particularly appealing in terms of potential future pilot sites and PRB suitability in general.

4. To make recommendations concerning the usefulness of PRB technology, and the need for further research and development

This final aim and the theme it encompasses runs through the latter chapters of this report. There are a number of specific recommendations, assumptions, constraints and limitations (see Section 5.2) that have been made regarding the technology and the results presented here. Extending the research philosophy ethic enlarged upon in the introductory section of this final chapter, this report has made "preliminary" positive findings regarding the usefulness of the technology and has also made a number of positive and pragmatic suggestions regarding the need and specifics of future research and development.

In all, the research team believes that there has been a positive and substantive attainment of the aims set out in the original research proposal approved by the WRC. In general, this research outcome bodes well for any future research into PRB technology that may be pursued.

5.2 CONTRAINTS AND LIMITIATIONS

One of the constraints of this study, to a certain extent, is that due to its scope limitations it has not been able to properly assess the effect that the South African deep groundwater will have on PRB functioning. Notwithstanding this, some elements and dynamics of deep groundwater environments have been considered and assessed (the effect of lower temperatures on microbial activity for example) and the study has provided a thorough and comprehensive review of tools developed internationally that can potentially deal with deep groundwater environments.

This study has not aimed to provide a detailed and comprehensive demonstration of PRB technology to the extent that an unreserved endorsement and recommendation can be made regarding their potential use in the South African environment. Instead, the report has looked to defer to the wide body of international literature to achieve this aim, and has provided a limited analytical demonstration of their use and efficiencies. This to provide a solid platform for the envisaged future work and research areas identified below.

Sections 5 and 6 particularly have gone to considerable length to highlight and discuss both the limitations and constraints that have emerged from the experimental runs and, developed from this, areas for further research. These are no repeated here and instead a more general recommendatory outline and summary is presented.

5.3 RECOMMENDATIONS: TAKING THE RESEARCH FURTHER

- While the research and the technology as it stands may seem more suited to sites that are characterised by surface or near surface groundwater pollution, the tools outlined in Section 3 of this report for dealing with deep groundwater environments, should be investigated in greater detail.

- The next logical step for taking the results and detail derived from this study further must be the selection of a site for (i) the development of a detailed pilot design and installation plan where both shallow and deep groundwater areas can be targeted; (ii) the installation and operation of a pilot site, and (iii) the monitoring, analyses and reporting of the functioning of that site. In the researchers' opinion, ideally, a uranium contaminated site should be selected from the Far West Rand region where there is a long history of uranium

contamination as well as a database covering uranium contamination. In addition, the dolomitic environment that charaterises this area would prime further research. Preliminary sites in this area have already been identified.

Secondly, a site characterised by organic contamination should be identified for the installation of a pilot PRB set up. A site in the Eastern Cape that has received much media attention recently from illegal (organic) waste disposal and that has now fallen under the care of the Department of Environmental Affairs and Tourism is a suggested candidate.

- Geohydrological characterisation and an understanding of the interplay between this and the optimal functioning of a PRB have emerged as critical elements, particularly as relates to any future work around PRBs in South Africa. It is a given that the scenario described in the point above would have to include a geohydrological characterisation and an effecient factoring in of geohydrological characteristics into the design and installation plan development.

- One of the suggested outputs of this research has been the potential development of a decision tree of sorts to deal with site specific contamination (at, for instance, a stream or impoundment impacted on by material from a tailings dam). This decision tree would then effectively guide management action at the site, in terms of PRB treatment.

  Conceivably, this tree would contain branches and action routings related to the parameters such as "water depth", "flow direction", "contaminant type" that would inform the path of the (management) action. It was deemed too early in the research to develop such a tree as not enough is know about the parameters active on site.

  This decision tree should be one of the products of the recommended next resaerch phase outlined above. Once the *in situ* dynamics of a particular site are understood (for instance, will a particular dolomitic substrate prove suitable for instalallation of a groundwater remediation tool similar to those described in the literature?; or what is the optimum barrier thickness to deal contaminated groundwater containing a uranium concentration of X?) the management assessment and action can be guided.

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CHAPTER 7 APPENDICES

APPENDIX 1 CHEMICAL CHARACTERISTICS (DATA SHEETS) FOR THE ORGANIC CONSTIUENTS OF THE TEST CONTAMIN ANT

ALAMINE 336

1-Octanamine, N,N-dioctyl-

- **Formula:** $C_{24}H_{51}N$
- **Molecular Weight:** 353.67
- **CAS Registry Number:** 1116-76-3
- **Chemical StructureOther Names:** Trioctylamine; Alamine 336; Tri-n-octylamine; Tri-N-caprylylamine; Tricaprylamine; Tricaprylylamine; Alamine 336S; Alamine 3365; 336S; Alamine 308

Condensed phase thermochemistry data

Quantity	Value	Units	Method	Reference	Comment
$?_fH°_{liquid}$	-587.5 ± 3.8	kJ/mol	Ccr	Steele, Chirico, et al., 1996	*ALS*
$?_fH°_{liquid}$	-585.3 ± 2.1	kJ/mol	Ccb	Lebedeva, 1966	*ALS*

Constant pressure heat capacity of liquid

$C_{p,liquid}$ (J/mol*K)	Temperature (K)	Reference	Comment
750.8	298.15	Steele, Chirico, et al., 1993	*DH*

Phase change data

Quantity	Value	Units	Method	Reference	Comment
T_{boil}	639.2	K	N/A	Weast and Grasselli, 1989	*BS*
T_{boil}	630.15	K	N/A	Merz and Gasiorowski, 1884	Uncertainty assigned by TRC = 4. K; *TRC*
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
T_{fus}	238.55	K	N/A	Ralston, Hoerr, et al., 1944	Uncertainty assigned by TRC = 1. K; *TRC*
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
$?_{vap}H°$	110. ± 15.	kJ/mol	V	Steele, Chirico, et al., 1996	*ALS*

Reaction thermochemistry data

Quantity	Value	Units	Method	Reference	Comment
$?_cH°$	-16145.4 ± 3.6	kJ/mol	Ccr	Steele, Chirico, et al., 1996	liquid phase
$?_cH°$	-16147.9 ± 2.1	kJ/mol	Ccb	Lebedeva, 1966	liquid phase

KEROSENE

Synonyms

- Kerosine
- Navy fuel JP-5
- Light petroleum
- Fuel oil No. 1
- Lamp oil
- Kerosine, petroleum

Physical properties.

Melting pt. (°C) -46 **Solubility in water** Insoluble **Boiling pt. (°C)** 175 - 325 **Flash point (°C)** 38 - 72 **Specific gravity** 0.8 **Autoignition temp. (°C)** 220 **V.P. (mm Hg)** 5 **Upper explosive limit (%)** 5 **Vapor density** 4.5 **Lower explosive limit (%)** 0.7

Registry numbers.

CAS 8008-20-6 **NFPA ratings (0-4) EINECS** 232-366-4 **Health** 0 **RTECS** QN9650000 **Flammability** 2 **RCRA Reactivity** 0 **UN** 1223 **UN Guide** 128 **Exposure limits UN Hazard Class** 3
NIOSH REL: TWA 100 mg/m^3
CAS Number 8008-20-6 is listed on the TSCA inventory.

Description.

Colorless to yellowish, oily liquid with a strong, characteristic odor.

Hazards.

Reacts with oxidizers. Class II Combustible Liquid.

ISODECANOL

Synonyms

- Isodecyl alcohol (mixed isomers)

Formula	$C_{10}H_{21}OH$
Formula mass	158.3

Physical properties.

Melting pt. (°C)	7	**Solubility in water**	Insoluble
Boiling pt. (°C)	220	**Flash point (°C)**	104
Specific gravity	84	**Autoignition temp. (°C)**	285
V.P. (mm Hg)	1	**Upper explosive limit (%)**	
Vapor density	5.5	**Lower explosive limit (%)**	0.8

Registry numbers.

CAS	25339-17-7	**NFPA ratings (0-4)**	
EINECS	246-869-1	**Health**	0
RTECS	NR0960000	**Flammability**	1
RCRA		**Reactivity**	0
UN	3082		
UN Guide	171	**Exposure limits**	
UN Hazard Class	9		

CAS Number 25339-17-7 is listed on the TSCA inventory.

Description.

Viscous, colorless liquid with a characteristic odor.

Hazards.

Decomposes on heating producing acrid smoke and fumes. Reacts with strong oxidizers.

APPENDIX 2 CHEMICAL COMPOSITION OF SALDHANA STEEL IRON ORE (MILL SCALINGS)

Total oil free moisture free basis	%m/m
Total iron (Fe)	65.26
Ferrous Iron (Fe)	59.19
Silica (SiO_2)	0.24
Alumina (Al_2O_3)	0.09
Sodium (Na)	<0.01
Potassium (K)	<0.01
Calcium (Ca)	0.12
Magnesium (Mg)	0.02
Manganese (Mn)	0.18
Nickel (Ni)	<0.01
Chromium (Cr)	0.01
Copper (Cu)	<0.01
Titanium dioxide (TiO_2)	<0.01
Vanadium (V)	<0.01
Zinc (Zn)	<0.01
Tin (Sn)	<0.02
Carbon (C)	0.08
Moisture	3.93
Oil	0.01
Sulphur (S)	0.02
Phosphorus (P)	0.004
Chloride (Cl)	0.003
Flouride (F)	0.008
Arsenic (As)	<0.001

Size distribution (oil moisture free)

Micron		%m/m
	+10000	Nil
10000	+2360	3.5
2360	+300	74.8
300	+150	17.4
150	+75	3.6
75		0.7

Note: 1. Ferrous iron includes metallic iron
2. Values reported as < are below detection limits

APPENDIX 3 SUPPLEMENTARY INFORMATION ON IRON CORROSION

Corrosion processes are the required chemical underpinning of contaminant remediation by metallic iron. Until recently, the science of corrosion was concerned almost exclusively with studying the process in order to minimize, and if possible eliminate, corrosion reactions. Corrosion results in rusting of the iron and steel in cars, pipes, bridges, buildings, and other structures. It is perhaps the most expensive aspect of infrastructure deterioration in modern society. Although corrosion is familiar to everyone as rusting, few are aware of the extremely complex reactions occurring within the corroding metals, at their surfaces and, in the case of electrochemical corrosion, in the surrounding electrolyte solutions. To understand how these reactions can be used for remediating contaminants requires at least a fundamental awareness of the manner in which corrosion reactions proceed. Zero-valence-state metals, such as metallic iron (Fe(0), can serve as electron donors for the reduction of oxidized species.

These metals are unstable in the natural environment and have to be created using high temperature metal refining processes (EPA, 1998). Zero-valence-state metals tend to revert to a form that is more thermodynamically stable; for example, iron metal oxidizes to Fe_2O_3 in the earth's oxygen-rich atmosphere. At low temperatures the rate of simple atmospheric oxidation of iron and steel is negligible, however, due to the formation of oxide films that inhibit further surface exposure. When a metal is immersed in an aqueous salt solution, as would be the case for a reactive barrier of iron chips or filings in an aquifer, an electrochemical corrosion mechanism will occur. Electrons are given up by the metal in one area (the anodic region) forming soluble cations of the metal, and taken up by oxidized species that become reduced, at another part of the metal surface (the cathodic region).

The instability of the iron itself can provide the necessary energy for oxidation-reduction reactions without external energy input, provided suitable coupled electron-accepting reactions can occur with reducible species at the cathode. Typically dissolved oxygen is the preferred oxidant, or electron acceptor, during aerobic corrosion processes. These systems can, however, become anoxic or anaerobic if oxygen is depleted by the reactions. When present, inorganic contaminants such as chromate (CrO_4^{2-}) or highly halogenated organic compounds such as PCE and TCE can serve as the oxidants.

accept electrons, and become reduced. As long as electron acceptors are present, corrosion processes and electron transfer within the metal can continue. An electrochemical corrosion cell (ECC) can form in a number of ways, including:

- The simple contact of two different metals. One will become the anode, the other the cathode. The position of the metals in the galvanic series determines the direction of electron flow; i.e., which becomes the anode and which the cathode.
- When anodic and cathodic regions develop on the same metal surface. This can result from compositional variations within the metal (i.e., other metal contaminants or inclusions with differing galvanic potentials), surface defects, differences in grain structure orientation, stress/strain differences, and chemical variations in the surrounding electrolyte solution (Manahan, 1994).

These electron transfer processes within a metal or between contacting metals are said to occur within the external circuit of the electrochemical cell. An internal circuit is also required to complete the cell. This requirement is fulfilled by the contacting electrolyte solution. This electrolyte can consist of water containing salts (such as ground water) and reducible, (electron-accepting), solute(s). In some cases the water itself can accept electrons via reductive dissociation. This is easily observed when the zero-valent metal is very low in the galvanic series, such as Mg.

When Mg metal is added to even deionized water (no solutes present), bubbles of H_2 gas rapidly appear on the Mg surfaces. Mg is so low in the galvanic series that the water itself serves as the electron acceptor and is rapidly dissociated. As you proceed to metals higher in the galvanic series, the dissociation of water becomes less and less pronounced. The ECC is basically a low-power version of the same type of circuit that is established in batteries. Figure 2.1 shows a simple ECC in a beaker of electrolyte solution with the external circuit resulting from the contact of two dissimilar metals, tin and iron. The electrons travel through the external circuit from the anode (Fe^0) to the cathode (Sn^0), where they can reduce oxidized species.

Some of the potential corrosion and contaminant reduction reactions in zero-valent iron systems are:

$Fe^0 \rightarrow Fe^{2+} + 2e^-$ Anode (2.1)

$2H^+ + 2e^- \rightarrow H_{2\,(gas)}$ Cathode (2.2)

$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_{2\,(gas)}$ Net reaction (2.3)

and, when oxygen is present (aerobic system)

$4Fe^0 \rightarrow 4Fe^{3+} + 12e^-$ Anode (2.4)

$12H^+ + 3O_2 + 12e^- \rightarrow 6H_2O$ Cathode (2.5)

$4Fe^0 + 3O_2 + 12H^+ \rightarrow 4Fe^{3+} + 6H_2O$ Net reaction (2.6)

where the increase in pH due to proton consumption (Equation 2.6) results in the precipitation of the Fe^{3+} as $Fe(OH)_3$. Should chromate be present as an oxidized species

$Fe^0 \rightarrow Fe^{3+} + 3e^-$ Anode (2.7)

$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-$ Cathode (2.8)

$Fe^0 + CrO_4^{2-} + 4H_2O \rightarrow Fe(OH)_3 + Cr(OH)_3 + 2\,OH^-$ Net reaction (2.9)

APPENDIX 4 INORGANIC COMPONENT: REACTIVE MATERIAL COMPOSITIONS & RAW COLUMN ELUTION DATA

Table 7.1 **Column A: Filter sand (52g) 0.0% Iron**

Aliquot Number	*tbegin (hh:mm)*	*tend (hh:mm)*	*Elution time (min)*	*mass (g)*	*Vol thru column (ml)*	*No. Pore volumes*	*pH*	*Eh (mV)*	*Avg vol flow rate (ml/min)*
A1	10:17	10:37	0	52.33	52.3	3.8	7.93	168	2.62
A2	10:37	10:49	20	56.73	109.1	7.9	8.02	165	4.73
A3	10:49	11:05	32	53.99	163.1	11.8	8.02	161	3.37
A4	11:05	11:26	48	52.59	215.6	15.6	7.90	159	2.50
A5	11:26	11:47	69	49.85	265.5	19.3	7.93	157	2.37
A6	11:47	12:08	90	51.58	317.1	23.0	7.73	85	2.46
A7	12:08	12:27	111	53.22	370.3	26.9	7.90	116	2.80
A8	12:27	12:47	130	53.23	423.5	30.7	7.86	115	2.66
A9	12:47	13:06	150	60.97	484.5	35.1	7.81	88	3.21
A10	13:06	13:27	169	52.73	537.2	39.0	7.73	162	2.51
A11	13:27	13:33	190	49.11	586.3	42.5	7.75	69	8.19

Table 7.2 **Column B: Granulated iron (4.10g) + Filter sand (48g) 7.9% Iron**

Aliquot Number	*tbegin (hh:mm)*	*tend (hh:mm)*	*Elution time (min)*	*mass (g)*	*Vol thru column (ml)*	*No. Pore volumes*	*pH*	*Eh (mV)*	*Avg vol flow rate (ml/min)*
B1	10:17	10:37	0	52.54	52.5	3.8	7.89	151	2.63
B2	10:37	10:58	20	64.06	116.6	8.4	7.80	156	3.05
B3	10:58	11:09	41	54.34	170.9	12.4	7.86	151	4.94
B4	11:09	11:26	52	52.67	223.6	16.2	7.86	146	3.10
B5	11:26	11:47	69	56.02	279.6	20.2	7.81	143	2.67
B6	11:47	12:08	90	49.24	328.9	23.8	7.76	88	2.34
B7	12:08	12:27	111	52.03	380.9	27.6	7.85	65	2.74
B8	12:27	12:47	130	53.23	434.1	31.4	7.80	20	2.66
B9	12:47	13:06	150	54.85	489.0	35.4	7.72	45	2.89
B10	13:06	13:13	169	51.32	540.3	39.1	7.84	70	7.33
B11	13:13	13:33	176	48.32	588.6	42.6	7.75	39	2.42

Table 7.3 **Column C: Steel wool (4.06g) + Filter sand (48g)7.8%Iron**

Aliquot Number	*tbegin (hh:mm)*	*tend (hh:mm)*	*Elution time (min)*	*mass (g)*	*Vol thru column (ml)*	*No. Pore volumes*	*pH*	*Eh (mV)*	*Avg vol flow rate (ml/min)*
C1	10:17	10:37	0	49.89	49.9	3.6	7.93	116	2.49
C2	10:37	10:58	20	48.07	98.0	7.1	7.72	-14	2.29
C3	10:58	11:16	41	45.39	143.4	10.4	7.69	-10	2.52
C4	11:16	11:27	59	57.11	200.5	14.5	7.76	6	5.19
C5	11:27	11:47	70	48.61	249.1	18.0	7.81	62	2.43
C6	11:47	12:08	90	56.89	306.0	22.2	7.87	58	2.71
C7	12:08	12:27	111	49.3	355.3	25.7	7.95	60	2.59
C8	12:27	12:47	130	50.1	405.4	29.4	8.09	29	2.51
C9	12:47	13:07	150	54.87	460.2	33.3	8.23	23	2.74
C10	13:07	13:27	170	51.24	511.5	37.1	8.22	40	2.56
C11	13:27	13:47	190	64.44	575.9	41.7	8.19	23	3.22

APPENDIX 5 ANALYTICAL RESULTS FOR COLUMN SOLUTIONS

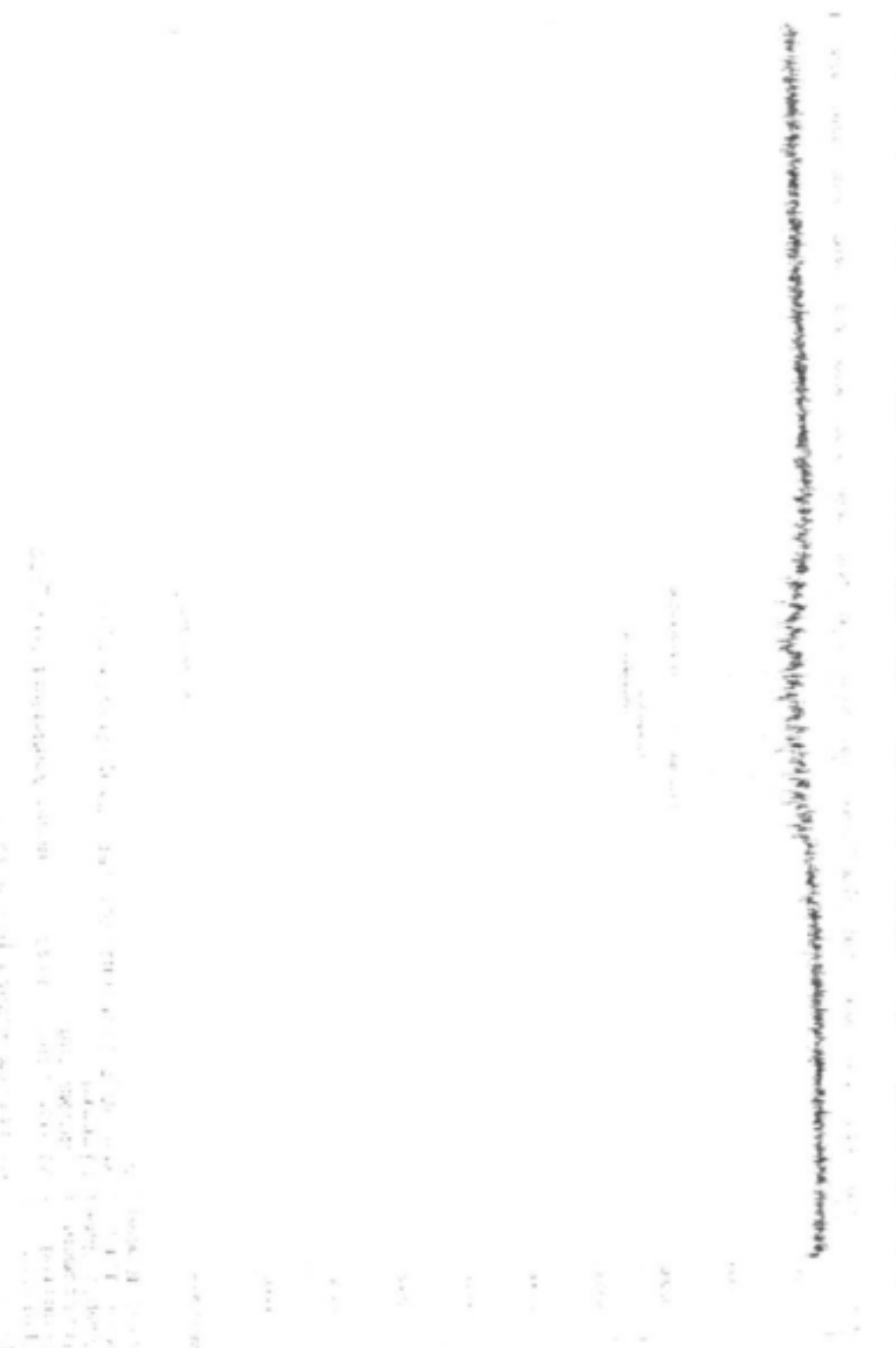
Table 7.4 Laboratory analytical results for column solutions (Lakefield Research)

Sample ID	U [µg/L]	pH [unit]	Cond [mS/m]	T.Alk [mg/L #]	HCO3 [mg/L *]	Cl [mg/L]	SO4 [mg/L]	Ca [mg/L]	Mg [mg/L]	Na [mg/L]	Fe ICP [mg/L]
Sample A1	13	7.9	67.6	43	26	25	197	45	32	38	< 0.02
Sample A2	41	7.8	75.8	34	21	26	245	51	39	43	< 0.02
Sample A3	53	7.8	76.3	33	20	24	246	50	39	43	< 0.02
Sample A4	59	7.8	76.4	33	20	24	247	53	40	44	< 0.02
Sample A5	58	7.9	76.4	33	20	24	248	53	40	44	< 0.02
Sample A6	60	7.8	76.4	33	20	24	252	51	40	43	< 0.02
Sample A7	63	7.9	76.4	33	20	27	274	52	39	45	< 0.02
Sample A8	64	7.9	76.4	34	20	24	250	51	39	44	< 0.02
Sample A9	68	7.8	76.4	33	20	24	247	51	39	43	< 0.02
Sample A10	71	7.9	76.5	33	20	25	250	52	40	44	< 0.02
Sample A11	73	7.9	76.5	33	20	25	253	53	41	45	< 0.02
Sample A12	73	7.9	76.5	--	--	--	--	--	--	--	--
Sample B1	3.9	8.2	44.5	64	39	25	88	32	17	27	< 0.02
Sample B2	28	7.9	76.7	33	20	24	243	50	38	43	< 0.02
Sample B3	46	7.9	77.0	33	20	25	251	51	39	44	< 0.02
Sample B4	53	7.9	77.0	33	20	25	251	52	39	44	< 0.02
Sample B5	53	7.9	76.8	33	20	25	250	53	40	44	< 0.02
Sample B6	53	7.9	76.8	33	20	25	252	54	40	45	< 0.02
Sample B7	56	7.9	76.7	33	20	25	258	51	39	44	< 0.02
Sample B8	58	7.9	76.8	33	20	24	252	51	40	44	< 0.02
Sample B9	63	7.9	76.7	33	20	25	253	52	40	45	< 0.02
Sample B10	61	7.9	76.7	33	20	26	255	51	39	43	< 0.02
Sample B11	70	7.9	76.7	33	20	25	254	51	40	45	< 0.02
Sample B12	66	7.9	76.7	33	20	25	251	52	40	43	< 0.02
Sample C1	< 2.1	8.4	31.4	76	47	21	30	24	9.6	21	< 0.02
Sample C2	< 2.1	8.0	70.1	36	22	24	213	48	34	41	0.03

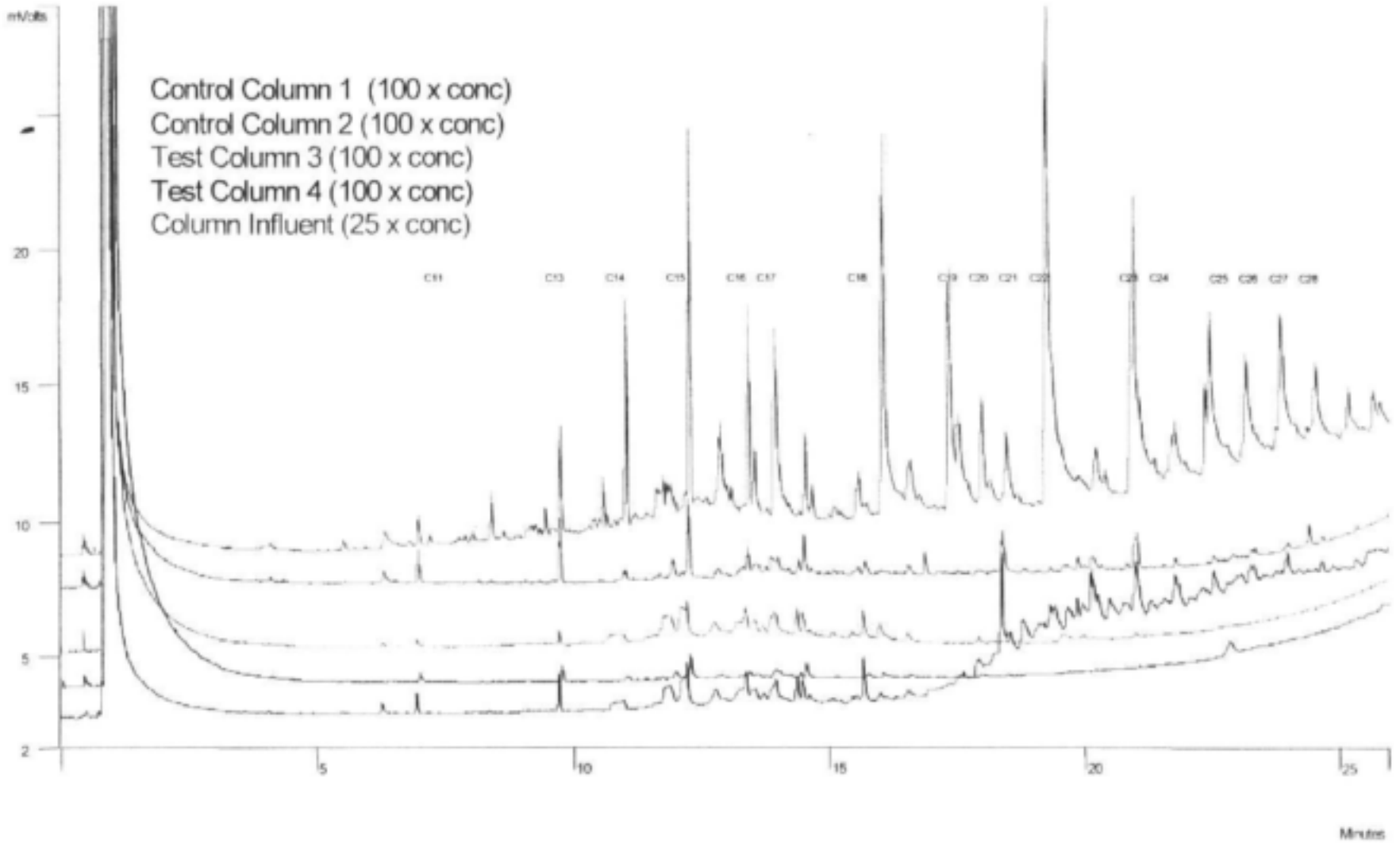
Sample ID	U [µg/L]	pH [unit]	Cond [mS/m]	T.Alk [mg/L #]	HCO3 [mg/L *]	Cl [mg/L]	SO4 [mg/L]	Ca [mg/L]	Mg [mg/L]	Na [mg/L]	Fe ICP [mg/L]
Sample C3	< 2.1	7.9	76.0	30	18	24	241	52	39	44	0.83
Sample C4	< 2.1	7.9	76.3	31	19	25	249	52	40	43	0.39
Sample C5	< 2.1	7.9	76.3	31	19	25	252	51	40	44	0.40
Sample C6	< 2.1	7.9	76.3	31	19	25	254	51	39	43	0.11
Sample C7	< 2.1	8.0	76.4	32	20	25	253	52	39	44	0.10
Sample C8	< 2.1	8.0	76.2	32	20	24	248	51	39	44	0.06
Sample C9	3.1	8.0	76.4	32	20	24	253	50	39	42	0.13
Sample C10	< 2.1	8.0	76.5	33	20	25	253	51	40	44	< 0.02
Sample C11	< 2.1	8.0	76.5	33	20	26	252	51	39	44	0.05
Sample C12	3.0	7.9	76.8	--	--	--	--	--	--	--	--
Sample A1	< 2.1	--	67.6	iss	iss	26	196	44	--	38	--
Sample B1	< 2.1	--	44.6	iss	iss	24	86	32	17	27	< 0.02
Sample C1	< 2.1	--	31.8	iss	iss	iss	iss	25	9.5	22	< 0.02
Sample C4	< 2.1	--	--	--	--	25	251	52	40	44	--

APPENDIX 6 GCMS SCAN OF SOLVENT (N-HEXANE) EXTRACTION OF A SAMPLE OF THE FREE PHASE MATERIAL FROM THE TEST CONTAMINANT

APPENDIX 7 GCMS SCAN OF INFLUENT MATERIAL (BTEX COMPOUNDS)



APPENDIX 8 GCMS OF ORGANIC COMPOUNDS AFTER SOVENT EXTRACTION (N-HEXANE) AFTER PASSAGE THROUGH THE COLUMNS


mVolts
Control Column 1 (100 x conc)
Control Column 2 (100 x conc)
Test Column 3 (100 x conc)
Test Column 4 (100 x conc)
Column Influent (25 x conc)
C11
C13
C14
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
20
15
10
5
2
5
10
15
20
25
Minutes

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