

CRANFIELD UNIVERSITY

Moathodi Wise Letshwenyo

PHOSPHORUS REMOVAL IN PASSIVE TREATMENT
TECHNOLOGIES FOR TERTIARY WASTEWATER TREATMENT

School of Applied Science

Department of Environmental Science and Technology

PhD Thesis

Academic Year: 2010 - 2013

Supervisors: Professor Bruce Jefferson and Dr Ewan McAdam

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degree of Doctor of Philosophy

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ABSTRACT

The treatment of phosphorus at small sewage works requires alternative approaches to the traditional chemical precipitation and biological removal pathways, as such approaches do not align well to the requirements at such a scale in relation to the use of chemicals, increased energy demands and/or increased sludge production. At small sewage works, constructed wetlands are often used as a tertiary treatment for solid removal and some associated biological degradation. The current work aims to assess the potential to upgrade such systems for phosphorus removal by replacing the traditional media with a reactive alternative. This was accomplished through a series of laboratory and pilot trials to establish the most appropriate media and understand the underlying mechanisms. Determination of key properties, such as retention capacity, mechanical strength and regeneration potential, identified steel slag and phosphateTM as media that were suitable for in depth investigation. Both were shown to be effective at phosphorus removal if sufficient contact time was provided such that 1 mg L⁻¹ effluent concentrations was achieved when an empty bed contact time of 48 hours was used. A detailed investigation of the media revealed that steel slag worked through a two-step process where initially calcium was dissolved into the water from the surface of the media and then precipitated with the phosphorus to form calcium phosphate.

The presence of alkalinity in steel slag bed inhibited the precipitation of phosphorus through calcium, as carbonates were precipitated instead. There was also a risk associated with the leachability of aluminum and flushing of retained phosphorus during the treatment of wastewater with very low phosphorus concentrations from the bed.

In the case of PhosphateTM, the binding agent resulted in very high effluent pH and the formation of colloidal phosphates that needed to be filtered out to enable low effluent phosphorus concentrations to be achieved.

The results indicated that both media have the potential to remove phosphorus from tertiary effluents, but the issues of leachability of aluminum from steel slag bed and

Abstract

the release of retained phosphorus should be investigated further before full scale trials. The colloidal phosphorus observed escaping effluent from phosphateTM bed and that the elevated effluent pH should be solved before full scale trials.

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Contents

| | | |
|-------|--|----|
| 1 | CHAPTER 1: INTRODUCTION | 2 |
| 1.1 | Background..... | 2 |
| 1.2 | Aims and objectives | 3 |
| 1.3 | Thesis plan..... | 4 |
| 1.4 | References..... | 5 |
| 2 | PHOSPHORUS REMOVAL IN REEDS BEDS WITH REACTIVE MEDIA | 8 |
| 2.1 | Introduction | 8 |
| 2.2 | Conventional technologies for P removal from wastewater | 9 |
| 2.2.1 | Chemical precipitation | 9 |
| 2.2.2 | Biological P removal | 10 |
| 2.3 | P removal through reed beds and reactive media..... | 10 |
| 2.3.1 | Key properties influencing choice of media..... | 12 |
| 2.3.2 | Properties seldom used for screening..... | 14 |
| 2.3.3 | Phosphorus removal mechanisms | 16 |
| 2.3.4 | Competition for P removal with other ions | 21 |
| 2.4 | Identified gaps from review | 22 |
| 2.5 | Acknowledgements..... | 22 |
| 2.6 | References..... | 23 |
| 3 | Chapter 3: MEDIA SCREENING FOR DETERMINATION OF KEY PROPERTIES INFLUENCING PERFORMANCE FOR PHOSPHORUS REMOVAL FROM TERTIARY EFFLUENTS..... | 33 |
| 3.1 | Introduction | 33 |
| 3.2 | Materials and methods | 36 |
| 3.3 | Results and discussion..... | 39 |
| 3.3.1 | Influence of elemental composition on performance | 39 |
| 3.3.2 | Fixed bed columns..... | 43 |
| 3.3.3 | Link to large scale | 44 |
| 3.3.4 | Batch regeneration..... | 46 |
| 3.3.5 | Phosphorus Sequential Extraction | 47 |
| 3.3.6 | Media mechanical strength vs. density..... | 48 |
| 3.4 | Conclusions | 50 |

Contents

| | | |
|-------|---|-----|
| 3.5 | Acknowledgements..... | 51 |
| 3.6 | References..... | 51 |
| 4 | DISSOLUTION OF CALCIUM FROM STEEL SLAG IN PHOSPHATE MITIGATION; INFLUENCE OF BACKGROUND WASTEWATER CHARACTERISTICS..... | 57 |
| 4.1 | Introduction | 57 |
| 4.2 | Materials and methods | 58 |
| 4.3 | Results and discussion..... | 58 |
| 4.3.1 | Media characterisation | 58 |
| 4.3.2 | Steel slag dissolution | 59 |
| 4.4 | Conclusion | 71 |
| 4.5 | Acknowledgements..... | 72 |
| 4.6 | Reference | 72 |
| 5 | EVALUATION OF STEEL SLAG AND PHOSFATE™ AS REACTIVE MEDIA FOR PHOSPHORUS REMOVAL FROM TERTIARY EFFLUENTS..... | 78 |
| 5.1 | Introduction | 78 |
| 5.2 | Materials and methods | 80 |
| 5.3 | Results and discussion..... | 84 |
| 5.3.1 | Influence of media pH and surface acidity or basicity on performance | 84 |
| 5.3.2 | Leachability in DI water and controlled pH..... | 85 |
| 5.3.3 | Effect of competing ions | 87 |
| 5.3.4 | Detailed batch experiments | 89 |
| 5.3.5 | Fixed bed column studies..... | 90 |
| 5.3.6 | Tracer studies | 100 |
| 5.3.7 | Phosphorus sequential extraction | 102 |
| 5.4 | Conclusion | 104 |
| 5.5 | Acknowledgements..... | 105 |
| 5.6 | References..... | 105 |
| 6 | PHOSPHORUS REMOVAL FROM LOW AND HIGH CONCENTRATED PHOSPHORUS EFFLUENTS USING STEEL SLAG..... | 112 |
| 6.1 | Introduction | 112 |
| 6.2 | Materials and methods | 114 |
| 6.3 | Results and discussion..... | 117 |
| 6.3.1 | Phosphorus removal from tertiary effluents | 117 |

Contents

| | | |
|-------|---|-----|
| 6.3.2 | Effect of empty bed contact time on steel slag efficiency | 123 |
| 6.3.3 | Influence of leaching metals on media performance | 125 |
| 6.3.4 | Retention of other anions by steel slag bed | 130 |
| 6.3.5 | Tracer studies | 131 |
| 6.3.6 | Phosphorus sequential extraction | 132 |
| 6.3.7 | Steel slag regeneration and P recovery..... | 133 |
| 6.4 | Toxicity effect of the two media | 137 |
| 6.5 | Conclusion | 138 |
| 6.6 | Acknowledgements..... | 139 |
| 6.7 | References..... | 139 |
| 7 | DISCUSSIONS | 145 |
| 7.1 | Which phosphorus removal pathways were involved in the two media?..... | 145 |
| 7.1.1 | Media dissolution into Ca^{2+} and OH^- ions..... | 145 |
| 7.1.2 | Formation of precursors (OCP and ACP) | 145 |
| 7.1.3 | CaCO_3 Precipitation | 146 |
| 7.1.4 | Other P removal pathways..... | 147 |
| 7.2 | Key observations | 148 |
| 7.2.1 | Contact time influences performance..... | 148 |
| 7.2.2 | Media regeneration and P recovery..... | 149 |
| 7.2.3 | Fine colloids of P in the effluent..... | 149 |
| 7.2.4 | Release reaction | 149 |
| 7.3 | In what situation can reactive media be used to remove phosphorus?..... | 149 |
| 7.4 | What influence does media selection have on the process?..... | 150 |
| 7.5 | What is the influence of sewage characteristics on P removal?..... | 151 |
| 7.5.1 | Alkalinity | 151 |
| 7.5.2 | Aluminum, Calcium, Iron and Magnesium Concentrations | 151 |
| 7.5.3 | The influence of wastewater pH | 152 |
| 7.6 | What are the main implementation challenges?..... | 152 |
| 7.6.1 | Elevated pH | 152 |
| 7.6.2 | Regeneration and regenerant strength | 153 |
| 7.6.3 | Leachability..... | 154 |
| 7.7 | References..... | 154 |
| 8 | CONCLUSIONS | 158 |

Contents

| | | |
|-----|------------------|-----|
| 8.1 | Future work..... | 159 |
|-----|------------------|-----|

LIST OF FIGURES

| | |
|--|----|
| Figure 3.1: Breakthrough curves of different media from rapid small scale columns experiments----- | 43 |
| Figure 3-2: Impact of batch regeneration cycles on P retention capacity ----- | 46 |
| Figure 3-3: Phosphorus sequential extraction results ----- | 47 |
| Figure 3-4: Bulk density and mechanical strength at failure ----- | 49 |
| Figure 4-1: Impact of alkalinity on steel slag dissolution in NaHCO ₃ solution----- | 60 |
| Figure 4-2: Impact of alkalinity on steel slag dissolution in CaCO ₃ solution, low and high P strength effluents----- | 62 |
| Figure 4-3: Variation of pH with alkalinity, low and high strength effluents----- | 64 |
| Figure 4-4: Impact of P concentration on P removal with time using steel slag----- | 65 |
| Figure 4-5: Variation of residual P concentration with time during steel slag bed batch tests----- | 66 |
| Figure 4-6: Impact of media dosage on P removal from high and low P effluents----- | 67 |
| Figure 5-1: Impact of media pH, acidity and basicity on P retention capacity of steel slag and phosphate TM ----- | 85 |
| Figure 5-2: Influent and effluent TP, SRP from steel slag and phosphate TM bed----- | 91 |
| Figure 5-3: Change of pH with number of bed volumes treated by steel slag and phosphate TM beds----- | 94 |
| Figure 5-4: Impact of effluent pH on P retention onto phosphate TM and steel slag beds----- | 94 |
| Figure 5-5: Correlation of metals in steel slag influent and effluent with bed volume of wastewater treated----- | 96 |

List of figures

| | |
|--|---------|
| Figure 5-6: Correlation of metals in phosphate TM influent and effluent with bed volume of wastewater treated----- | 98 |
| Figure 5-7: Exit age distribution curve of steel slag and phosphate TM beds----- | 101 |
| Figure 5-8: Phosphorus sequential extraction results from phosphate TM and steel slag beds----- | 102 |
| Figure 6-1: Results of P removal from tertiary effluents at sites A, B and C----- | 118-119 |
| Figure 6-2: Change of pH with number of bed volumes treated at sites A, B and C---- | 122 |
| Figure 6-3: Impact of EBCT on P removal from wastewater using steel slag----- | 124 |
| Figure 6-4: Impact of pH on P removal using steel slag----- | 125 |
| Figure 6-5: Correlation of metals with bed volume treated in influent and effluent into and out of steel slag bed treating high phosphorus wastewater----- | 126 |
| Figure 6-6: Correlation of metals with bed volume treated in influent and effluent into and out of steel slag bed treating high phosphorus wastewater----- | 129 |
| Figure 6-7: Exit age distribution curve for sites A and B at 12 and 48 hours nominal residence times----- | 131 |
| Figure 6-8: Phosphorus sequential extraction results----- | 133 |
| Figure 6-9: Impact of feeding cycles on steel slag bed during regeneration----- | 133 |
| Figure 6-10: Impact of regeneration cycles on phosphorus recovery----- | 135 |
| Figure 6-11: Impact of pH on phosphorus recovery from spent regenerant----- | 136 |
| Figure 6-12: Impact of contact time on phosphorus recovery from regenerant----- | 137 |
| Figure 7-1: Typical reactions during steel slag and Phosphate TM dissolution into calcium ions and phosphorus precipitation----- | 145 |

List of figures

Figure 7-2: Other phosphorus removal pathways by steel slag and phosphateTM-----148

LIST OF TABLES

| | |
|---|----|
| Table 2-1: Results from previous studies of different media used in constructed wetlands ----- | 11 |
| Table 2-2: Results from different studies showing P retention capacities of different media under varying conditions ----- | 13 |
| Table 2-3: Examples of properties seldom included during media screening performance ----- | 14 |
| Table 2-4: Toxicity or leachability results from previous studies conducted on some media ----- | 15 |
| Table 2-5: Experimental results from previous studies under different conditions showing media P retention capacity and removal mechanisms----- | 18 |
| Table 2-6: Results of competing effect between P and other ions from previous studies----- | 21 |
| Table 3-1: Results from previous studies on media under different experimental conditions----- | 34 |
| Table 3-2: Protocol for P sequential extraction----- | 38 |
| Table 3-3: Batch equilibrium isotherm and elemental composition results----- | 39 |
| Table 3.4: X-ray diffraction results of mineralogy and elemental composition----- | 42 |
| Table 3-5: Breakthrough curves analysis results----- | 44 |
| Table 3-6: Scale up results from rapid small scale columns to full scale----- | 45 |
| Table 3-7: Summary of key results from media screening process----- | 49 |
| Table 4-1: X-Ray diffraction results from steel slag and comparative results from other studies----- | 59 |
| Table 4-2: Ca: P molar ratio from high and low P effluents----- | 69 |

List of tables

| | |
|---|-----|
| Table 4-3: Reactions occurring in solutions during calcium phosphate precipitation | 70 |
| Table 5-1: Results of ochre and steel slag by different researchers | 79 |
| Table 5-2: Protocol for P sequential extraction | 83 |
| Table 5-3: Leachability test results in DI water and controlled pH | 86 |
| Table 5-4: Single solute and multisolute batch equilibrium tests results | 88 |
| Table 5-5: Impact of initial concentration and pH on P retention | 89 |
| Table 5-6: Elemental composition of fresh and exhausted Phosphate TM and steel slag | 97 |
| Table 5-7: X-ray diffraction results showing mineralogy in fresh and exhausted Phosphate TM and steel slag | 99 |
| Table 5-8: Influent and effluent concentrations of ions Phosphate TM and steel slag beds | 99 |
| Table 6-1: Previous studies results on P removal using steel slag | 113 |
| Table 6-2: Protocol for P sequential extraction | 116 |
| Table 6-3: Elemental composition of fresh and exhausted steel slag treating low and high phosphorus wastewater | 127 |
| Table 6-4: X-ray diffraction results of fresh and exhausted steel slag treating low and high phosphorus wastewater | 128 |
| Table 6-5: Influent and effluent levels of other ions at sites | 130 |

ABBREVIATIONS AND NOTATION

μm – micrometre

ACP – Amorphous calcium phosphate

Ag – Silver

Al – Aluminum

Ba – Barium

BOF – Blast Oxygen Furnace

Ca – Calcium

Ca^{2+} - Calcium ion

CaCO_3 – Calcium Carbonate

CaO – Calcium Oxide

Cd – Cadmium

CEC – Cation exchange capacity

Cl – Chlorine

CO_2 – Carbon dioxide

CO_3^{2-} Carbonate ion

COD – Chemical Oxygen Demand

Cu – Copper

DCP – Dicalcium phosphate

DI – Deionised Water

Dissolved reactive phosphorus

Abbreviations and notation

EAF – Electric Arc Furnace

EBCT – Empty bed contact time

EEC – European Economic Committee

EU – European Union

F – Fluoride ion

Fe – Iron

FS – Furnace Slag

HAP – Hydroxyapatite

HCO_3^- - Bicarbonate ion

Hg – Mercury

LUB – Length of unused bed

M – Moles

MCP – Mono calcium phosphate

Mg – Magnesium

Mn – Manganese

NaOH – Sodium hydroxide

NH_4Cl – Ammonium Chloride

$\text{NH}_4\text{H}_2\text{PO}_4$ – Ammonium dihydrogen phosphate

Ni – Nickel

NO_3^- - Nitrate ion

OCP – Octacalcium phosphate

Abbreviations and notation

OH^- - Hydroxide ion

P – Phosphorus

P_2O_5 – Phosphide

Pb – Lead

qe – equilibrium concentration

RSSC – Rapid small scale columns

SEM – Scanning electron microscopy

Si – Silica

SO_4^{2-} Sulphate ion

SRP – Soluble reactive phosphorus

TCP – Tricalcium phosphate

TP – Total phosphorus

VFA – Volatile fatty acids

Zn – Zinc

CHAPTER 1: INTRODUCTION

1 CHAPTER 1: INTRODUCTION

1.1 Background

Phosphorus (P) is an essential element for all living organisms and plays a major role biochemically for cell growth in plants and algae (Zhou et al., 2005). Consequently excessive P disposal into water bodies such as lakes, rivers, reservoirs and estuaries can trigger accelerated growth of organisms such as algal blooms leading to ecosystem deterioration due to eutrophication, (Hussain et al., 2011). Whilst algae do not pose any problems for water treatment at low concentrations, when the population blooms significant difficulty occurs (Henderson et al., 2008). Accordingly, bodies such as the European Union have developed stringent laws to control the level of P into receiving environments. The EU directive 91/271/EEC sets limits of total phosphorus (TP) in effluent wastewater of 1 or 2 mg TP L⁻¹ in sensitive areas depending on the equivalent population of the discharge area. In some regions, these consents are further reduced to 0.5-0.8 mg TP L⁻¹ (Hussain et al., 2011) with some very stringent consent set at 0.03 and 0.07 mg TP L⁻¹ in the USA (Bernard and Steichen, 2006).

Conventional technologies for P removal include chemical precipitation and enhanced biological P removal. Concerns over the cost of energy, sludge produced and high carbon foot print necessitates consideration into alternative treatment processes. For example, energy requirements for extended aeration, sequencing batch reactor and carousel oxidation ditch systems are 2.39, 1.13 and 0.51 kWh m⁻³, respectively (Brix, 1999). In addition, the production of greenhouse gases (carbon dioxide, methane, nitrogen dioxide) from these technologies promotes global warming (Charpentier and Martin, 1996; Foley et al., 2010). Crystallisation process has been reported to be a success in removing P from wastewater, with successful pilot studies conducted (Joko, 1984) with effluent concentration ranging between 0.3 and 1.0 mg P L⁻¹. The disadvantage of this method is its complexity and the increase in salinity of the effluent (Joko, 1984), for the success of the method is influenced by lime dosing resulting in chemical costs and elevated pH which need lowering before effluent is discharged.

Various other approaches have been trialled including reverse osmosis, contact filtration and electrodialysis (Xiong et al., 2008), and magnetic devices (Gong and Zhao, 2014) but the economics associated with these methods have made them unattractive through the requirements of additional chemicals, post correction of pH or a high energy demand.

Passive technologies such as constructed wetlands and filtration systems have emerged as alternative technologies in areas where conventional systems are uneconomic to construct, onsite treatment is required or where small sewage works are required. In addition, a wetland system requires less or no energy with typical energy demands of $< 0.1 \text{ kWh m}^{-3}$ (Brix, 1999). A number of potential media have been suggested (Drizo et al., 1999; Zhu et al., 2003), but the differences in performance evaluation approaches between the studies have made comparison difficult. Practical issues such as mechanical strength and reusability have not been substantially investigated and, as such, no clear guidance exists on how to design passive treatment systems with reactive media.

1.2 Aims and objectives

The aim of the research was to understand the potential for enhancing phosphorus removal in passive tertiary treatment technologies using reactive media. To achieve this aim, a series of specific objectives have been addressed:

- 1) To screen available media to establish the key properties for enhanced P removal.
- 2) To investigate the influence of background wastewater characteristics on steel slag dissolution into calcium ions.
- 3) To further evaluate the two media chosen from the initial screening process for P removal from tertiary effluent.
- 4) To understand the design limits for phosphorus removal and practical implications of the use of reactive media.

1.3 Thesis plan

The thesis chapters are presented in the form of a series of papers, each linked to the research objectives and formatted as journal papers for publications. All papers were written by the first author, Moatlhodi Wise Letshwenyo and edited by Professor Bruce Jefferson. Experimental works were conducted at Cranfield University by Moatlhodi Wise Letshwenyo.

Chapter 2, *Phosphorus removal in reed beds with reactive media*, focuses on the role played by reactive media during P retention in passive systems. This chapter is aimed at reviewing the available literature on media performance to establish appropriate media characteristics and identify knowledge gaps.

Chapter 3, *Media screening for determination of key properties influencing performance for phosphorus removal from wastewater*, investigates the parameters concerning selection of media from the available list through laboratory batch and rapid small scale column tests. A total of six media were screened, from which two were selected for further testing.

Chapter 4, *Dissolution of calcium from steel slag in phosphate mitigation; influence of background wastewater characteristics* looks into the dissolution of steel slag in different water backgrounds. Experiments were conducted to study the release of Ca^{2+} ions under different alkalinity concentrations. This was followed by studying dissolution in real wastewater effluents with high and low P concentrations. Lastly, the regeneration potential of steel slag using laboratory rapid small scale columns was conducted.

Chapter 5, *Evaluation of steel slag and PhosphateTM as reactive media for phosphorus removal from tertiary effluents*, evaluates the performance of steel slag and phosphateTM for P removal from tertiary effluent. The performance of the two media was evaluated firstly through laboratory experiments to investigate the influence of media pH, acidity and basicity and pH controlled leachability tests. Evaluation was also based on the competitive effect between P, carbonates and sulphates, and the influence of P concentration and pH on media performance. This was complimented by

pilot scale trials using tertiary effluent where P retention, leachability and retention of other ions was monitored. Tracer studies and sequential P extraction were conducted as well.

Chapter 6, *Performance evaluation of steel slag for phosphorus removal from high and low strength phosphorus tertiary effluents*, compares the performance of steel slag for P removal from tertiary effluents with low and high concentrations of phosphorus across a range of empty bed contact times to establish the key design criteria. The work was complemented by tracer studies at 12 and 48 hours of empty bed contact time. This was followed by a sequential extraction experiment for the media sampled from those two beds to evaluate the removal mechanisms involved.

Chapter 7, *Discussion*, looks into the key findings of this work to address commonly encountered questions concerning the use of reactive media in constructed wetlands.

Chapter 8, *Conclusions*, concludes the findings of the study.

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CHAPTER 2: PHOSPHORUS REMOVAL IN REED BEDS WITH REACTIVE MEDIA

2 PHOSPHORUS REMOVAL IN REEDS BEDS WITH REACTIVE MEDIA

2.1 Introduction

Phosphorus (P) is one of the main nutrients for all living species and plays a role in biochemical functional groups for the growth of cells in plants including algae (Zhou et al., 2005). In many freshwater environments, P is the limiting nutrient with limits required to remain below 0.1 mg TP L^{-1} to inhibit excessive growth of algae (Hussain et al., 2011). Consequently, disposal of phosphorus rich effluents into surface water such as lakes, rivers, reservoirs and estuaries promotes algal blooms (eutrophication) (Hussain et al., 2011). Eutrophication results in oxygen deficiency in surface waters leading to detrimental effects on aquatic life and water quality (Chi et al., 2010). At low concentrations, algae do not pose any problems for water treatment; however blooms resulting from phosphorus enrichment can affect water treatment (Henderson et al., 2008). Accordingly, stringent laws have been developed by bodies such as the European Union to control the level of P concentrations into receiving environments. The EU directive 91/271/EEC sets limits of total phosphorus (TP) in effluent wastewater of 1 or 2 mg P L^{-1} on an annual average basis in sensitive areas depending on the equivalent population of the discharge area. In some regions, these consents are as low as 0.5-0.8 mg TP L^{-1} (Hussain et al., 2011), with current discussion leading to a proposed level of as low as 0.1 mg L^{-1} in the next five years. In the USA, some control measures are even more stringent with effluent TP concentrations of between 0.03 and $0.07 \text{ mg TP L}^{-1}$ (Bernard and Steichen, 2006).

Conventional technologies for P removal, such as enhanced biological phosphorus removal, membrane filtration, chemical precipitation and reverse osmosis, have been used. These technologies are associated with operational and maintenance costs, and large volumes of sludge production which makes treatment, handling and disposal costly. In response new cost effective, sustainable and environmental friendly technologies are needed for phosphorus removal. Consequently, adaptations of passive systems such as constructed wetlands are emerging as the technology requires low

financial investment and operational costs, and exerts a low energy demand (Yousefi and Bandpei, 2010). For instance, the energy requirements for both vertical and horizontal flow systems are $< 0.1 \text{ kWh m}^{-3}$ (Brix, 1999).

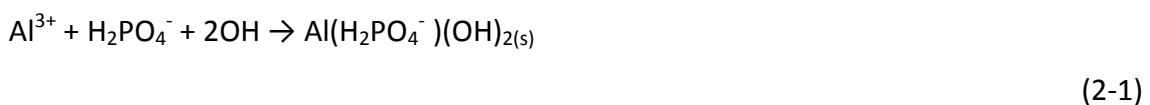
The major concern for using this technology is the unavailability of phosphorus retention media. An evaluation of P retention capacities for various media (artificial, engineered and industrial by-products) has been conducted through laboratory batch and column experiments (Drizo et al., 1999; Zhu et al., 2003; Brix and Arias, 2005). This review focuses on media for P removal from tertiary effluents using passive systems as alternative technologies for the future. The review investigates the key properties that are considered during media selection and the parameters that influence media performance.

2.2 Conventional technologies for P removal from wastewater

Conventional technologies widely used for P removal from wastewater are chemical precipitation and enhanced biological phosphorus removal (Morse et al., 1998). Enhanced biological phosphorus removal is achieved through adapting environmental conditions to favour bacteria that store high amounts of P as poly-phosphates (Rittmann et al., 2011). Chemical precipitation involves the use of metal salts to precipitate P into insoluble compounds and separated as sludge.

2.2.1 Chemical precipitation

Chemical precipitation through the use of coagulants is widely used for P removal (De-Bashan and Bashan, 2004) and includes use of ferric or ferrous chloride, aluminium hydroxide, alum and lime (CaO) (De-Bashan and Bashan, 2004). The addition of a precipitating chemical means that more sludge is produced than in biological nutrient removal. An illustration of the precipitation reaction to form aluminum phosphate hydrate ($\text{Al}(\text{H}_2\text{PO}_4^-)(\text{OH})_{2(s)}$) is as follows (Nir et al., 2009);



Chemical dosing is commonly based on a fixed rate or is flow proportional with limited examples of P load proportional dosing. The use of coagulants requires chemical storage and sludge treatment leading to increased costs which are strongly linked to the supply price of the different chemicals available. The sludge has a high P content which can be used as a fertiliser; however the strong bonding between the metal salt and phosphorus has resulted in inconclusive evidence of its efficiency as a fertiliser (Morse et al., 1998).

2.2.2 Biological P removal

Biological P removal is achieved in activated sludge by inclusion of sequential anaerobic and aerobic zones leading to the development of luxury uptakes of phosphorus. The process requires volatile fatty acids (VFA) to proceed which are generated in the anaerobic zone. A COD: P > 40:1 ratio is often quoted to be required and as such the process only works with high strength wastewater sources (Mulkerrins et al., 2004). Additional carbon can be supplemented through pre fermenter zones to ensure sufficient VFA is formed. The VFA production stage is temperature sensitive such that back up chemical precipitation is common to ensure sufficient treatment.

2.3 P removal through reed beds and reactive media

Implementation of P removal at small sewage works (typically less than 2000 P.E.) is limited to chemical precipitation. However, the use of chemicals and the associated increased frequency of sludge collection make the option undesirable. Consequently, alternatives that do not require chemicals and regular maintenance are required. In many cases, such works are suitable for inclusion of constructed wetlands which represent a passive technology for enhanced solid removal and some associated biological degradation. The technology is most commonly configured as a horizontal flow gravel bed (Brix et al., 2001). Phosphorus removal occurs through uptake onto the media, biofilm and plants although removal is known to be limited and insufficient to meet a 1 - 2 mg TP L⁻¹ standard (Brix, 1999). In such cases, chemical dosing is included where the gravel bed accumulates the precipitated solids. Enhancement of the technology has been proposed through the use of reactive media to provide additional uptake through adsorption or precipitation. Traditionally, sands or naturally available

materials such as gravel and limestone were used to enhance adsorption, however short operating periods have limited their efficacy (Brix et al., 2001). Different types of media have been investigated including natural materials (sands, gravel, and clay), industrial or waste byproducts (fly ash, steel slag, blast furnace slag, and ochre) and engineered materials (polymeric adsorbents, ion exchange resins).

Comparison of the available data indicates that manmade and industrial by-products outperform natural media (Table 2.1). For example, gravel and blast furnace granulated slag both treating the same wastewater had efficiencies of 9.0 and 64.0%, respectively (Korkusuz et al., 2004). The media size plays a role as slag particles ranged between 0 - 3.0 mm compared to 7-30 mm for gravel. However the composition of the different media was the dominant impact as the steel slag contains high concentrations of Ca, Al and Fe enabling different pathways for removal compared to the gravel.

Table 2.1: Results from previous studies of different media used in constructed wetlands

| Natural materials | | | | |
|--------------------------------|--------------------------|------------------------------------|--|--------------------------------|
| Media and size (mm) | Plants | % removal or media capacity | Comments | Reference |
| Limestone (2-14) | Phragmites | 17.1 | Only Arundo plants were able to assimilate P in their mass. The presence of phragmites had no effect on P removal | Hamouri et al.,(2006) |
| | Arundo | 33 | | |
| | Unplanted | 17 | | |
| Gravel (> 2) and sand (0.05-2) | Phragmites | 0.3 g kg ⁻¹ media | Injection of Ca, Al and Fe did not improve the P sink in the wetlands (was only effective in the first few months) | Karczmarczyk and Renman,(2011) |
| Gravel (7- 30) | Phragmites | 9 | Effluent P concentration fluctuated and was greater than influent concentrations | Korkusuz et al., (2004) |
| Gravel (8- 12) | Phragmites | 45 | Removal efficiency of coarser media was lower than that of finer media | Mantovi et al.,(2003) |
| Gravel (3 – 6) | Phragmites | 60.6 | | |
| Fine gravel (5.0) | Pseudacorus | 67.5, 71.6, 74.9 | Effect of plants was 4.5-11.9% | Yousefi and Bandpei, (2010) |
| Fine gravel (5.0) | unplanted | 63 | | |
| Coarse gravel (27) | Pseudacorus | 46.9, 49.1, 52.3 | Effect of plants was 2.9-8.3% | |
| Coarse gravel (27) | unplanted | 44 | | |
| Sand clay loam | Cattails and reed canary | 40.5±5.8 | There was no difference in P removal between the two types of media. Media sizes not mentioned. | Yates and Prasher,(2009) |
| Sand soil | Cattails and | 41.9±2.4 | | |

| reed canary | | | | |
|--|------------|---------------------------|---|------------------------|
| Industrial by products | | | | |
| Oil shale ash (sedimentation filter) | | 52 | No correlation observed between P loading and P removal efficiency | Vohla et al., (2011) |
| Oyster shell (2.0) | unplanted | 87.76 – 96.8 as SRP or TP | P removal decreased as hydraulic loading rate increased | Wang et al., (2013) |
| Blast furnace granulated slag (0-3), gravel at the bottom (7-30) | Phragmites | 64 | Effluent TP was always comparable to 2.0 mg TP L ⁻¹ , Turkish standard. | Korkusuz et al.,(2004) |
| BOF slag (20) | unplanted | 35- 62 | P removal decreased with increasing initial P concentration | Bowden et al.,(2009) |
| Man-made products | | | | |
| Filtralite-p TM (0-4.0) | | 52 mg P kg ⁻¹ | CaCO ₃ , Ca-P, Mg-P precipitates were visible and identified on the media. | Adam et al.,(2006) |
| Light weight aggregate(0-2, 0-4, 2-4) | | >95 | | Vohla et al.,(2011) |

SRP = soluble reactive phosphorus, TP = total phosphorus

2.3.1 Key properties influencing choice of media

The efficacy of different media is normally determined through laboratory experiments. The elemental composition, mineralogy and media size have been identified as key parameters that influence media capacity (Drizo et al., 1999). Specifically, the presence of metals such as aluminum, calcium and iron has been used as a selection tool (Arias et al., 2001; Drizo et al., 2002; Wei et al., 2008; Cucarella and Renman, 2008). Calcium is considered a more important component than iron or aluminum as under the pH conditions normally encountered adsorption/complexation is thought to be limited (Brix et al., 2001) such that precipitation of calcium phosphates is considered the main pathway (Chazarenc et al., 2007). The presence of carbonates is also considered, as it provides a competing pathway for the available calcium and therefore reduces the phosphate uptake (Johansson and Gustafsson, 2000). The efficacy of the different media is normally determined through batch or small scale column uptake experiments. The reported uptake is consequently influenced by media size and the initial P concentration used during the test (Table 2.2). The conditions used are commonly different from those experienced in field conditions and therefore

translation of the reported capacities is required. For instance, phosphorus concentrations in tertiary effluents hardly exceed 10 mg TP L^{-1} and sometimes are very dilute, yet laboratory experiments are conducted with P levels exceeding 100 mg L^{-1} . Media sizes of less than 1.0 mm have been tested, yet it is accepted that media of less than 5 mm will lead to excessive clogging in field systems (Chazarenc et al., 2007). This has been supported by Westholm (2010), who suggests using media sizes of between 4-7 mm, highlighting that specific surface areas of such media will be reduced, hence has less retention capacity compared to common laboratory tests. This is reflected in guidance where recommended European guidelines suggest 5-10 mm with specific countries such as Austria and Czech Republic opting for 4-8 mm (Yousefi and Bandpei, 2010).

Table 2.2: Results from different studies showing phosphorus retention capacities of different media under varying conditions

| Media | Type of solution and concentration (mg P L^{-1}) | Media size (mm) and elemental composition | Mode of test | Capacity | Reference |
|-------------------|---|---|------------------|----------------|-------------------------------|
| EAF slag | Synthetic (5,10,25,100) | 5-10 > 10 | Batch | 0.09 to 0.28 | Barca et al., (2012) |
| | Spiked real wastewater (5,10,25, 100) | 5-10, > 10, Ca, Al, Fe, Si, Mn, Mg | Batch | 0.12 to 0.63 | Barca et al., (2012) |
| BOF slag | Synthetic (5,10,25,100) | (5-10), > 10 | Batch | 0.03 to 2.49 | Barca et al., (2012) |
| | Spiked real wastewater (5,10,25, 100) | (5-10, >10), Ca, Al, Fe, Si, Mn, Mg | Batch | 0.14 to 2.5 | Barca et al., (2012) |
| FS slag | Synthetic (11-107) | (5-10) Al, Ca, Fe, Mg, Si, Mn | Column | 8.3 | Claveau-Mallet et al., (2013) |
| Slag microspheres | Synthetic (75-1000) | (0.6-1.18) Al, Ca, Fe, Mg, Si, Mn | Batch and column | 10.95 and 2.27 | Lee et al., (2012) |
| EAF slag | Synthetic (1-320 l) | (2.5-10) Ca, Fe, | Batch tests | 0.31-3.93 | Drizo et |

| | | | | | |
|-------------------------|---------------------------|-------------------------------------|------------------------|--|---------------------------|
| Steel slag | Real effluent | Mg, Si, Al, Mn | and column | and 1.35 | al.,(2002) |
| | | | Field trials | 1.23 g P kg ⁻¹ | Pratt and Shilton, (2010) |
| Basic oxygen steel slag | Synthetic (1-300) | >300 μm , >5 Ca, Al, Fe, Mn, Mg, Si | Batch and column | 8.39 g P kg ⁻¹ | Bowden et al., (2009) |
| BOF slag | (10-500) | (0.6) Ca, Al, Fe, Si, Mg | Batch | 0.99-43.1, 0.98-41.6, 0.82-37.6 mg P g ⁻¹ | Xue et al., (2009) |
| Blast furnace slag | Synthetic (180) | (0.03-0.02) Si, Fe, Al, Ca, Mg, | Batch | 6.37nmg P g ⁻¹ | Oguz, (2004) |
| Shell sand | Synthetic (5-1500) | (< 1.0) Ca, Fe, Al, Mg | Batch | 8000 mg P kg ⁻¹ | Sovik and Klove, (2005) |
| Ochre | Real wastewater | 6.4-9.5 | Horizontal flow trough | 5.2±1.6 and 0.77±0.09 g TP kg ⁻¹ | Dobbie et al., (2009) |
| Ochre pellets | Synthetic solution (11.2) | (1.18) A, Ca, Fe | Column diameter 100 mm | P < 1.0 mg P L ⁻¹ | Littler et al., (2013) |
| | Synthetic (28-560) | 0.045-0.063, 0.063-0.125, 1-2, 2-4 | Batch | 5.81 mg P g ⁻¹ | Littler et al., (2013) |

2.3.2 Properties seldom used for screening

Selected media for P retention should be selective in removing phosphorus and have a larger capacity, be easily handled and have high physical and mechanical strengths, and in addition be nonhazardous (White et al., 2011), (Table 2.3)

Table 2.3: Examples of properties seldom included during media screening for performance

| Property | Influence to performance | Reference |
|--------------|--|--|
| Strength | Failure due to static force in the bed. Clogging problem | White et al., (2011) |
| CEC | Link to retention capacity, some say no link with capacity | Lee et al., (1997); Drizo et al., (1999) |
| Leachability | Leachability limits the usability value of the media | Wei et al.,(2008) |

| | | |
|--------------|---|----------------------|
| Media pH | High pH correlates with CaP precipitation and 4-7.5 adsorption process | Bowden et al.,(2009) |
| Regeneration | Performance enhanced, replacement and disposal costs saved, P recovery. | Pratt et al., (2011) |

In addition, media that can be regenerated to save replacement costs and also recover P for use as fertilizer are recommended. However, the better retention media often do not release the retained P in most cases, making regeneration and recovery difficult.

Some of the studies have included leachability tests of the targeted media to find their suitability for use (Table 2.4). During such studies, either batch or column studies are employed during the investigations. To illustrate, trials with ochre revealed no issues during column experiments, whereas batch results revealed that some of the mandatory metal compliance levels were exceeded (Dobbie et al., 2009; Fenton et al., 2009).

The material's pH can have both a positive and negative impact on media performance. Materials such as steel slags have been reported to elevate effluent pH because of OH⁻ release. For example, steel slag reported increasing pH from an influent value of 7.1 to effluent value of 10.3 (Chazarenc et al., 2007). Elevated effluent pH is reported as an indication that the P retention capacity of the material has not been exhausted (Chazarenc et al., 2007). The effluent pH should then be lowered before being discharged into the receiving environment. Minerals such as CaCO₃ and Ca (OH)₂ contribute to pH elevation during dissolution at the same time as the release of Ca²⁺ ions. Blast furnace granulated slag and steel slag have been observed to have pH values of 8.4 and 10.2-10.6, respectively (Korkusuz et al., 2007). EAF slag pH was reported to be 10.9 by Penn and McGrath (2011).

Table 2.4: Toxicity or leachability results from previous studies

| Media | Metals | Test | Remarks | Reference |
|----------|--|--------|--|-------------------------|
| F S Slag | Fe, Mn, Zn, Cu, Cd, Pb, Ni, Ag, Ca, Al | Column | 1) Potential of leachability if influent is acidic. 2) Tests conducted using distilled water indicated low leachability except for Ca and Al which were 116 and 16.6 mg L ⁻¹ respectively. | Claveau-Mallet .,(2013) |

| | | | | |
|-----------------------------|---|----------------------|---|-------------------------------|
| B Slag | Fe, Mn, Zn, Cu, Cd, Pb, Ni, Ag, Ca, Al | Column | <p>3) When neutralising capacity of the materials extinguishes pH will not rise hence possibility of leaching</p> <p>1) Potential of leachability if influent is acidic</p> <p>2) Tests conducted using distilled water indicated low leachability except for Ca and Al which were 159 and 66.9 mg L⁻¹ respectively.</p> <p>3) When neutralising capacity of the materials extinguishes pH will not rise hence possibility of leaching</p> | Claveau-Mallet et al., (2013) |
| Red mud granular adsorbents | Ag, As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Zn | Column | 1) All concentrations were lower than thresholds set in China | Yue et al., (2010) |
| Ochre | Al, Cd, Cr, Cu, Fe, Ni, Pb, Zn | Flow through troughs | 1) Values less than 0.25 mg L ⁻¹ , which is Environmental Quality Standard for protecting less sensitive life in the aquatic environment | Dobbie et al., (2009) |
| Ochre | Fe, Cu, Mg, Zn, Na, Mn, K, Cl | Batch | 2) Fe, Cu, Mg, Zn were found to be above the mandatory limit | Fenton et al., (2009) |
| EAF Slag | Ca, Fe, Zn, Cu | Pans | 1) High metal concentrations were observed 15 to 30 minutes after beginning the experiments, and remained high thereafter. | Bird and Drizo, (2009) |

Foot note: Fe = Iron, Mn = Manganese, Zn = zinc, Cu = copper, Cd= cadmium, Pb = lead, Ni = nickel, Ag = silver, Ca = calcium, Al = aluminum, Hg = mercury

2.3.3 Phosphorus removal mechanisms

The dominant removal mechanism has been indicated to be controlled by pH (Chazarenc et al., 2007). High pH is associated with CaP precipitation, whereas low pH favours association to Fe and Al. However, there are a number of complex pathways due to competition and transformation of the precipitate from amorphous calcium phosphate to hydroxyapatite leading to conflicting reports and indications of the key requirements. Different P removal mechanisms have been reported for the same media. For instance, CaP precipitation and adsorption onto Fe/oxide/hydroxides have been reported for slag (Table 2.5). This is most apparent in cases where the influent P is relatively low as expected in sewage effluents. For instance, CaP precipitation was

reported to be efficient when the P concentration exceeded 0.5 mg L^{-1} , below which adsorption became the key removal pathway (Koiv et al., 2010). To maximise, both mixed media systems have been tested with trials containing steel slag, anthracite and vermiculite (Wu et al., 2011). Trials were reported for a system treating a feed P of 0.9 to 1.5 mg L^{-1} leading to $82.45 \pm 9.52\%$ removal when all the three media were used and 90.26 ± 4.48 and $77.17 \pm 23.34\%$ removal, respectively when just steel slag and anthracite were used.

Table 2.5: Results from previous studies under different conditions showing media P capacity and removal mechanisms

| Media | Composition | Experiment | Capacity (mg g ⁻¹ media) | P retention mechanism | Remarks/Observations | Reference |
|--|---|---|--|---|--|---------------------------|
| Apatite (Four apatite materials sourced from different areas.) | Al, Ca, Mg, Fe, P, Si differed for each area | Batch and column, using synthetic and field trial using effluent from constructed wetlands. | Batch (1.09, 0.41) 0.37, 0.31, 0.28 apatite), 50% retention by lab column, field columns reduced P from 10 to 2 mg L ⁻¹ | Crystallization | Columns used had smaller diameter compared to media diameter. Media diameter was 2.5-10 mm, hence minimum column diameter should be 200 mm (Column diameter at least 20 times media diameter), diameter used was 100 mm. | Bellier et al., (2006) |
| Steel slag filters | Iron-titanium oxides, Calcium-magnesium silicates | Full scale | 1.23 g P kg ⁻¹ media | Adsorption onto Fe amorphous Fe oxyhydroxides | Exhausted media had more Fe on surface than fresh media | Pratt and Shilton, (2010) |
| Limestone (6 different types) | Limestone selected for further evaluation had 75% CaCO ₃ . | Lab batch, column and field trials | Lab columns removed 64% of P. During field trials performance decreased to 18% removal | Precipitation | Lab experiments using synthetic solutions cannot effectively represent full scale systems. | Shilton et al., (2005) |

| | | | | | | |
|-------------|------------------------|-------------|--|--|--|----------------------|
| Melter slag | Al, Fe, Mg, Ti | SEM/EDS/XRD | N/A | <ol style="list-style-type: none"> 1) Adsorption onto Fe oxides/oxyhydroxides 2) Precipitation, some stable Fe/P/O precipitates are formed on the surface coating slag and to a lesser extent Ca/P/O precipitates. 3) Organic sequestration on the slag coating | <p>During P sequestration using 1 M HCl to target Ca-P, it was found that much higher P was extracted though slag was found to contain Ca carbonates and Ca phosphates. It was concluded that 1M HCl is none selective in removing Ca-P, overestimates Ca-P hence unreliable.</p> | Pratt et al., (2007) |
| EAF Slag | Fe, Ca, Mg, Si, Al, Ti | | <p>Batch (0.31-3.93) Column (1.35)</p> | <ol style="list-style-type: none"> 1) Fe-P had the largest P extracted (46.5%), Ca-p 913.6%), 26.5% as Ca-P in stable residual pool. | <p>Slag used was 2.5-10 mm in 103 mm inside diameter column. The rule of minimum column diameter to be at least 20x media diameter not observed, but that of 10 times media diameter. Shorter retention times are said not to favour HAP. HRT was 8.7 hours and HAP is favoured when HRT</p> | Drizo et al., (2002) |

Literature review

Chapter 2

| | | | | | | |
|--------------------------------------|---|--------------------------------|--|-----------------------|---|-----------------------------|
| Seed crystals (phosphate rock) | P ₂ O ₅ , CaO, F | Batch and Columns | 92-97% removal by columns | 1) Crystallization | > 12 hours. Efficiency affected by pH, Ca concentration than alkalinity. Batch results revealed efficiency decrease as alkalinity increased | Joko, (1984) |
| EAF Slag | Fe ₂ O ₃ , CaO, Al ₂ O ₃ , CO ₂ , | Bench scale and Pilot scale | 0.3 g P kg ⁻¹ media in bench scale and 2 g P kg ⁻¹ media in pilot scale | 1) Ca-P precipitation | Significant Fe released, CaO, P ₂ O ₅ , CO ₂ , leading to HAP or Ca-P formation. High effluent pH indicates P retention limit not reached | Chazarenc et al., (2007) |

2.3.4 Competition for P removal with other ions

Potential contaminants in wastewater that have been investigated as competitors for phosphorus include bicarbonates, sulphates, chlorides, nitrates and fluorides (Yin et al., 2011), as well as some unknown parameters in wastewater (Table 2.6). The most commonly reported influence is alkalinity as it provides competition for the release of calcium ions leading to the formation of calcium carbonate. Consequently, Barca et al., (2012) conducted experiments on the release of Ca^{2+} ions using DI water and real wastewater. The equilibrium capacities for the release of Ca^{2+} ions for steel slag ranged between 0.7 and 1.2 mg Ca g^{-1} media, whereas that of BOF slag ranged between 3.2 and 9.6 mg Ca g^{-1} media. Joko (1984) investigated the impact of alkalinity on the use of Ca^{2+} ions for P removal through calcium phosphate crystallisation in batch and column trials. Phosphorus removal was shown to decrease as alkalinity increased in the batch system. For instance, residual P increased from 0.2 mg L^{-1} to 1.25 mg L^{-1} as the alkalinity was increased from 15 to 550 mg L^{-1} at a constant contact time of 10 hours. Similarly, Kim et al., (2006) reported a decrease in P removal with increasing alkalinity using converter slag in a batch system. Residual P in the system increased from 1.0 to 2.1 mg P L^{-1} as alkalinity was increased from 50 to 500 mg L^{-1} , respectively after 10 hours.

Table 2.6: Competing effect between phosphorus and other ions from previous studies

| Media | Competitors | Mode of test | Remarks | Reference |
|--|---|----------------|--|----------------------|
| Calcium rich sepiolite (NOCS ₂) | SO_4^{2-} , NO_3^- , Cl^- , HCO_3^- , F | Batch isotherm | SO_4^{2-} , NO_3^- , Cl^- did not have effect but HCO_3^- , F reduced the media capacity significantly | Yin et al., (2011) |
| Calcareous materials (calcite and recycled crushed concrete) | HCO_3^- | Batch isotherm | Negative effect of HCO_3^- on P retention | Molle et al., (2003) |
| Slag microspheres | SO_4^{2-} , NO_3^- , Cl^- , HCO_3^- | Batch isotherm | SO_4^{2-} , NO_3^- , Cl^- had less influence. HCO_3^- , A 20mM bicarbonate reduced capacity by 21% and | Lee et al., (2012) |

| | | | | |
|----------|--------------------|----------------|---|-------------------------|
| Goethite | SO_4^{2-} | Batch isotherm | 100mM by 87% Phosphates were preferred to sulphates except at pH below 4 | Geelhoed et al., (1997) |
|----------|--------------------|----------------|---|-------------------------|

2.4 Identified gaps from review

- Comparison of the different media is difficult as no standardised test conditions were used leading to differences in media size, P concentration and background water chemistry between studies (Cucarella and Renman, 2009). Consequently, a direct comparative assessment is required to properly understand the relative merits of each media. In addition, there is a paucity of information existing in relation to mechanical strength, regeneration and leachability which is critical to understanding the potential to use reactive media in practice.
- Though alkalinity has been reported to influence the performance of some media e.g. co-precipitation with P, there are no studies on the dissolution of media into Ca^{2+} ions under different alkalinities. This is despite the fact that some media have natural alkalinity which might inhibit the release of calcium ions.
- There are reports which have suggested that low P in the feed might result in the already retained P being flushed out of the bed (Pant and Reddy, 2003; Bowden et al., 2009). Despite such suggestions, there are only a few reports available on studies conducted let alone studies comparing the performance of media treating low and high P concentrated effluents.
- There is a paucity of information related to the influence of contact time

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**CHAPTER 3: MEDIA SCREENING FOR DETERMINATION OF KEY
PROPERTIES INFLUENCING PERFORMANCE FOR PHOSPHORUS REMOVAL
FROM TERTIARY EFFLUENTS**

3 Chapter 3: MEDIA SCREENING FOR DETERMINATION OF KEY PROPERTIES INFLUENCING PERFORMANCE FOR PHOSPHORUS REMOVAL FROM TERTIARY EFFLUENTS

3.1 Introduction

Wastewater discharges into surface waters is one of the major concerns of excess phosphorus (P) loading which leads to eutrophication (Drizo et al., 2008). Organisations such as the European Union have made legislations for controlling P discharges, such that discharges from sites with a population equivalent to between 10 000 and 100000 should be less than 2 mg TP L⁻¹ and a limit of less than 1 mg TP L⁻¹ for those with more than 100000 P.E. at an average annual basis. In the next 5- 10 years, the need to treat discharges from small works is expected, along with a reduction in the discharge limits. The future discharges are linked to maintaining the ecological status of the receiving body prior to the discharge, such that limits below 1.0 mg L⁻¹ are likely, with some as low as 0.1 mg TP L⁻¹ (Hussain et al., 2011).

Phosphorus removal at small works is restricted to chemical precipitation with tertiary solids removal incorporated to retain the precipitated solids and limit the release of residual metals. In many cases, the tertiary process is based on the subsurface horizontal flow of constructed wetlands. Consequently, increasing interest is being reported in relation to replacing the standard gravel media with more reactive materials to enhance P retention. A range of materials including natural (limestone, clay, sand, apatite, dolomite), waste (water treatment residue, ochre,) and engineered (steel slag, fly ash, blast furnace slag) media have been tested (Vohla et al., 2011). In all cases the media contain high levels of calcium, iron or aluminum to drive the increased removal. However, many of the studies use small media sizes and high P concentration in batch tests which provide an unrealistic impression of efficacy compared to field use (Table 3.1). Typical field conditions include 5-10 mm diameter media treating P concentrations between 2-10 mg TP L⁻¹ suggesting a significant reduction compared to batch tests using media sizes of as low as 300 µm and P concentrations of up to 300 mg L⁻¹ (Table 3.1). Furthermore, only a few directly compared control trials have been conducted, limiting our understanding of the relative benefits of each media. This

extends beyond P uptake and includes practical issues such as mechanical strength, which has been known to limit usability of some media (White et al., 2011).

The effect of the initial P concentration on P removal using basic oxygen steel slag was investigated for P concentrations of between 0-1000 P mg L⁻¹ and a positive correlation was reported between P removal and the initial concentration (Bowden et al., 2009). In the case of media size, it was reported that P removal decreased with increasing media size for materials with particle diameters ranging from < 63 µm to 6.0 mm (Bowden et al., 2009). Similar experiments were conducted by Zhu et al., (2003) using light weight aggregate, who found that fine materials of size 0- 2.0 mm had a larger retention capacity than courser materials (0 – 4.0 and 2.0 – 4.0 mm).

The objective of the current study was to screen six media in terms of P removal, mechanical strength and reusability. The properties evaluated were elemental and mineralogy, P retention capacity, cation exchange capacity (CEC), determination of length of unused bed (LUB) of different media, regeneration potential and mechanical strength and density. Screening was conducted through different experimental set ups such as scanning electron microscope, X-ray diffraction, laboratory batch and column studies and other laboratory based experiments.

Table 3.1: Results from previous studies on media under different experimental conditions

| Media | Type of solution and concentration (mg P L ⁻¹) | Media size (mm) and elemental composition | Mode of test | Capacity (mg g ⁻¹ media) | Reference |
|----------|--|---|--------------|-------------------------------------|-----------------------|
| EAF slag | Synthetic (5,10,25,100) | 5-10 > 10 | Batch | 0.09 to 0.28 | Barca eat al., (2012) |
| | Spiked real wastewater (5,10,25, 100) | 5-10, > 10, Ca, Al, Fe, Si, Mn, Mg | Batch | 0.12 to 0.63 | Barca eat al., (2012) |
| BOF slag | Synthetic (5,10,25,100) | (5-10), > 10 | Batch | 0.03 to 2.49 | Barca eat al., (2012) |
| | Spiked real | (5-10, >10), Ca, | Batch | 0.14 to 2.5 | Barca eat al., |

| | | | | | | |
|-------------------------|---------------------------|-------------------------------------|------------------------|--|--|-------------------------------|
| | wastewater(5,10,25, 100) | Al, Fe, Si, Mn, Mg | | | | (2012) |
| FS slag | Synthetic (11-107) | (5-10) Al, Ca, Fe, Mg, Si, Mn | Column | 8.3 | | Claveau-Mallet et al., (2013) |
| Slag microspheres | Synthetic (75-1000) | (0.6-1.18) Al, Ca, Fe, Mg, Si, Mn | Batch and column | 10.95 and 2.27 | | Lee et al., (2012) |
| EAF slag | Synthetic 1-320 l) | (2.5-10) Ca, Fe, Mg, Si, Al, Mn | Batch tests and column | 0.31-3.93 and 1.35 | | Drizo et al.,(2002) |
| Steel slag | Real effluent | | Field trials | 1.23 g P kg ⁻¹ | | Pratt and Shilton, (2010) |
| Basic oxygen steel slag | Synthetic (1-300) | >300 μm , >5 Ca, Al, Fe, Mn, Mg, Si | Batch and column | 8.39 g P kg ⁻¹ | | Bowden et al., (2009) |
| BOF slag | (10-500) | (0.6) Ca, Al, Fe, Si, Mg | Batch | 0.99-43.1, 0.98-41.6, 0.82-37.6 mg P g ⁻¹ | | Xue et al., (2009) |
| Blast furnace slag | Synthetic (180) | (0.03-0.02) Si, Fe, Al, Ca, Mg, | Batch | 6.37 mg P g ⁻¹ | | Oguz, (2004) |
| Shell sand | Synthetic (5-1500) | (< 1.0) Ca, Fe, Al, Mg | Batch | 8000 mg P kg ⁻¹ | | Sovik and Klove, (2005) |
| Ochre | Real wastewater | 6.4-9.5 | Horizontal flow trough | 5.2±1.6 and 0.77±0.09 g TP kg ⁻¹ | | Dobbie et al., (2009) |
| Ochre pellets | Synthetic solution (11.2) | (1.18) A, Ca, Fe | Column diameter 100 mm | P < 1.0 mg P L ⁻¹ | | Littler et al., (2013) |
| | Synthetic (28-560) | 0.045-0.063, 0.063-0.125, 1-2, 2-4 | Batch | 5.81 mg P g ⁻¹ | | Littler et al., (2013) |

3.2 Materials and methods

The six materials investigated were gravel, limestone, PhosphateTM, bauxsol, blast furnace slag and EAF steel slag. All the media were supplied by Wessex Water with the exception of PhosphateTM which was supplied by Severn Trent Water. Small batches of gravel, limestone and the two slags were ground to 0.5 – 1.0 mm and sieved using BS 410 sieves. The media were then washed in DI water and dried before use.

During mechanical strength testing, a media size of 5.0 mm was chosen since it has been recommended as the minimum size to be used in constructed wetlands to minimise clogging (Chazarenc et al., 2007). As such, the force at failure would give an indication of the minimum force at failure likely to be experienced in the bed.

A media size of 0.5 – 1.0 mm was used during the normalised size experiments to reflect the choices of small rapid trials whilst maintaining requirements associated with media size to wall ratio that ensures wall effects are minimised.

Mechanical strengths were determined through measuring the compressive failure force of six media pieces of each type of material using Instron 5500R machine. The bulk density was determined through volume displacement in triplicate as described by Molle et al., (2003). Elemental composition was determined using scanning electron microscopy (SEM), D5005, Phillips XL ESEM- EDS and mineralogy using X-Ray diffraction spectrometry.

Cation exchange capacity was measured using 2.5 g of media (0.5 – 1.0 mm) which was placed into a 50 mL centrifuge bottle. A 30 mL solution of 0.1 M buffered Barium chloride at pH 8.1 was added and shaken for 1 hour. The procedure was repeated twice and three supernatants collected for determining the exchanged cations. The solid portion was shaken again with 30 mL of 0.02 M magnesium sulphate solution for 2 hours. The mixture was filtered through 0.45µm filter paper. Absorbed barium exchanges with magnesium and precipitated as barium sulphate. The result was subtracted from the initial barium content with the difference defining the CEC of the media. The barium concentration was measured using a Flame Atomic absorption spectrometer Perkin AAnalyst 800.

For P solution preparation, a known amount of Tris (hydroxymethyl amino methane) buffer was dissolved in deionised (DI) water to make a solution of pH 7.25. A known amount of ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) was dissolved into the liquid to make a 5.6 mg TP L^{-1} synthetic wastewater. All chemicals used were of analytical grade.

For batch kinetic experiments, duplicate sets of 2.0 g media were placed into 250 mL Erlenmeyer flasks and 100 mL of P solution added with controls containing only DI water. The mixtures were shaken on a SSL1 Stuart orbital shaker at 160 rpm before being filtered through $0.45 \mu\text{m}$ Glass microfiber WhatmanTM filter papers supplied by Fisher Scientific.

For batch equilibrium experiments, different media amounts were placed in different 250 mL Erlenmeyer flasks and 100 mL of P solution added. Experiments were conducted in duplicates and controls contained a phosphorus solution only. The mixtures were shaken on the same shaker described previously at 160 rpm for 24 hours. Experimental data was fitted onto linearized Langmuir, Freundlich and Temkin isotherm models as described by Kumar and Kirthika (2009).

Continuous flow experiments were conducted in 25 mm diameter Perspex columns of 200 mm length operated in a down-ward flow. Media was placed in the column in batches of 2.0 mm and compacted to make sure that porosity was even. This was repeated until a depth of 100 mm was attained. Air and fines were removed through upward flow pumping using a peristaltic pump at a 100 ml min^{-1} flow rate. The media was left for 24 hours to allow gravity settling. Phosphorus solution was fed in down flow mode at 2.45 ml min^{-1} (20 minutes empty bed contact time (EBCT)). Samples were collected at certain bed volumes and analysed immediately. Monitoring continued until the bed was exhausted and the length of unused bed (LUB) was calculated from the equation described by Worch (2012). The capacity was determined by integrating the area above the breakthrough curve. Scaling up to pilot columns was checked through the proportional and constant diffusivity models as described by MWH (2005) and Worch (2012).

Batch regeneration trials were conducted in duplicates. Media weighing 1.0 g and 100 mL of 5.6 mg TP L⁻¹ solution were placed into 250 ml Erlenmeyer flasks and shaken for 24 hours at 160 rpm. Each media was rinsed three times with deionised water. A 150 mL 0.1 M sodium hydroxide (NaOH) solution was added to each flask and shaken again for 24 hrs. The mixture was filtered and any materials retained on the filter put back into the flasks. The residue was fed again with P solution and the procedure repeated for three cycles.

Phosphorus sequential extraction

Samples of exhausted media were collected from the columns and air dried. The experiment was conducted in triplicates using 1.0 g of media. The media was placed into 250 mL Erlenmeyer flasks, appropriate chemicals (Table 3.2) were added, and shaken for 24 hours on an orbital shaker at 160 rpm.

Each sample was washed twice with 25 mL supersaturated sodium chloride solution between each step to remove P that could have been retained by media and filtrates placed into relevant bottles to make 100 mL solutions. Mixtures were filtered through 0.45 µm filter papers and solutions placed into separate bottles.

Table 3.2: Protocol for P sequential extraction (adopted from Korkusuz et al., 2007 and Drizo et al., 2008)

| Fraction | Extractant | Procedure |
|----------------------|--------------------------|--|
| Loosely bound P | 1M NH ₄ Cl | 50mL of extractant and shaken for 24 hours |
| Al bound P | 0.1 M NaOH | 50mL of extractant and shaken for 24 hours |
| Fe bound P | 0.5 M NaHCO ₃ | 50mL of extractant and shaken for 24 hours |
| Ca bound P | 1 HCl | 50mL of extractant and shaken for 24 hours |
| Stable residual pool | Concentrated HCl | 50mL of extractant and shaken for 24 hours |

The amount of total phosphorus, TP, extracted in (mg g⁻¹) was calculated according to the following formula:

$$TP = \frac{CxV}{M} \quad (3-1)$$

Where C is extracted phosphorus in mg L⁻¹, V is extractant in mL and M is media sample in grams.

Analytical methods

The solution's pH was determined through Jenway 3540 pH and a conductivity meter. The meter was calibrated with pH 4, 7 and 10 buffer solutions each time before use. Phosphorus was determined through molybdenum blue method and measured photometrically.

3.3 Results and discussion

3.3.1 Influence of elemental composition on performance

Calcium (Ca) was the predominant component in the industrial products (blast furnace and steel slag) and natural materials (limestone and gravel). To illustrate, the calcium concentration was 380, 340, 330 and 247.1 mg g⁻¹, respectively in blast furnace slag, limestone, gravel and steel slag compared to less than 60 mg g⁻¹ in the case of the manmade materials (phosphateTM and bauxsol), (Table 3.3).

Table 3.3: Batch equilibrium isotherm, and elemental composition results

| Media | Steel slag (mg g⁻¹) | phosphateTM (mg g⁻¹) | BFS (mg g⁻¹) | Limestone (mg g⁻¹) | Bauxsol (mg g⁻¹) | Gravel (mg g⁻¹) |
|--------------|---|---|--|--|--|---------------------------------------|
| Al | 44.1 (10) | 18.1 (20) | 53 (3.2) | 10 (0) | 62 (90) | 10 (10) |
| Ca | 247.1 (97) | 60 (20) | 380 (380) | 340 (380) | 52 (10) | 330 (320) |
| Fe | 131 (128.5) | 410 (481) | 2.9 (0) | 0 (0) | 120 (190) | 9.7 (10) |
| P | 5.5 (31) | 0 (5) | 0 (2.9) | 0 (0.5) | 3.1 (27) | 0 (1.1) |

| Media | Media capacity (mg TP g ⁻¹ media) | CEC (cmol (+) kg ⁻¹) | Δ Al (mg g ⁻¹) | Δ Ca (mg g ⁻¹) | Δ Fe (mg g ⁻¹) | Δ P (mg g ⁻¹) | Calcium used/TP retained |
|-------------------------|--|----------------------------------|----------------------------|----------------------------|----------------------------|---------------------------|--------------------------|
| Steel slag | 0.51±0.02 | 8.2 | -34 | -150 | +2.5 | +25.5 | 5.9 |
| phosphate TM | 0.47±0.01 | 18.9 | +1.9 | -40 | +71 | +5 | 8.0 |
| BFS | 0.1±0.0 | 1.9 | -49.8 | 0.0 | -0.3 | +2.9 | 0 |
| Limestone | 0.07±0.0 | 1 | -10 | +40 | 0.0 | +0.5 | n.d. |
| Bauxsol | 0.46±0.02 | 14.2 | +28 | -42 | +70 | +23.9 | 1.8 |
| Gravel | 0.12±0.01 | 2.4 | 0.0 | -10 | +0.3 | +1.1 | 9.1 |

- = Decrease in media concentration

+ = Increase in media concentration

() = Exhausted media concentration

The second most prevalent component was iron at 410, 210 and 131 mg g⁻¹ for PhosphateTM, bauxsol and steel slag, with all other media containing less than 100 mg g⁻¹. Similarly all media had relatively low aluminium levels, with the maximum observed for bauxsol and BFS at 62 and 53 mg g⁻¹, respectively.

Analysis of the exhausted media revealed changes in the elemental composition and phosphorus uptake (Table 3.3). All saturated media had a decrease in Ca concentration except blast furnace slag and limestone. Steel slag, bauxsol, PhosphateTM and gravel revealed Ca decreases of 150, 42, 40 and 10 mg g⁻¹, respectively. The corresponding phosphorus increases were 25.5, 23.9, 5 and 1.1 mg g⁻¹ media consisting of a Ca decrease / TP increase ratios 5.9, 1.76, 8 and 9.1, respectively. This is indicative of calcium dissolution mechanisms, whereby the released calcium reacts with phosphorus and carbonates, with a proportion precipitating onto the media surface. The remaining solids remain in suspension which was confirmed by visual inspection of the liquid phase which became cloudy as the test proceeded. The Ca: TP ratios are consistent with previous studies in the range of 1.25 to 6.22 (Barca et al., 2012) from electric arc furnace slag and blast oxygen furnace slag.

In terms of the other key components, the levels of aluminium (Al) decreased by 49.8, 34 and 10 mg g⁻¹ in BFS, steel slag and limestone, respectively. These results suggest Al could have been involved in P uptake or was leaching from these media. The other media indicated increases of Al except gravel and this could have been due to the decrease in the total mass of the media whilst Al remained the same. This was also true in the case of iron (Fe), with only blast furnace revealing a slight decrease. Drizo et al., (2002) made the same observations where FeO in EAF steel slag had increased from 30.2±1.2 to 32.5±1.2% in fresh and exhausted media, respectively.

X-ray diffraction results indicate that gravel and limestone were predominantly calcite materials (Table 3.4). Bauxsol was dominated by iron and aluminium, and PhosphateTM was also a predominant iron material. Both industrial products (BFS and steel slag) were dominated by calcium minerals.

New minerals were formed after media exhaustion containing phosphates which was an indication of P retention. The minerals present in exhausted steel slag were Ca₁₀(PO₄)₆(OH)₂, Ca₂(Mg,Fe(PO₄)₂·H₂O), Fe,Mn(AlPO₄(OH)·H₂O (Table 3.4).

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) was also identified in fresh slag so it could have been a seed for P precipitation. The structures of some of the minerals suggest that after P was retained by a particular divalent ion, the resultant compound was further attached to some other metals oxides/hydroxides with a strong affinity for phosphorus. In the case of the exhausted PhosphateTM, CaHPO₄ and FePO₄·2H₂O were identified; suggesting calcium and iron were the P removal mechanisms. Iron retains P mainly through ligand exchange where the phosphorus molecules replace hydroxides or water molecules in the oxide; therefore no Fe is expected to change, except due to leaching. New minerals revealed by exhausted bauxsol were AlPO₄, Al(PO₃)₃, Fe(PO₄)₂(OH)₆·H₂O and FePO₄·2H₂O. Even though calcium had decreased in exhausted bauxsol, there was no calcium related mineral identified, suggesting a different dominant mechanism compared to the steel slag.

Table 3.4: X-ray diffraction results of mineral composition of the six media (fresh and exhausted).

| Natural materials | | | |
|--|--|--|--|
| Fresh gravel | Exhausted gravel | Fresh limestone | Exhausted limestone |
| CaCO ₃ /CaO.CO ₂ | CaCO ₃ | CaCO ₃ | CaCO ₃ |
| CaCO ₃ | CaCO ₃ /CaO.CO ₂ | CaCO ₃ /CaO.CO ₂ | CaCO ₃ /CaO.CO ₂ |
| FeO | CaHPO ₄ .2H ₂ O/2CaO.P ₂ O ₅ .5H ₂ O | | CaP |
| SiO ₂ | CaHPO ₄ | | AlH ₂ P ₃ O ₁₀ .H ₂ O |
| Man-made materials | | | |
| Fresh Bauxsol | Exhausted Bauxsol | Fresh PhosphateTM | Exhausted phosphateTM |
| Fe ₂ O ₃ | Fe ₂ O ₃ | CaCO ₃ | FeO(OH) |
| Al ₂ O ₃ | AlPO ₄ | FeO ₃ .H ₂ O | Fe ₂ O ₃ .2H ₂ O |
| CaCO ₃ | Ca ₃ Al ₂ O ₆ | FeO(OH) | CaHPO ₄ |
| Ca ₃ Al ₂ O ₆ | Al(PO ₃) ₃ | Fe ₃ O ₄ | FePO ₄ .2H ₂ O |
| | Fe ₄ (PO ₄) ₂ (OH) ₆ .H ₂ O | | |
| | FePO ₄ .2H ₂ O | | |
| Industrial by-products | | | |
| Fresh BFS | Exhausted BFS | Fresh steel slag | Exhausted steel slag |
| 2CaO.Al ₂ O ₃ SiO ₂ | Ca(H ₂ PO ₄).H ₂ O | CaCO ₃ | Mg ₂ P ₂ O ₇ |
| Ca ₂ Al ₂ SiO ₇ | CaHPO ₄ .2H ₂ O/CaO.P ₂ O ₇ .H ₂ O | FeO | CaMg |
| Ca ₂ MgSiO ₇ | Ca ₂ Al ₂ SiO ₇ | CaO ₂ .8H ₂ O | Ca ₄ O(PO ₄) ₂ /4CaO.P ₂ O ₅ |
| | K ₂ Ca ₄ Al ₈ (PO ₄) ₈ (OH) ₂ .H ₂ O | Mg ₂ P ₂ O ₇ | CaO ₂ .8H ₂ O |
| | FePO ₄ | Ca ₁₀ (PO ₄) ₆ (OH) ₂ | Ca ₁₀ (PO ₄) ₆ (OH) ₂ |
| | | CaMg ₂ | Ca ₅ (PO ₄) ₃ F |
| | | CaSi ₂ | FeO |
| | | 2CaO. Al ₂ O ₃ .SiO ₂ | CaSi ₂ |
| | | Fe ₂ SiO ₄ | |
| | | Ca ₂ Al ₂ O ₃ SiO ₂ | |

There was a high link between P retention capacity and CEC (Table 3.3). To illustrate steel slag, PhosphateTM and bauxsol P retention capacities were 0.51±0.02, 0.47±0.01, and 0.46±0.02 mg TP g⁻¹ media, respectively and corresponding CEC were 8.2, 14.2, and 18.9 cmol (+) kg⁻¹. In contrast, media with low CEC such as limestone, blast furnace slag and gravel all revealed low capacities (0.07, 0.1 and 0.1 mg TP g⁻¹ media respectively). CEC values of these media were 1, 1.9 and 2.4 cmol (+) kg⁻¹, respectively. The same trend was observed from rapid small scale columns where retention capacities at breakthrough were 0.64, 0.17, 0.05, 0.04, 0.02 and 0.01 mg g⁻¹ for steel slag, PhosphateTM, bauxsol, gravel, blast furnace slag and limestone, respectively. These results are in agreement with those reported by Lee et al., (1997), however in contrast

to Drizo et al., (1999) who suggested no strong link between CEC and theoretical P retention capacity.

Observed equilibrium capacities (Table 3.3) were, in most cases similar to those reported in literature. For instance, Drizo et al., (2002) reported a range of 0.31-3.93 mg P g⁻¹ media for steel slag. Similarly, removal capacities of 0.5 mg P g⁻¹ media for Phosphate™ were reported (Fenton et al., 2009), 0.58 mg g⁻¹ media for bauxsol (Huang et al., 2008) and 0.089 mg P g⁻¹ media for limestone (Tang et al., 2009). In contrast, in the case of limestone, a much lower level was observed compared to previous studies where between 0.3-20 mg P g⁻¹ media had been observed (Johansson, 1999).

3.3.2 Fixed bed columns

The breakthrough curves revealed larger LUB for blast furnace slag, limestone, gravel and Phosphate™ (Figure 3.1).

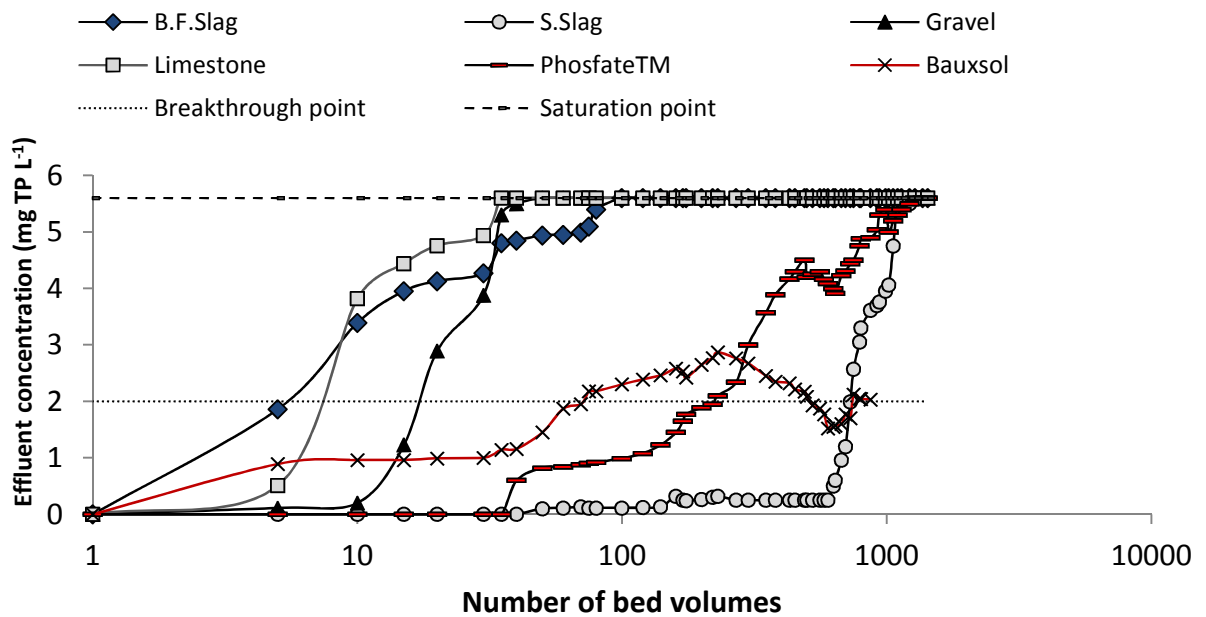


Figure 3.1: Breakthrough curves of different media from rapid small scale column experiments.

The observed LUB in decreasing order were 95, 82, 79, 53 and 34 mm for blast furnace slag, Phosphate™, limestone, gravel and steel slag, respectively (Table 3.5). Bauxsol LUB

was not determined as the effluent concentration was fluctuating most of the time and the experiment was not run to completion. Gravel, BFS, PhosphateTM and limestone breakthrough curves indicated slower rates of P removal which led to longer LUB than steel slag which indicated a faster rate of P removal.

The performance of fixed bed reactors is sometimes quantified in terms of media usage rate, defined as a mass of media in the bed/ (flow rate x time). This gives an indication of how much water is treated by a unit mass of media. Media with larger capacities such as steel slag, PhosphateTM and bauxsol had smaller minimum usage rates than those with smaller capacities such as blast furnace slag, gravel and limestone (Table 3.5). Capacities at saturation were in agreement with equilibrium batch isotherm results except for steel slag and phosphateTM, which were larger.

Table 3.5: Breakthrough curve analysis results

| Media | Media mass(g) | Bed volume at breakthrough | Bed volume at saturation | LUB (mm) | Capacity at saturation (mg g ⁻¹ media) | Capacity at breakthrough (mg g ⁻¹ media) | Minimum media usage rate (g /bed volume) at breakthrough |
|-------------------------|---------------|----------------------------|--------------------------|----------|---|---|--|
| Steel slag | 95 | 730 | 1100 | 34 | 2.3 | 0.6 | 0.1 |
| BFS | 71 | 5.5 | 100 | 95 | 0.1 | 0.02 | 12.9 |
| Bauxsol | 54 | 75 | n.d. | n.d. | n.d. | 0.05 | 0.7 |
| Phosphate TM | 62 | 230 | 1280 | 82 | 2.3 | 0.2 | 0.3 |
| Gravel | 71 | 19 | 40 | 53 | 0.1 | 0.04 | 3.7 |
| Limestone | 73.4 | 7.5 | 35 | 79 | 0.04 | 0.01 | 9.8 |

n.d. = not determined

3.3.3 Link to large scale

Analysis was carried out to scale up column data to full scale systems treating wastewater of the same quality (Table 3.6). The results suggest that at full scale, steel

slag bed will operate for 1441 days or 4 years before reaching breakthrough and 2161 days or 6 years before all the media is exhausted. Shilton et al., (2006) reported a mean P effluent of 2.3 mg TP L⁻¹ over the first five years of a full scale filter bed using active slag filters and a reduced efficiency thereafter. These results are similar to this study. Shilton et al., (2006) utilised a retention time of 3 days compared to 2 days used in this study, which could have led to an increased operation time. In contrast, Drizo et al., (2002) estimated a life expectancy of 13-20 years for EAF slag. PhosphateTM is the second best media after steel slag with breakthrough scaled up to 432 days or 1.2 years and exhaustion after 2571 days or 7 years. All the other media revealed scaled up breakthrough times that were very small, suggesting that they were not appropriate for further study. Comparing the results in this study and reported findings from full scale studies, RSSC test results are realistic but a pilot plant should be conducted using real wastewater and recommended media sizes to be used at full scale before making any decisions. Biological degradation processes in full scale systems with longer EBCT can partially regenerate media and prolong bed life (Worch, 2012) hence RSSC can underestimate bed life.

Table 3.6: Scale up results from rapid small scale columns to full scale

| Model | Media | Column type | Media size(mm) | Breakthrough (Days) | Exhaustion (Days) |
|--------------------------|-------------------------|-------------|----------------|---------------------|-------------------|
| Proportional diffusivity | Steel slag | RSSC | 0.75 | 10 | 15 |
| | | Full scale | 10.8 | 1441 | 2161 |
| | Phosphate TM | RSSC | 0.75 | 3 | 18 |
| | | Full scale | 10.8 | 432 | 2571 |
| | BFS | RSSC | 0.75 | 0.08 | 1.4 |
| | | Full scale | 10.8 | 11 | 200 |
| Constant diffusivity | Gravel | RSSC | 0.75 | 0.26 | 0.56 |
| | | Full scale | 8.9 | 37 | 80 |
| | Limestone | RSSC | 0.75 | 0.1 | 0.49 |
| | | Full scale | 8.9 | 14 | 70 |
| | Bauxsol | RSSC | 0.75 | 1.0 | n.d. |
| | | Full scale | 8.9 | 149 | n.d. |

n.d. = not determined

3.3.4 Batch regeneration

Retention capacities were recovered from all media (Figure 3.2) with over 100% recovered from steel slag, bauxsol, gravel, limestone, and blast furnace slag. The same was observed by Pratt et al., (2011), where 100% capacity was recovered from exhausted active slag filters and was linked to the formation of new active sites through protonation on the media's surfaces. Drizo et al., (2002) reported an increase from 1.35 to 2.35 g kg⁻¹ media after resting EAF steel slag for 4 weeks. Recovery of retention capacities meant that the media have the potential for regeneration and re use and thereby reducing replacement costs.

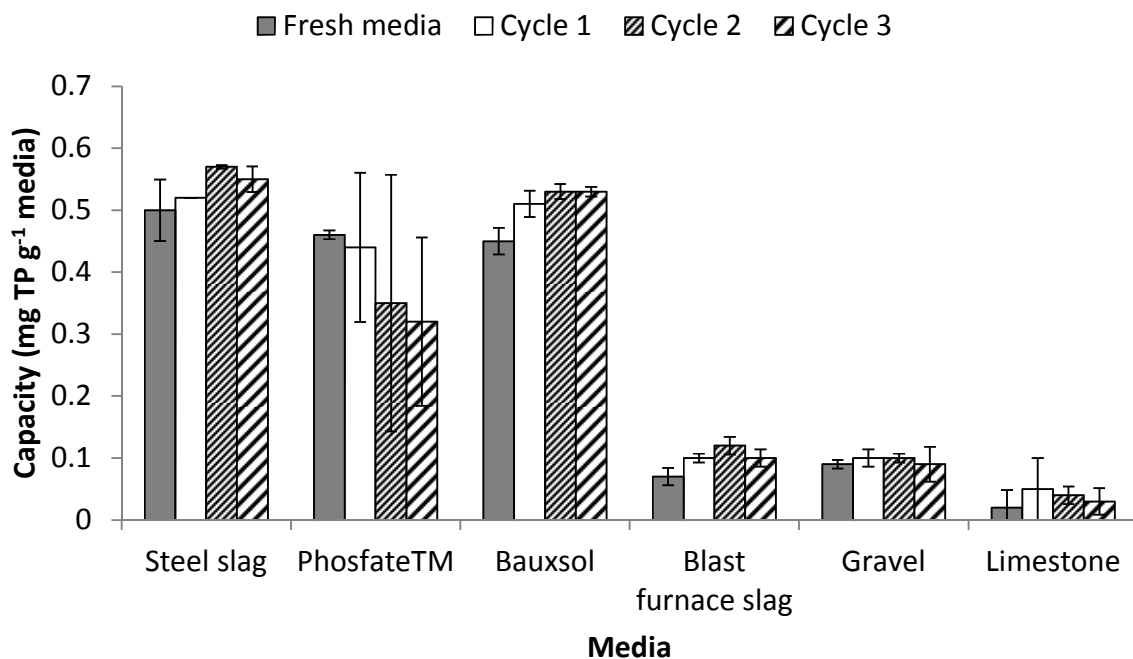


Figure 3.2: Impact of batch regeneration cycles on P retention capacity (initial P concentration = 5.6 mg TP L⁻¹, media size 0.5-1.0 mm, 0.1 M NaOH as regenerant)

Phosphate™ revealed a decline in retention capacity with each regeneration cycle. This limits the regeneration cycles of the media. Though capacities were recovered from blast furnace slag, gravel and limestone, they were still smaller compared to those from steel slag, Phosphate™ and bauxsol.

3.3.5 Phosphorus Sequential Extraction

Sequential extraction of the exhausted media indicates that the main P removal mechanisms by steel slag are through calcium precipitation, retention onto iron oxide surfaces and the stable residual pool fraction (Figure 3.3). The corresponding amounts extracted from these fractions were 0.49 ± 0.05 , 0.85 ± 0.006 and 0.5 ± 0.0024 mg TP g^{-1} media, respectively. The formation of new minerals in the exhausted media such as $((Ca_2(Mg,Fe)(PO_4)_2 \cdot H_2O)$, manganoan $(Fe,Mn)ALPO_4(OH)_2 \cdot H_2O$ and hydroxylapatite $(Ca_{10}(PO_4)_6(OH)_2))$ as identified during the elemental and mineralogy determination are in agreement with these results. The concentration of calcium was identified to have decreased in exhausted media, hence agreeing with the results that CaP precipitation was one of the best removal mechanisms. The iron pool had more P extracted than other fractions, suggesting that it was the main pool of retained phosphorus in steel slag. Shilton et al., (2013) have reported phosphorus bound to some mineral phases of weathered slag granules such as iron precipitates, iron-magnesium precipitates and the amorphous iron oxyhydroxides that resulted from chemical weathering of fresh slag. The findings by Shilton et al., (2013) are in general agreement with the results of steel slag. In contrast others have identified the Ca pool as the main fraction (Drizo et al., 2008).

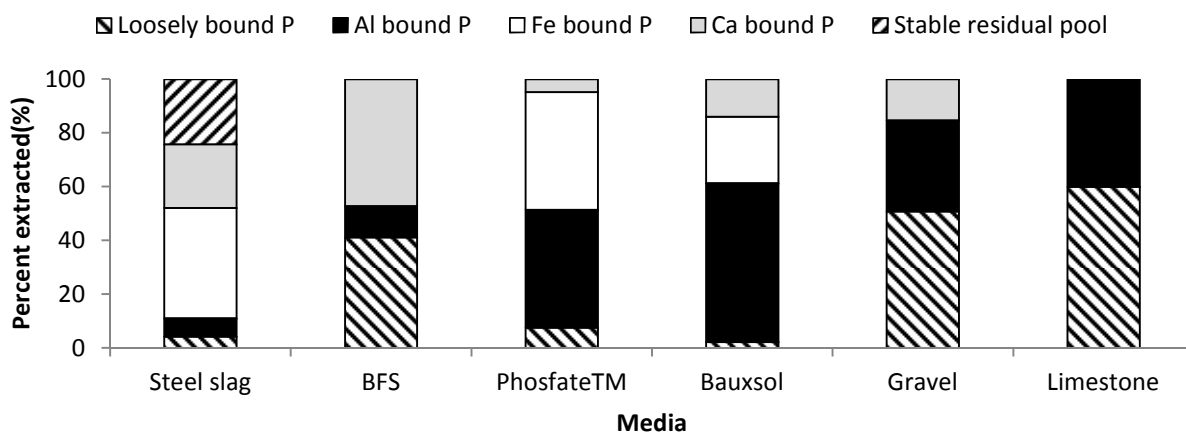


Figure 3.3: Phosphorus sequential extraction results (media diameter 0.5-1.0 mm)

In the case of man-made materials, P removal was mainly associated with the aluminium and iron fractions. PhosphateTM revealed equal amounts of P were extracted from Al and Fe pools with 0.46 ± 0.005 and 0.46 ± 0.004 mg TP g⁻¹ media, respectively compared to bauxsol at 0.81 ± 0.0 and 0.34 ± 0.003 mg TP g⁻¹, respectively. The results of bauxsol are consistent with X-ray diffraction results reported earlier, where aluminum phosphate (AlPO₄), aluminum phosphate oxide (Al (PO₃)₃), strengite (FePO₄·2H₂O) and delvauxite (Fe₄ (PO₄)₂(OH)₆·H₂O) were identified in exhausted bauxsol.

The amounts of P loosely bound to limestone, gravel and blast furnace slag were 0.03 ± 0.001 , 0.03 ± 0.003 and 0.07 ± 0.005 mg TP g⁻¹ media, respectively. Other noticeable extractions from limestone and gravel were from Al, 0.02 ± 0.001 and 0.02 ± 0.0 mg TP g⁻¹, respectively. Though limestone and gravel had revealed higher Ca concentrations, there was less or no P extracted from the fraction. Limestone results were in agreement with earlier elemental and mineralogy results from which aluminum in exhausted limestone had decreased by 10 mg g⁻¹ and aluminum hydrogen phosphate hydrate mineral was identified (AlH₂P₃O₁₀·H₂O). Gravel results are in agreement with SEM and X-ray-diffraction results where calcium concentration had decreased by 10 and CaHPO₄·2H₂O and CaHPO₄ were identified in the saturated media. Removal through Al fraction could have been due to ligand exchange in the same manner as through iron oxides/hydroxides. Removal mechanisms in BFS were calcium precipitation, some of the phosphorus was loosely bound and Al retained as 0.08 ± 0.006 , 0.07 ± 0.005 and 0.02 ± 0.001 mg TP g⁻¹ respectively. X-ray diffraction did not identify aluminum phosphate minerals from both gravel and BFS; however phosphorus was extracted from the Al pool during sequential extraction.

3.3.6 Media mechanical strength vs. density

Higher density media were shown to also have larger failure strengths such that industrial by-products had larger failure strengths followed by natural materials and lastly man-made materials (Figure 3.4). In descending order, failure strengths were 1.87 ± 1.02 , 1.48 ± 0.66 , 0.67 ± 0.27 , 0.65 ± 0.2 , 0.05 ± 0.02 and 0.02 ± 0.0 kN, respectively for blast furnace slag, steel slag, limestone, gravel, bauxsol and PhosphateTM. The corresponding densities were 3.21 ± 0.01 , 2.9 ± 0.01 , 2.32 ± 0.01 , 2.69 ± 0.02 , 2.19 ± 0.01

and $2.29 \pm 0.01 \text{ g cm}^{-3}$, respectively. The density of steel slag was similar to that reported by Shilton et al., (2005) of steel smelter slag which was 3.04 g cm^{-3} .

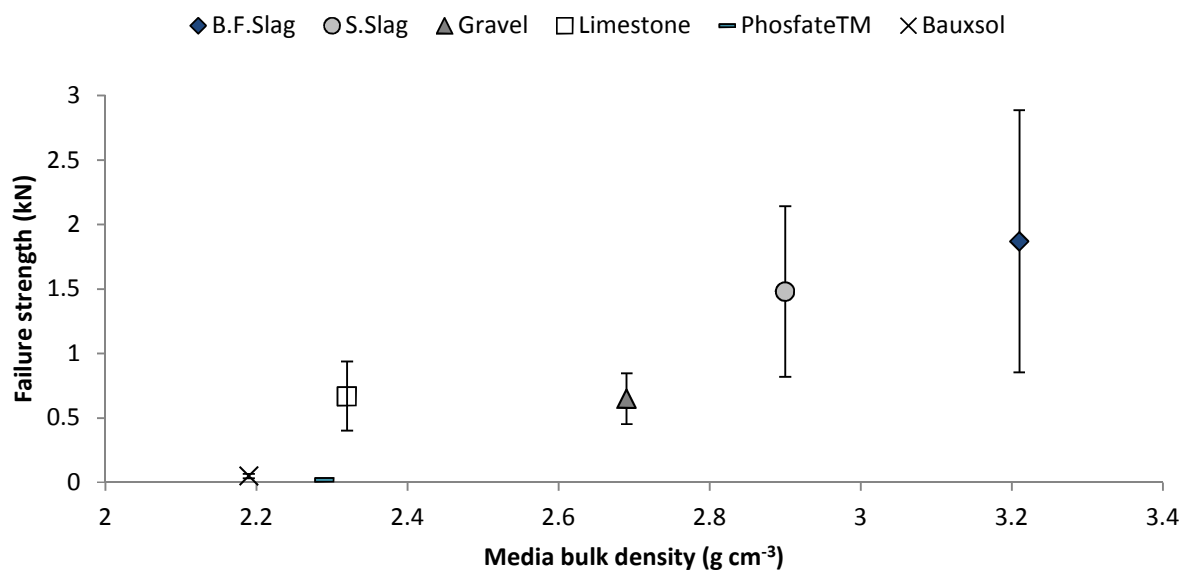


Figure 3.4: Bulk density and mechanical strength at failure

The density of limestone was closer to that reported by Shilton et al., (2005), which was 2.68 g cm^{-3} . Industrial products and natural materials are likely to withstand the static forces encountered in a reed bed.

After screening the six media, the results were compared and the best two performing media were chosen for further evaluation (Table 3.7).

Table 3.7: Summary of key results of media screening process.

| Media | P retention capacity (mg g^{-1}) | Recovered P retention capacity (%) | Mechanical strength (kN) | Al, Fe and Ca elements in descending order | |
|------------|---|------------------------------------|--------------------------|--|------------|
| | Batch mode | Column mode | | | |
| Gravel | 0.12 | 0.1 | 100 | 0.65 | Ca, Al, Fe |
| Limestone | 0.07 | 0.04 | 100 | 0.67 | Ca, Al |
| Bauxsol | 0.46 | Clogging | 100 | 0.05 | Fe, Al, Ca |
| Phosphate™ | 0.47 | 2.3 | 95 | 0.02 | Fe, Ca, Al |

| | | | | | |
|--------------------|------|-----|-----|------|------------|
| Steel slag | 0.51 | 2.3 | 100 | 1.48 | Ca, Fe, Al |
| Blast furnace slag | 0.1 | 0.1 | 100 | 1.87 | Ca, Al, Fe |

Steel slag was observed to be the best of all the six media as it has larger P retention capacity, can be regenerated and exhibited sufficient mechanical strength for use in typical constructed wetlands. No other media provided a complete set of required properties with failure strength being an issue for PhosphateTM and bauxsol, and low overall capacity for other media. PhosphateTM was chosen for further study due to its capacity and discussion undertaken with the supplier to increase its mechanical strength ahead of the longer term trials.

3.4 Conclusions

In this study, six media were screened to establish key properties that influence performance on phosphorus removal from tertiary effluent.

- Steel slag, PhosphateTM and bauxsol were found to have larger P retention capacities than blast furnace slag, limestone and gravel.
- Industrial by-products (steel slag and blast furnace slag) showed higher mechanical strengths followed by natural materials (limestone and gravel), with man-made products (PhosphateTM and bauxsol) revealing the lowest mechanical strengths.
- The retention capacities of all the media were during batch regeneration trials with some revealing over 100% recovery.
- The results from rapid small scale columns revealed that scaling up to full scale is possible.

From the screening process, it was found that steel slag and PhosphateTM were the best two media and were therefore chosen for further evaluation for P removal from tertiary effluents. Though limestone, gravel and blast furnace slag revealed higher mechanical strength, PhosphateTM had larger P retention capacity which was 5 times more than that of these materials.

3.5 Acknowledgements

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**CHAPTER 4: DISSOLUTION OF CALCIUM FROM STEEL SLAG IN
PHOSPHATE MITIGATION; INFLUENCE OF BACKGROUND WASTEWATER
CHARACTERISTICS.**

4 DISSOLUTION OF CALCIUM FROM STEEL SLAG IN PHOSPHATE MITIGATION; INFLUENCE OF BACKGROUND WASTEWATER CHARACTERISTICS.

4.1 Introduction

Phosphorus (P) is an essential element for plant growth and it is often the limiting nutrient in aquatic plants (Diaz et al., 1994). Excessive release into water bodies results in algal blooms or eutrophication which degrades water quality and imbalances the ecosystem (Biswas et al., 2008; Barca et al., 2012). Phosphorus is an important component of many industrial products, the use of which ends up in waste which is discharged into industrial and domestic wastewater (Biswas et al., 2008). As a result, strict controls have been put in place to limit the amount of P discharged into the environment. Waste from conventional systems, such as enhanced biological P removal and chemical precipitation, contains impurities such as aluminium or ferric phosphate, hence cannot be reused (Midorikawa et al., 2008). In addition biological P removal technologies are technologically and economically unsuitable for use at a smaller scale, hence the option of passive systems (De- Bashan and Bashan, 2004). Recent studies have focussed on the upgrading of passive systems, such as constructed wetlands for P removal from tertiary effluents through the inclusion of reactive media. To date, steel slag has emerged as the most promising candidate with the predominate mechanism being attributed to a two-step process of initial calcium dissolution followed by precipitation of calcium phosphate (Chazarenc et al., 2007). Comparisons between synthetic and real wastewaters have revealed inconsistencies (Cucarella and Renman, 2009) indicating that the background water chemistry influences the overall process. Previous studies have investigated the dissolution step in deionised water and real wastewater (Barca et al., 2012; Engstrom et al., 2013) however no studies have reported looking at how the background components influence the process limiting translation across different sites without the use of individual pilot trails.

The objective of this work was to investigate the influence of alkalinity and P strength on steel slag dissolution into calcium ions. The experiments were conducted through laboratory batch tests.

4.2 Materials and methods

Elemental composition was determined through Scanning Electron Microscopy (SEM), Phillips XL 30 ESEM-EDS and mineralogy using Siemens X-ray Diffraction, D5005, energy dispersive X-ray spectrometry (EDXS).

For dissolution of steel slag, a fresh steel slag sample (of 5.0 – 12.5 mm diameter) was washed in DI water and left to dry. Known amounts of sodium bicarbonate (NaHCO_3) or calcium carbonate (CaCO_3) were dissolved in deionised (DI) water to simulate alkalinities of 50, 75, 100 and 180 mg L^{-1} as CaCO_3 . The experiments were conducted by placing 20 g media and 100 mL solution in 250 mL Erlenmeyer flasks, and the controls contained media and DI water. The other flasks contained high (8.2 mg TP L^{-1}) and low (0.99 mg TP L^{-1}) strengths effluents of 82 and 200 mg L^{-1} alkalinity respectively. The experiments were conducted in duplicates. Flasks were shaken on an orbital shaker at 160 rpm and removed at predetermined times. The mixtures were filtered through 0.45 μm filter papers. The pH was measured using a Jenway pH and conductivity meter 3540 after calibration. Solutions were preserved by adding 5 mL of pH 4.0 nitric acid and stored at 4°C until analysis. Calcium concentration was determined using a Flame Atomic absorption spectrometer (Perkin AAnalyst 800).

4.3 Results and discussion

4.3.1 Media characterisation

X-ray diffraction analysis indicated that the oxides present in the steel slag samples were FeO and $\text{CaO} \cdot 8\text{H}_2\text{O}$ (Table 4.1). Background phosphates were present as $\text{Mg}_2\text{P}_2\text{O}_7$, and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ which can act as a seed for phosphorus crystal growth (Bellier et al., 2006). Compared to other materials reported by Barca et al., (2012), the composition was similar except that in this study there was CaCO_3 present and other minerals that were not oxides (CaMg_2 and CaSi_2).

Table 4.1: X-Ray diffraction results from steel slag and comparative results from other studies (Other experiment results adopted from Barca et al., (2012))

| This study | Other steel slag dissolution experiments conducted | |
|--|--|----------------|
| | EAF Slag (W %) | BOF Slag (W %) |
| Mineral | | |
| CaCO ₃ | Fe ₂ O ₃ (51.4) | 33.5 |
| FeO | CaO (34.9) | 60.4 |
| CaO ₂ .8H ₂ O | SiO ₂ (16.5) | 16.1 |
| Mg ₂ P ₂ O ₇ | Al ₂ O ₃ (13.1) | 2.6 |
| Ca ₁₀ (PO ₄) ₆ (OH) ₂ | MnO (8.1) | 5.4 |
| CaMg ₂ | MgO (4.4) | 5.5 |
| CaSi ₂ | | |
| 2CaO. Al ₂ O ₃ .SiO ₂ | | |
| Fe ₂ SiO ₄ | | |
| Ca ₂ Al ₂ O ₃ SiO ₂ | | |

The percent composition of minerals in this study could not be determined, hence the amount of calcium likely to be liberated was not known. Barca et al., (2012) did not measure other minerals identified in this study which makes comparison of the materials difficult.

4.3.2 Steel slag dissolution

4.3.2.1 Influence of alkalinity using NaHCO₃ solution for steel slag dissolution.

The dissolution of steel slag under different alkalinities and DI water with time is presented (Figure 4.1) since it has been reported that the release of calcium from the material is a slow release process. For the control experiment (DI water), the released calcium ions (Ca²⁺) increased with time such that between day 1 and 4 the concentration of Ca increased from 20±0.5, to 32.5±10 mg L⁻¹, respectively, reaching 40.7 ±0.2 mg L⁻¹ on day 7. This was an indication that the dissolution of steel slag was positively correlating with time (R² = 0.7).

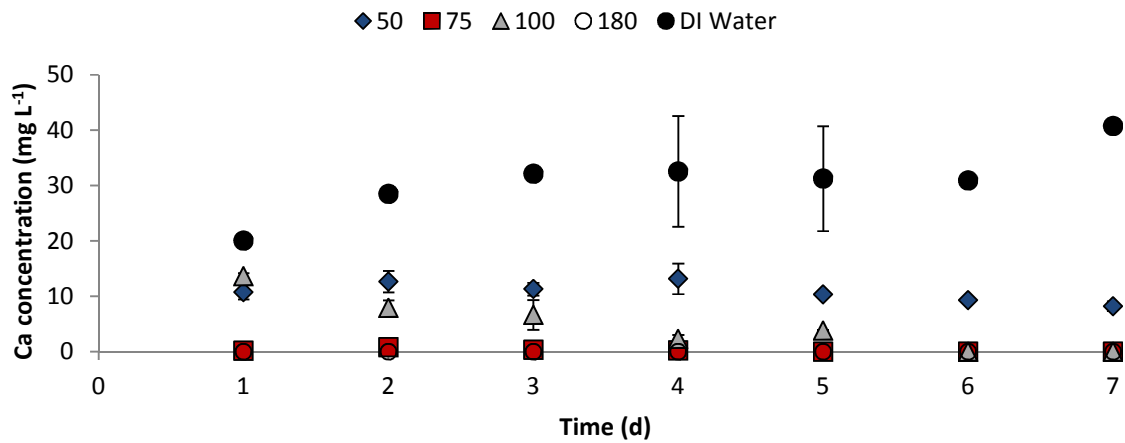


Figure: 4.1: Impact of alkalinity on steel slag dissolution into calcium ions in NaHCO₃ solution at (50, 75, 100, 180 mg L⁻¹ as CaCO₃) and DI water as control

In contrast, in the presence of 50 mg L⁻¹ alkalinity there was a reduced release of Ca at between 8.2±0.4 and 13±2.8 mg L⁻¹ with slight decrease overtime (Figure 4.1). Though there were cases of fluctuations, in general, the concentration of Ca²⁺ ions decreased with time. There were no residual Ca²⁺ ions in the solution when the alkalinity was increased to 75 mg L⁻¹ as the highest value was 0.8±0.1 mg L⁻¹ at day 2. It was expected that there would be no Ca²⁺ ions when alkalinity was increased to 100 mg L⁻¹ as CaCO₃, however surprising results were observed. The concentration was 13.6±0.6 mg L⁻¹ on the first day and had decreased to 3.8±0.2 mg L⁻¹ by day 5, and none thereafter. There were no residual Ca²⁺ ions in the solution when alkalinity was increased to 180 mg L⁻¹.

The comparison of the release in the different waters is consistent with the released Ca²⁺ ions reacting with available carbonates to form CaCO₃ according to the following equations;



The presence of background alkalinity in the media also contributed to the slow release of Ca^{2+} ions. Since the source of alkalinity had no calcium ions, all Ca^{2+} ions for precipitating CaCO_3 were sourced from dissolution of steel slag.

4.3.2.2 Influence of effluent phosphorus strength, and alkalinity as CaCO_3 on steel slag dissolution.

In contrast to when NaHCO_3 was used, when CaCO_3 solution was used, no residual Ca^{2+} ions were present during the first 2 days when alkalinity was 50 mg L^{-1} , however was $6.9 \pm 0.6 \text{ mg L}^{-1}$ on day 3 and $1.4 \pm 0.3 \text{ mg L}^{-1}$ on day 7 (Figure 4.2). The same trend was observed when alkalinity was increased to 75 mg L^{-1} , with a maximum concentration of $6.2 \pm 0.7 \text{ mg L}^{-1}$ at day 4 and then decreasing to $2.0 \pm 0.7 \text{ mg L}^{-1}$ at day 7. The calcium ions present in the alkaline solution were reacting in a reversible reaction with CO_3^{2-} and were at equilibrium; hence Ca^{2+} ions were not released. This is in agreement with findings (Molle et al., 2003) on the investigations of P removal by calcareous materials.

When real wastewater was used, the background Ca^{2+} ions in low and high phosphorus effluents were similar; 30.0 ± 0.6 and $31.8 \pm 1.2 \text{ mg L}^{-1}$, respectively. The corresponding alkalinities were 200 and $82 \text{ mg L}^{-1} \text{ CaCO}_3$, respectively. The residual Ca^{2+} concentrations were fluctuating with time in both systems. After 12 hours of shaking, the concentrations were similar at 38.5 ± 0.4 and $36.9 \pm 0.0 \text{ mg L}^{-1}$ from the low and high strength systems, respectively. During the preceding days, the concentration in the low strength system decreased with time such that after 7 days the concentration was $29.1 \pm 0.2 \text{ mg L}^{-1}$.

For the high phosphorus effluent, the concentration of Ca^{2+} ions increased with time and later was observed to be decreasing from a background concentration of 31.8 ± 1.2 to a maximum value of $43.5 \pm 6.5 \text{ mg L}^{-1}$ by day 5, after which it stabilised at 40.6 ± 4.1 and $39.9 \pm 2.0 \text{ mg L}^{-1}$ on day 6 and 7, respectively. Overall, there were more residual Ca^{2+} ions in the high phosphorus effluent than in the low phosphorus effluent even though the P concentration was 8.3 times higher than in low strength system. The levels of alkalinities of the two systems were 82 mg L^{-1} and $200 \text{ mg L}^{-1} \text{ CaCO}_3$, respectively. Most of the Ca^{2+} ions were consumed by carbonate species (alkalinity) to precipitate CaCO_3 , however the consumption was higher in the low phosphorus system

than the high phosphorus system. The presence of calcium ions in the filtrate suggests that the solution was supersaturated with Ca^{2+} ions. The final pH in the high phosphorus system was below 8.0 most of the time, which did not favour HAP crystallisation. This explains why the concentration of Ca^{2+} ions was high. This means that P retention was mainly through retention onto metal oxides surfaces (Bowden et al., 2009). Gehlenite ($\text{Ca}_2\text{Al}_2\text{O}_3\text{SiO}_2$) mineral, which was present in steel slag, contributed to the slow release of calcium ions. It releases calcium ions at pH 4, than at 7 and 10 (Engstrom et al., 2013).

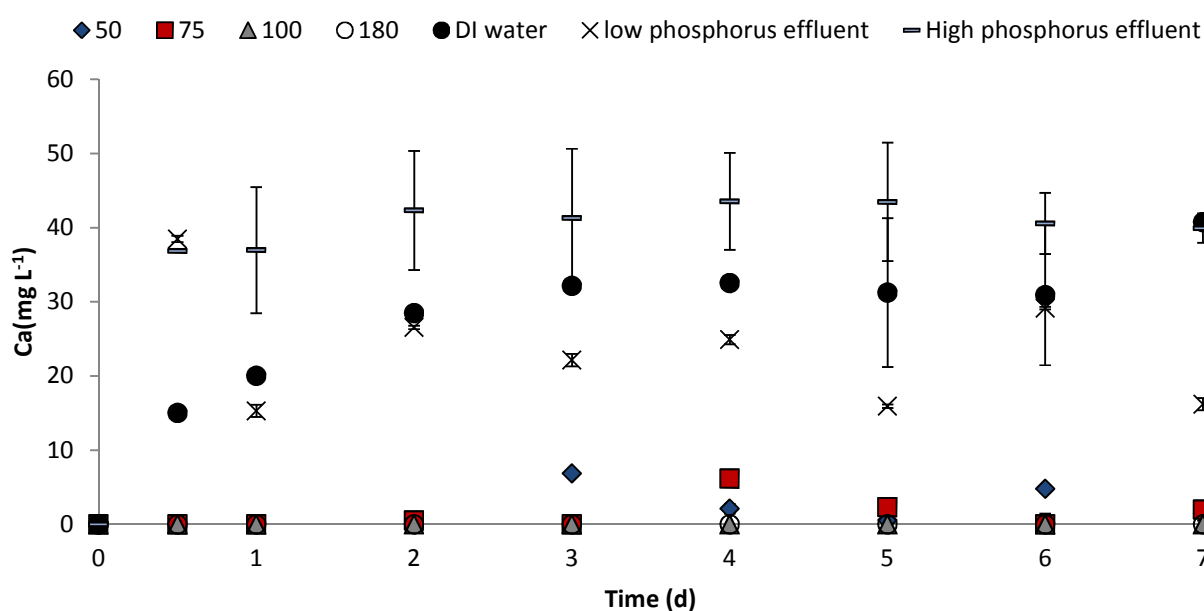


Figure 4.2: Impact of alkalinity on steel slag dissolution in CaCO_3 solution, low and high P effluents and DI water ($C_0 = 8.2 \text{ mg TP L}^{-1}$ for high strength and $0.99 \text{ mg TP L}^{-1}$ for low strength and 82 and $200 \text{ mg L}^{-1} \text{ CaCO}_3$ alkalinity respectively).

The results further confirm that alkalinity in the form of NaHCO_3 or CaCO_3 solutions inhibits the release of Ca^{2+} ions from the steel slag. There were only few instances where the ions were present in the solution at lower alkalinities (50 and 75 mg L^{-1} as CaCO_3). The Ca^{2+} ions were not released due to supersaturation when CaCO_3 solution was used but were consumed to precipitate CaCO_3 when NaHCO_3 solution was used. Low and high strength systems further confirmed that the level of alkalinity

contributes to the dissolution of steel slag as the level of Ca^{2+} ions were low in the system with higher alkalinity than lower alkalinity.

Impact of alkalinity on final pH

The initial pH was 9.9, 9.0, 9.9, and 10.1, corresponding to alkalinities of 50, 75, 100 and 180 mg L^{-1} CaCO_3 , respectively. The pH values decreased with time (Figure 4.3) such that on day 3, the corresponding pH values were 8.4, 8.5, 8.5 and 8.5, respectively. After 5 days of shaking, the pH values remained stable 8.6, 8.6, 8.5 and 8.4 units. The low and high phosphorus effluent's initial pH values were 9.6 and 7.4 units, respectively. The corresponding pH values after 3 days were 8.8 and 7.8, which showed a decrease by 0.8 units and increase by 0.4 units, respectively. After 5 days, the pH values were 9.0 and 8.0, respectively for low and high phosphorus systems, with low phosphorus showing a slight increase. In general, alkalinity inhibits pH elevation. Johansson and Gustafsson (2000) reported that a pH decrease was a function of adding phosphorus to blast furnace slag. Since the phosphate ions were replaced by carbonate ions, the results were therefore in agreement with the observations by Johansson and Gustafsson (2000). The same was observed by Joko (1984), in that high calcium and phosphate concentrations resulted in the reaction of the two, and a net lowering of pH. This was confirmed by Molle et al., (2003) on the investigation on calcareous materials and their chemical reactions. The pH of the system influences the distribution of carbonate species in aqueous systems. In an alkaline environment, the equilibrium system follows the following pattern as described by Rau et al., (1999).



Since the pH of all the systems were between 7.9 and 9.2, the dominant species was HCO_3^- with a smaller fraction as CO_3^{2-} . This means that HCO_3^- ions were beginning to convert to CO_3^{2-} ions, hence the system was not yet saturated with CaCO_3 , confirming that low Ca^{2+} release was due to inhibition by high alkalinity in the low P concentrated

wastewater. It has been reported that within the carbonate system, pH and HCO_3^- control most reactions in natural waters (MWH, 2005). Long retention times may allow counter ions of calcium source mineral such as CO_3^{2-} to increase in concentration resulting in further prevention of dissolution of the mineral, hence low calcium ion supply (Penn and McGrath, 2011). This was the case in this study as the longest retention time was 7 days.

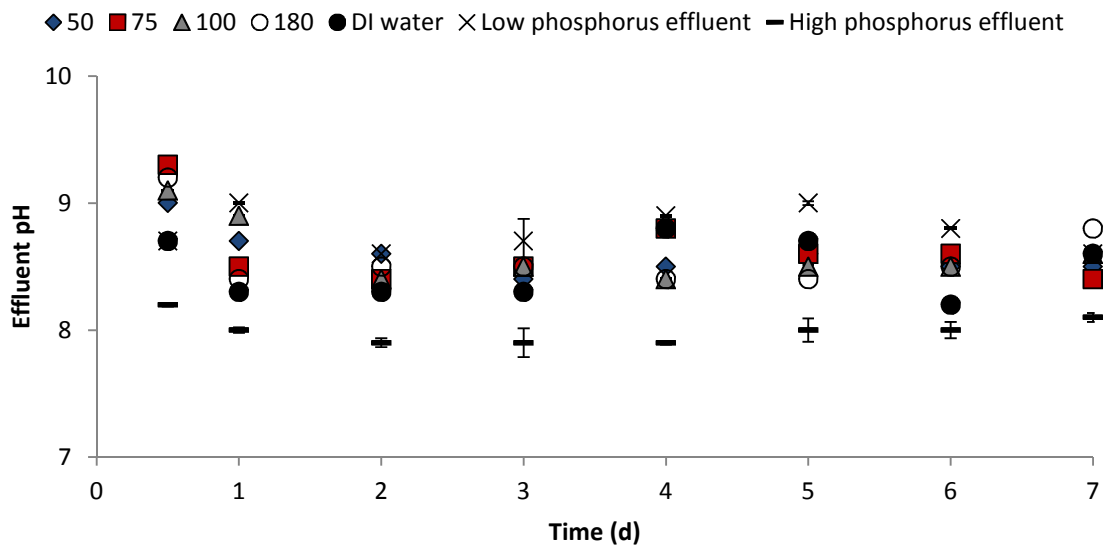


Figure 4.3: Variation of pH with alkalinity, low and high P effluents and DI water during steel slag dissolution

4.3.2.3 Batch kinetics using low and high phosphorus tertiary effluents

Phosphorus retention capacities increased with increasing time in the case of the high strength effluent system (Figure 4.4). To illustrate, the retention capacity increased from 0.01 mg TP g⁻¹ after 12 hours to 0.03±0.001 mg TP g⁻¹ after 7 days. In the case of low strength effluent, the capacity stabilised at around 0.003 mg TP g⁻¹ media from the second day until the experiment was completed.

The lowest capacity observed from a low phosphorus system was due to higher alkalinity. Some of the Ca²⁺ ions in the effluent and those released by the media were reacting with CO_3^{2-} to precipitate CaCO₃. High phosphate concentrations inhibit CaCO₃ formation while co-precipitation has been observed at low P concentration (Kleiner,

1988). This is confirmed by these results, where high P concentration in low alkalinity effluent had higher P retention capacity compared to low P effluent which had higher alkalinity. Another reason for low retention capacity is the lower P concentration in low P effluent system. The Initial P concentration and P retention capacity (mg TP g^{-1} media) are very positively correlated (Bowden et al., 2009); this agrees with these findings.

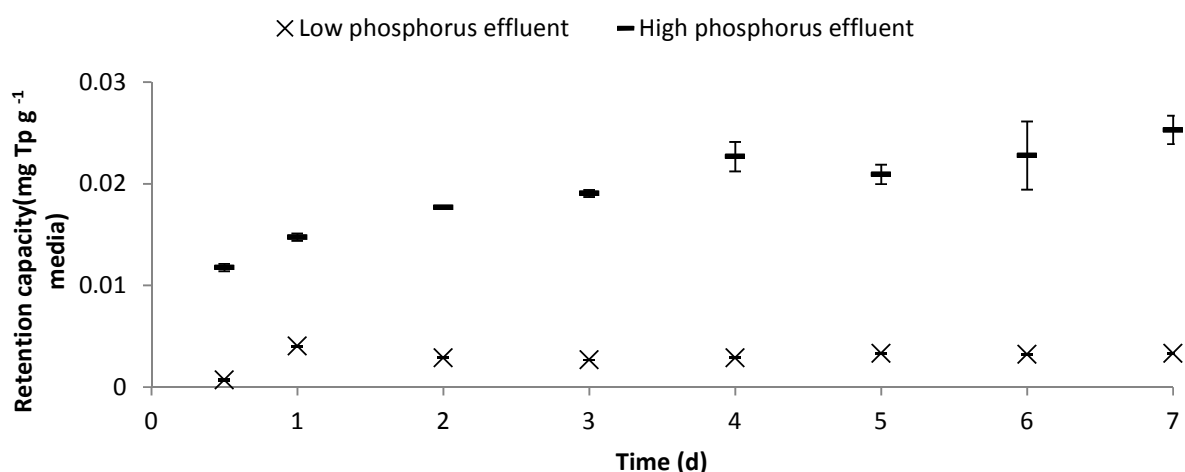


Figure 4.4: Impact of P concentration on P removal with time using steel slag (Initial P concentration high P = 8.2 mg TP L^{-1} , low P concentration = $0.99 \text{ mg TP L}^{-1}$).

Phosphorus precipitation has been shown to be low when the Ca^{2+} concentration is less than 50 mg L^{-1} and the pH is less than 8.0 (Joko, 1984). Since no pH elevation was observed in the high strength system, it is possible that limited CaP precipitation was occurring. This was confirmed by the concentrations of residual phosphorus in the systems which ranged between 5.9 ± 0.07 to $3.1 \pm 0.3 \text{ mg TP L}^{-1}$ from initial concentration of 8.2 mg TP L^{-1} (Figure 4.5). In the low phosphorus system, the residual P concentration range was 0.85 ± 0.01 to $0.33 \pm 0.0 \text{ mg TP L}^{-1}$ from an initial value of $0.99 \text{ mg TP L}^{-1}$ (Figure 4.5). This was despite the pH in the system being above 8.0 and even reaching 9.0. The efficiencies of the two systems after 7 days were 62.2 and 58%, respectively. Low efficiencies were due to low pH in the case of the high strength system and high alkalinity in the case of the low strength system. These results are similar to those observed by Joko (1984) in that P removal during batch tests were

observed to decrease as alkalinity was increased from 15 mg L⁻¹ to 550 mg L⁻¹ as CaCO₃ using NaHCO₃ as the source of alkalinity. The same was reported by Kim et al., (2006), in that the rate of P removal decreased with increasing alkalinity when a converter slag was used as reactive media, suggesting that alkalinity inhibits ACP crystallisation. This suggests that amorphous calcium phosphate (ACP) and CaCO₃ formations were competing for Ca²⁺ ions. In addition, Joko (1984) reported that under steady state conditions, when column tests were conducted for the same experiment, it was observed that effluent pH decreased as alkalinity decreased and concluded that pH was affecting the efficiency of P removal instead, but not alkalinity. If Ca²⁺ ions were the limiting factor, the solution pH would have to be elevated to approximately 10 to decrease the solubility of calcium phosphate, hence increasing CaP precipitation. For CaP precipitation, Ca²⁺ concentration should be 40 - 60 mg L⁻¹ for P levels between 15-20 mg P L⁻¹ (Bellier et al., 2006). The maximum P level in this study was 8.2 mg TP L⁻¹, confirming that calcium ions were consumed for other purposes such as CaCO₃ precipitation.

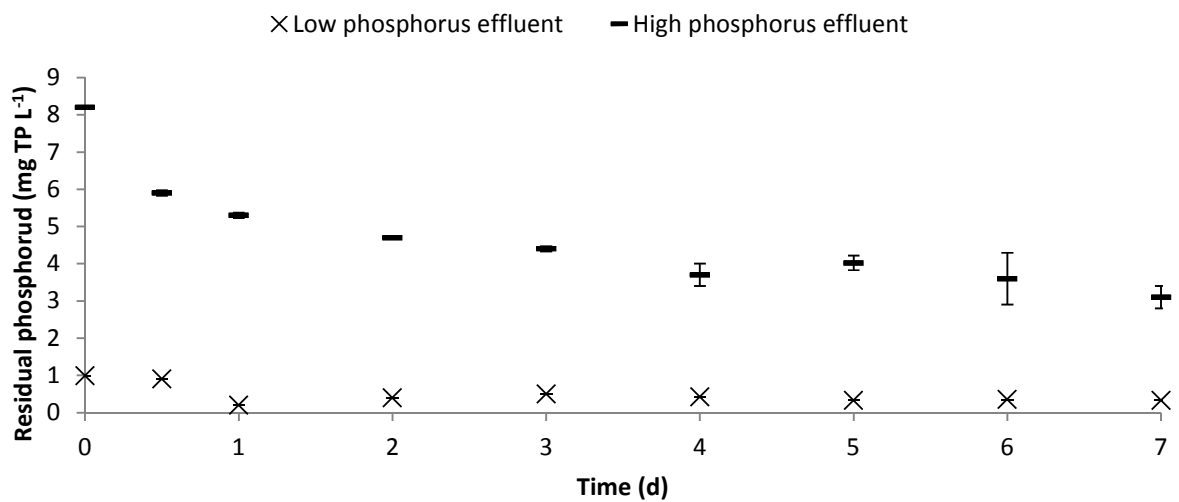


Figure 4.5: Variation of residual phosphorus concentration with time during steel slag batch tests

4.3.2.4 Batch equilibrium isotherm for P removal from high and low phosphorus effluents

Phosphorus removal increased as media dosage increased during the batch experiment with the high phosphorus effluent (Figure 4.6). From an initial dosage of 25 g L⁻¹, P removal was 19.9% and increased to 33.6% when the dosage was increased to 50 g L⁻¹ with a maximum removal of 87.1% at 100 g L⁻¹. The same results were observed by Chen et al., (2009) for P removal and recovery through crystallisation of hydroxyapatite using xonotlite as a seed crystal. High removal efficiencies corresponded to high residual Ca²⁺ ions observed at those media dosages. For example, the highest P removal of 87.1% at 100 g L⁻¹ dosage corresponded to 79.9 mg L⁻¹ residual Ca²⁺ ions (Figure 4.6). Background Ca²⁺ ions (40.1 mg L⁻¹) present in the wastewater also contributed to higher efficiency being observed.

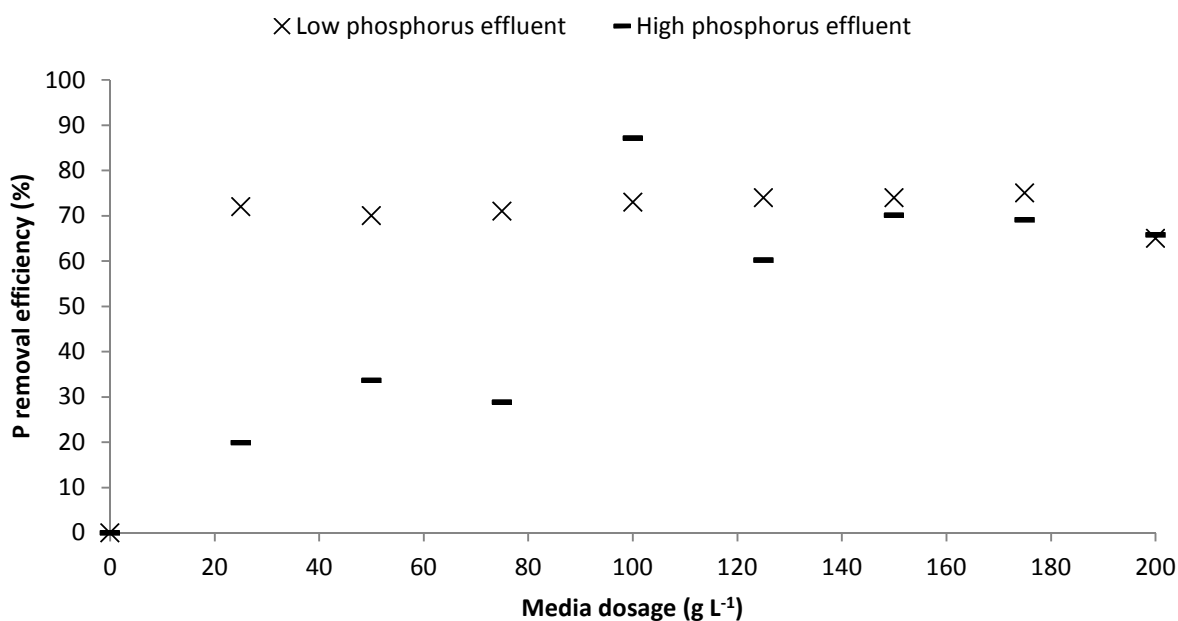
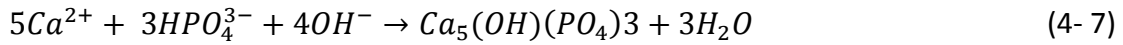


Figure 4.6: Impact of media dosage on P removal from high and low P effluents (C₀= 7.3 and 0.99 mg TP L⁻¹, 160 rpm, 48 hours shaking)

In the case of the low phosphorus effluent, P removal was constant with no significant increase observed but with increased media dosage. The minimum and maximum values were 65 and 75%, respectively corresponding to media dosages of 200 and 175 g L⁻¹. There were no residual Ca²⁺ ions in the case of low strength effluent suggesting all the available Ca²⁺ was used up during the reactions.

Ca/TP molar ration for kinetics and batch retention***Batch kinetics***

The Ca^{2+} : TP molar ratio ranged between 3.3 and 6.0 in the high strength system compared to between 33.4 and 63.6 for the low strength system (Table 4.2). Johansson and Gustafsson (2000) reported molar ratios of 2.9 to 4 for P removal by crystalline slags, similar to high strength results. Similar results were also reported by Chazarenc et al., (2007), where a molar ratio of 5.9 ± 0.2 was observed for EAF slag, and justified the higher ratio to other forms of CaP precipitation taking place. Theoretically, a Ca^{2+} : P ratio of 1.67 is required for hydroxyapatite (HAP) formation (Barca et al, 2012), however Kim et al., (2006) reported a ratio of 1.78 for P retention on converter slags indicating HAP crystallisation as it was within the 1.33 to 1.95 range reported in other studies. The large ratio observed in the current cases were due to some calcium ions being consumed by alkalinity as well as other forms of CaP precipitation such as octacalcium phosphate (OCP) and ACP other than HAP formation. The HAP reaction is reported to occur at a slow rate and species such as ACP and OCP act as precursors, hence a large Ca: P ratio (Lu et al., 2010) with OCP commonly reported as an intermediate phase in the HAP formation (Tervahauta et al., 2014). The other reason might be due to CaCO_3 precipitation and the presence of calcite or dolomite bearing media contributing to the high ratio (Bellier et al., 2006). This is confirmed by the presence of calcite in steel slag. In the case of the low strength system, alkalinity was a contributing factor as the same finding was reported by Joko (1984) in that alkalinity decreases P removal efficiency by CaP precipitation in a batch system. The pH was not a factor since the optimum value of 8.0 was exceeded at all times. Barca et al., (2012) reported ratios between 1.65 to 1.71 for P concentrations of between 5 and 100 mg P L^{-1} . Since residual Ca^{2+} ions were present at the end of their experiments, this indicates that there were still available ions for CaP precipitation even if CaCO_3 could have been precipitated. Various studies have suggested that phosphate and calcium ions react to precipitate calcium phosphate (Joko, 1984; Johansson and Gustafsson, 2000; Barca et al., 2012).



According to the above equation, Ca^{2+} ion concentration can limit HAP precipitation if the molar ratio of residual $PO_4\text{-P}$ concentration to residual Ca^{2+} concentration is higher than 0.6 (Barca et al., 2012). For both high and low strength effluents, the relationship was checked and the ratio was less than 0.6. This confirms that other forms of CaP precipitation were taking place as well as alkalinity consuming calcium ions. Barca et al., (2012) found that for P concentrations $> 10 \text{ mg P L}^{-1}$, Ca^{2+} limited HAP precipitation when EAF steel slag was used but not for BOF slag when treating synthetic P solutions of between 5-100 $\text{mg PO}_4\text{-P L}^{-1}$. The difference with this study is the source of P solution as real wastewater was used in this study which had background Ca^{2+} ions. When Barca et al., (2012) used real wastewater; it was found that Ca^{2+} ions limited HAP precipitation when a 100 $\text{mg PO}_4\text{-P L}^{-1}$ solution was used. This further confirms that pH was the limiting factor in a high phosphorus system and alkalinity consuming Ca^{2+} ions in a low phosphorus system.

Table 4.2: Ca: TP molar ratio from high and low P effluents

| Batch kinetics (Ca:P) | | |
|------------------------------------|-------------------------|--------------------------|
| Time (d) | Low phosphorus effluent | High phosphorus effluent |
| 0.5 | 36 | 3.3 |
| 1 | 33.4 | 5.5 |
| 2 | 43 | 5.2 |
| 3 | 57.4 | 6.0 |
| 4 | 50.7 | 4.3 |
| 5 | 52.8 | 4.7 |
| 6 | 38.1 | 4.3 |
| 7 | 63.6 | 5.2 |
| Batch equilibrium (Ca:P) | | |
| Media dosage (g L^{-1}) | Low phosphorus effluent | High phosphorus effluent |
| 25 | 27.7 | 5.1 |
| 50 | 25.5 | 0.4 |
| 75 | 29.2 | 1.9 |
| 100 | 32.1 | 2.4 |

| | | |
|-----|------|-----|
| 125 | 39.6 | 0.9 |
| 150 | 27.6 | 0.4 |
| 175 | 39.6 | 2.0 |
| 200 | 45.4 | 3.2 |

4.3.2.5 Batch equilibrium isotherm tests

Molar ratios of Ca^{2+} used/ P uptake for high phosphorus systems during batch tests were 5.1, 0.44, 1.9, 0.9, 0.4, 2.0 and 3.2, respectively for media dosages 25, 50, 75, 100, 125, 150, 175 and 200 g L⁻¹ (Table 4.3). The ratio of 0.9 corresponding to a media dosage of 125 g L⁻¹ is closer to 1, suggesting CaHPO₄ formation (Khadhraoui et al., 2002). The ratio of 0.4 is close to 0.5 suggesting the formation of Ca (H₂PO₄)₂ (Table 4.3). The lower values reflect that some reaction products participate as reactants during the formation of other CaP precipitates, hence low ratios (Doherty et al., 2009). Similarly, high ratio values were a result of the formation of precursors such as OCP and ACP, which are intermediate phases in the formation of HAP.

Table 4.3: Reactions occurring in solutions during calcium phosphate precipitation adopted from Doherty et al., 2009.

| Equation | Product name | Ca: P | |
|--|----------------------------------|-------|--------|
| $Ca^{2+} + 2H_2O_4 \leftrightarrow Ca(H_2PO_4)_2$ | Monocalcium phosphate (MCP) | 0.5 | (4-8) |
| $Ca^{2+} + HPO_4^{2-} \leftrightarrow CaHPO_4$ | Dicalcium phosphate (DCP) | 1 | (4-9) |
| $3Ca^{2+} + 2PO_4^{3-} \leftrightarrow Ca_3(PO_4)_2$ | Tricalcium phosphate (TCP) | 1.5 | (4-10) |
| $2CaHPO_4 + 2Ca_3(PO_4)_2 \leftrightarrow Ca_8H_2(PO_4)_6$ | Octacalcium phosphate (OCP) | 1.3 | (4-11) |
| $Ca_3(PO_4)_2 + 2Ca^{2+} + HPO_4^{3-} + H_2O$ $\leftrightarrow Ca_5(PO_4)_3OH + 2H^-$ | Hydroxyapatite (HAP) | 1.67 | (4-12) |
| $Ca_9(HPO_4)_6 \leftrightarrow Ca^{2+}$ | Amorphous calcium phosphate(ACP) | 1.5 | (4-13) |

The results are similar to those reported in the literature which ranged between 2.9 and 4 (Johansson and Gustafsson, 2000); 1.2 to 1.7 for EAF slag (Barca et al., 2012); 1.25 to 6.22 for blast oxygen furnace slag (Barca et al., 2012). An explanation for the difference has been previously given, in that molar ratios less than 1.67 indicate

phosphate retention on the media whereas ratios > 1.67 indicate CaCO_3 precipitation (Barca et al., 2012).

In the case of the low phosphorus system, the molar ratios were very high as the range was between 25.5 and 45.4 (Table 4.3). Calcium ions were used by alkalinity to precipitate CaCO_3 . This was confirmed by the results of the high phosphorus system where P concentration was 8.2 compared to 0.99 mg TP L^{-1} in the low phosphorus system; however the high phosphorus system had residual Ca^{2+} , whereas the low phosphorus system did not indicate Ca^{2+} was limiting HAP precipitation.

4.4 Conclusion

The dissolution of steel slag was evaluated under different alkalinities and wastewater effluents with high and low phosphorus concentrations in order to investigate how these two parameters influence the release of calcium ions from the media.

- The release of Ca^{2+} ions decreased with increasing alkalinity when either NaHCO_3 or CaCO_3 solutions were used. This was further confirmed by real effluents where wastewater with a high level of alkalinity had no or less residual Ca^{2+} ions after reacting with the steel slag. The influence of P concentration on Ca^{2+} release could not be concluded as the level of alkalinity in the effluents differed significantly.
- During dissolution in DI, Ca^{2+} ions increased with time suggesting a slow release reaction.
- The phosphorus retention capacity during the treatment of high phosphorus concentrated wastewater was higher than that treating lower concentrated wastewater.
- The molar ratios of Ca^{2+} used/P uptake indicate that, beside HAP formation, there were other forms of CaP formations taking place as well as the formation of CaCO_3 . The formation of CaCO_3 competes with P for Ca^{2+} ions resulting in more calcium being needed and a reduction of P removal.

4.5 Acknowledgements

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CHAPTER 5: EVALUATION OF STEEL SLAG AND PHOSFATETM AS REACTIVE MEDIA FOR PHOSPHORUS REMOVAL FROM TERTIARY EFFLUENTS

5 EVALUATION OF STEEL SLAG AND PHOSFATE™ AS REACTIVE MEDIA FOR PHOSPHORUS REMOVAL FROM TERTIARY EFFLUENTS

5.1 Introduction

Phosphorus removal is conventionally achieved by chemical dosing or biological adaptation in order to meet a 1 – 2 mg TP L⁻¹ discharge level. These conventional approaches do not align to the preferred approach for small sewage wastes (sub 2000 P.E.) where the preference is for "fit and forget" technologies that minimises chemicals, energy and maintenance whilst providing the appropriate treatment.

Passive systems such as filtration beds and constructed wetlands are better aligned to this small work preference and consequently development of appropriate P removal in such systems is of considerable interest in current research activity (Heal et al., 2004; Vymazal, 2011). A number of potential media have emerged for use in passive systems which include ochre, granulated blast furnace slag, opoka, serpentine, steel slag and many others. Of these materials, steel slag has been investigated by a number of researchers (Drizo et al., 2006, Chazarenc et al., 2007, Bowden et al., 2009, Barca et al., 2012). Steel slag has emerged from these studies as the current leading option and has been tested at field and full scale (Shilton et al., 2005; Chazarenc et al., 2007), although to date there are only a few pilot scale studies reported (Weber et al., 2007). Other studies have also indicated that ochre provides potential for P removal (Heal et al., 2004; Fenton et al., 2009).

Various experiments have been conducted through different conditions resulting in different P retention capacities (Table 5.1). To illustrate, Dobbie et al., (2009) used media sizes ranging from 6.4 – 9.5 mm in line with the > 5.0 mm recommended (Chazarenc et al., 2007). Furthermore, different EBCT contact times have been used to check the performance or design limits (Dobbie et al., 2009). Some research was also conducted at pilot and field scale (Heal et al., 2004; Chazarenc et al., 2007).

Table 5.1: Results of Ochre and steel slag by different researchers.

| Media | Contact time (hr.) | Type of solution and concentration | Media size (mm) | Mode of test | Capacity (g kg ⁻¹ media) | Reference |
|----------------|----------------------|--|-----------------|-------------------------|-------------------------------------|--------------------------|
| Ochre | 7, 23 and 26 minutes | Wastewater | 6.4-9.5 | Field test | 26 | Dobbie et al., (2009) |
| Ochre | Not stated | Synthetic solution 20 mg P L ⁻¹ | 0.6 | HF trough (pilot scale) | < 1 mg P L ⁻¹ | Heal et al., (2004) |
| Ochre | 24 | 24.3 to 1137 mg P L ⁻¹ | < 2.0 | Batch | 21 | Fenton et al., (2009) |
| AMD sludge | 0.02 | 0.13 mg P L ⁻¹ | 2.0 – 4.0 | Columns | Minimum 60% removal | Sibrell et al., (2009) |
| BOF steel slag | 4 – 22 | 1-300 mg P L ⁻¹ | 20 | Columns | 8.39 | Bowden et al., (2009) |
| EAF steel slag | | Wastewater | 5-10 | Pilot scale | 2.0 | Chazarenc et al., (2007) |
| EAF slag | | wastewater | 5-10 | Batch | 0.3 | Chazarenc et al., (2007) |

The objective of this study was to further evaluate the performances of the two media chosen from the initial screening process for P removal from tertiary effluent. The evaluation was through the identification of some key properties such as competitive retention, influence of pH, basicity and acidity on P removal and leachability of metals from the two media. The experiments were conducted through batch mode to

evaluate key properties, with pilot studies aimed at simulating field conditions where real tertiary effluent and recommended media sizes were used.

5.2 Materials and methods

Materials

Steel slag was sourced from the steel works at Tarmac and size graded to 5 – 12.5 mm in line with standard constructed wetland practice (Walters et al., 2014 in Press). The media was washed in DI water and left to dry before use. PhosphateTM is a manufactured media from acid mine drainage wastewater (Ochre) and made into pellets by mixing with lime and Portland cement (Heal et al., 2004). The media was used as supplied (5-12.5 mm) and washed prior to use in DI water. Small batches of both media were sieved and those of steel slag ground further to 0.5 – 1.0 mm for rapid normalised batch experiments.

Surface acidity and basicity of media

Surface acidity and basicity were measured on reduced media size particles by mixing with either 0.1 N NaOH or 0.1 N HCl for 48 hours at 160 rpm on an orbital shaker (Stuart, SSL1 manufactured by BIBBY STERLIN LTD located in the wastewater laboratory). The excess base or acid was then measured by titrating the filtered solution (0.45 µm) until it reached either pH 4.5 or 8.3, respectively as per Kim et al., (2005). All measurements were conducted in triplicates.

$$\text{Basicity or acidity} \left(\frac{\text{meq}}{\text{g}} \right) = \frac{\text{mL of titrant used} \times \text{meq wt of titrant}}{\text{mL of sample} \times \text{mass of media (g)}} \quad (5 - 1)$$

The impact of the media on solution pH was determined through a batch test with deionised water at a solid-water ratio of 1:5, as described by Penn and McGrath, (2011). Flasks containing mixtures were shaken on an orbital shaker at 160 rpm for 30 minutes before settling for 5 minutes. Controls contained only DI water and all measured were conducted in triplicate.

Metal leachability tests

A fixed base liquid set to mimic the basic water chemistry of the sewage effluent used later was prepared for the leachability tests based on an electrical conductivity of 913 $\mu\text{S cm}^{-1}$ (by dissolving potassium chloride) and an alkalinity of 100 mg.L^{-1} as CaCO_3 using sodium bicarbonate (NaHCO_3). The latter was used rather than calcium carbonate to differentiate with hardness and as calcium dissolution was a key variable in the trials. Two grams of media (0.5 – 1.0 mm) were mixed with 100 mL of solution (1:50 ratio) and the pH altered between 4 – 12 with either nitric acid or sodium hydroxide before being mixed on an orbital shaker for 24 hours at 160 rpm. Samples were filtered through 0.45 μm Glass microfiber (WhatmanTM filters) and stored in nitric acid (pH 4) at 4°C prior to analysis. Metals were analysed by Flame Atomic absorption spectrometer (Perkin Analyst 800) for Al, Ca, Fe and Mg. The spectrometer was calibrated before each analysis, rinsed using DI water between analyses and measured in duplicate.

Selective retention for phosphates, carbonates and sulphate ions

A 5 mg TP L^{-1} , 100 mg L^{-1} as CaCO_3 and 70 mg $\text{SO}_4^{2-} \text{L}^{-1}$ solution was prepared. Ammonium dihydrogen orthophosphate, sodium bicarbonate and ammonium sulphate of analytical grade were used. There was no buffering to avoid the addition of anions which could further compete with P for retention.

Batch equilibrium experiment

Predetermined masses of media and 100 mL of solution were placed into 250 mL Erlenmeyer flasks and agitated for 48 hours at 160 rpm. Mixtures were filtered through 0.45 μm . The amount of P retained was calculated from the mass balance equation described by Kumar and Kirthika (2009).

$$qe = \left(\frac{C_0 - C_e}{M} \right) L \quad (5 - 2)$$

Where q_e (mg g^{-1}) is the amount adsorbed at equilibrium, C_0 (mg L^{-1}) is the initial concentration, C_e (mg L^{-1}) is the concentration at equilibrium, L is the volume of effluent in litres, M (g) is the mass of media.

Fixed bed columns studies

Fixed bed experiments were conducted in 250 mm diameter Perspex columns operated in a downward flow with a constant head of 0.3 m. 500 mm of media (0.025 m^3) was placed in the column in 50 mm batches and compacted to ensure even porosity. The columns were then washed with DI water to remove dust before being placed into service by feeding sewage effluent with a Watson Marlow 520S peristaltic pump. Flow rates were checked on a daily basis to make sure that EBCT had not changed.

Sampling

Influent and effluent samples were collected at regular bed volumes. During effluent sampling, valves were opened to flush stagnant wastewater before filling sampling bottles. Analyses were conducted at Cranfield University wastewater laboratory. Samples for metal analysis were filtered using $0.45 \mu\text{m}$ filter papers and preserved by adding nitric acid (pH 4.0), and stored at 4C for later analysis.

Tracer studies

Background conductivity of the wastewater was determined. A known mass of sodium chloride was dissolved in wastewater and conductivity determined as per the protocol of Chazarenc et al., (2003). A known volumetric concentration of sodium chloride was fed (via a pulse injection) into the beds at the inlet. Samples were immediately taken at the outlet. The normalised tracer curve and all other parameters were determined as per MWH, 2005; Headley and Kadlec, 2007; Bodin et al., 2012.

SEM and X-ray diffraction

Elemental composition and mineralogy were analysed using scanning electron microscopy (SEM and x-ray diffraction respectively).

Phosphorus sequential extraction

Samples of exhausted media were collected from the steel slag and Phosphate™ beds after 226 and 140 days of operation, respectively. The experiment was conducted in triplicates using 20 g of media. The media was placed in 250 mL Erlenmeyer flasks, appropriate chemicals (Table 5.2) were added, and shaken for 24 hours on an orbital shaker.

Table 5.2: Protocol for P sequential extraction (adopted from Korkusuz et al., 2007 and Drizo et al., 2008)

| Fraction | Extractant | Procedure |
|-------------------|--------------------------|--|
| Loosely bound P | 1M NH ₄ Cl | 50mL of extractant and shaken for 24 hours |
| Al bound P | 0.1 M NaOH | 50mL of extractant and shaken for 24 hours |
| Fe bound P | 0.5 M NaHCO ₃ | 50mL of extractant and shaken for 24 hours |
| Ca bound P | 1 HCl | 50mL of extractant and shaken for 24 hours |
| Stable residual P | Concentrated HCl | 50mL of extractant and shaken for 24 hours |

Each media sample was washed twice with 25 mL of supersaturated sodium chloride solution between each step to remove P that could have been retained again by media and filtrates placed into relevant bottles to make 100 mL solutions. Mixtures were filtered through 0.45 µm filter papers and solutions placed into separate bottles. The amount of total P (TP) extracted was calculated from the equation described below:

$$TP = \frac{CxV}{M} \tag{5-3}$$

Where TP is in mg g⁻¹ media, C_e is the effluent concentration in mg TP L⁻¹, V is the volume in litres and M is the media mass (g).

Sample and data analysis

Data was analysed using IBM Statistical Product and Service Solutions (SPSS) statistics. Mean, standard deviation, minimum and maximum values of the descriptive statistics

were calculated. Total phosphorus was determined through phosphomolybdenum blue method photometrically using NOVA 60 photometer. The method is analogous to EPA 365.2+3, American Public Health Association (APHA) 4500-PE, and DIN EN ISO 6878. Ammonium nitrogen ($\text{NH}_4\text{-N}$) was determined photometrically according to EPA 350.1, APHA-NH₃ D, and ISO 7150/1 and DIN 38406 E 5, method. Nitrates ($\text{NO}_3^- \text{-N}$) were analysed through 4-nitro-2, 6-dimethylphenol method and determined photometrically. Sulphates (SO_4^{2-}) were also determined photometrically according to EPA 375.4 and APHA 4500 – SO_4^{2-} E method. Nitrites (NO_2^-) were determined according to EPA 354.1, APHA 4500- NO_2^- B, and DIN EN 26777 D 10 method. The amount of P retained in the beds was determined through integration between the limits of influent and effluent concentrations. The amount escaping with the effluent was determined through integrating between the effluent graph and the X-axis ($y = 0$). Conductivity, pH and total dissolved solids were measured using a Jenway pH and conductivity meter, 3540, calibrated each time before measuring. The bicarbonate (alkalinity) concentration was determined through titration as described in Standard Methods for the Examination of Water and Wastewater, 1998. Metal analysis was carried as previously described.

5.3 Results and discussion

5.3.1 Influence of media pH and surface acidity or basicity on performance

The pH and surface basicity of PhosphateTM were 10.6 ± 0.01 units and 5.6 ± 0.01 meq g^{-1} media, respectively compared to 11.6 ± 0.2 units and 6.6 ± 0.02 meq g^{-1} media respectively for steel slag (Figure 5.1). The P retention capacities determined during media screening were 0.47 and 0.51 mg TP g^{-1} media, respectively. The material surfaces are alkaline and basic in nature. Fenton et al., (2009) and Ruihua et al., (2011) reported pH values of 8.7 and 8.0, respectively for Ochre and acid mine drainage sludge from which PhosphateTM is made. The difference with this study could have been due to processing and palletising of the material during the manufacturing of PhosphateTM, which includes the use of lime. The link between pH, acidity or basicity could not be concluded since the media have similar capacities, pH and basicity.

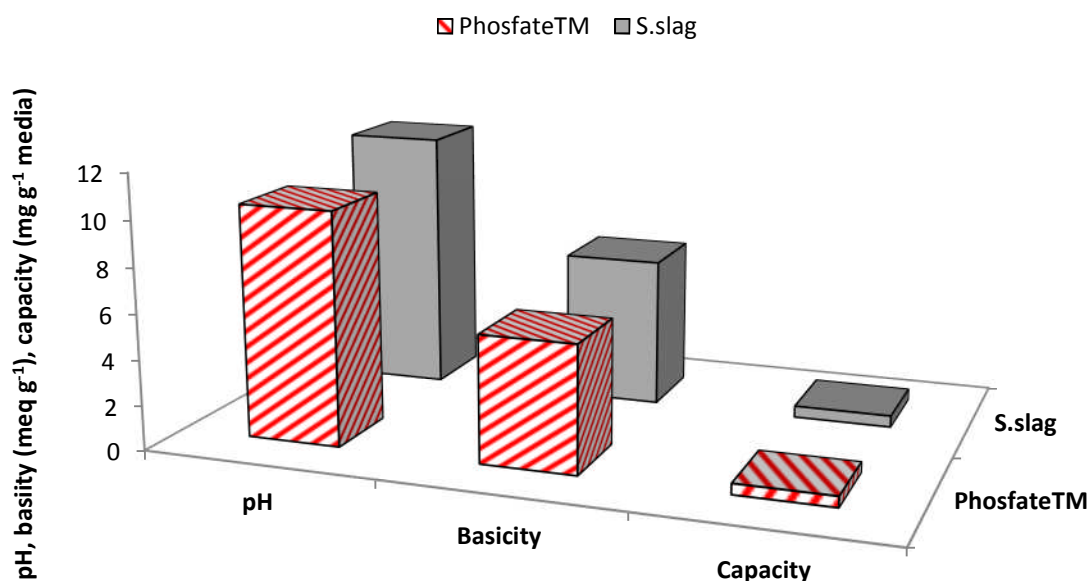


Figure 5.1: Impact of media pH, acidity and basicity on P retention capacity of steel slag and phosphateTM

5.3.2 Leachability in DI water and controlled pH

Leachability of Al, Fe and Mg in both DI and controlled pH were similar and low compared calcium which was high in controlled pH environment from both steel slag and PhosphateTM (Table 5.3). To illustrate, the maximum levels of Fe, Al, Mg and Ca in DI water were 0.2, 0.8, 1.4 and 4.2, respectively from PhosphateTM. The corresponding levels during controlled pH were 0.4, 0, 2.5 and 414 mg L⁻¹ at pH values of 6, all, 7 and 7, respectively.

Contrary to this study, Fenton et al., (2009) reported leachability of aluminium from two different supplies of ochre (from which PhosphateTM is manufactured) at 4.8±0.04 and 11.0±0.4 g kg⁻¹, as well as iron at 246.6±0.02 and 272.0±4.8 g kg⁻¹ from avoca and polkemmet ochre, respectively. In the case of calcium, the results from PhosphateTM are in agreement with the findings by Sibrell et al., (2009) for release from acid mine drainage sludge using DI water, and the highest level was 51.1 mg L⁻¹ and the minimum value being 0.5 mg L⁻¹.

Table 5.3: Results of leachability tests using DI water and controlled pH

| DI water test results concentration (mg L ⁻¹) | | | | | | |
|--|-------------------------|---------|--------|----------|---------|--------|
| Metal | phosphate TM | | | S. Slag | | |
| | Maximum | Minimum | Median | Maximum | Minimum | Median |
| Aluminum | 0.8 | 0 | 0.3 | 1.2 | 0.2 | 0.3 |
| Iron | 0.2 | 0 | 0 | 0.1 | 0 | 0 |
| Calcium | 42 | 0 | 30.4 | 41 | 15 | 31 |
| Magnesium | 1.4 | 0 | 0.1 | 0.5 | 0.02 | 0.04 |
| pH static test results concentration (mg L ⁻¹) | | | | | | |
| Media | Initial pH | Al | Fe | Ca | Mg | |
| phosphate TM | 4 | 0.0 | 0.0 | 261±25 | 2.2 | |
| | 6 | 0.0 | 0.4 | 47±1.7 | 0.2 | |
| | 7 | 0.0 | 0.0 | 414±34 | 2.5 | |
| | 8 | 0.0 | 0.0 | 109±9.5 | 1.7 | |
| | 10 | 0.0 | 0.0 | 18±1.0 | 0.4 | |
| | 12 | 0.0 | 0.1 | 1.1±0.06 | 0.03 | |
| Steel slag | 4 | 0.0 | 0.01 | 445±65 | 0.6 | |
| | 6 | 0.0 | 0.1 | 348±21 | 0.1 | |
| | 7 | 0.0 | 0.01 | 390±12 | 0.3 | |
| | 8 | 0.0 | 0.09 | 407±41 | 0.2 | |
| | 10 | 0.3 | 0.0 | 121±16 | 0.05 | |
| | 12 | 2.1 | 0.2 | 32±3 | 0.03 | |

In the case of steel slag, lower or acidic to near neutral pH values leached more calcium compared to alkaline values of 10 and 12. To illustrate, calcium concentrations were 445±65, 348±21, 390±12, 407±41, 121±16 and 32±3 mg L⁻¹ at pH 4, 6, 7, 8, 10 and 12, respectively (Table 5.3). The results shows that steel slag dissolution into calcium takes place more at acidic to near neutral conditions. Previous studies on the batch leachability of steel slag have shown that calcium is released from the media at higher concentrations (De Windt et al., 2011). For instance, 75 to 150 mg L⁻¹ of calcium was released during a trial using 0-1.0 mm media in ultrapure water (De Windt et al., 2011). In the case of Al, Fe and Mg, the results from steel slag were in agreement with the findings by De Windt et al., (2011) when DI water was used. De Windt et al., (2011) reported releases not exceeding 0.02, 0.1 and 1 mg L⁻¹, respectively in the case of Fe, Mg and Al.

The release of metals such as Al, Ca, Fe and Mg from reactive media is an indication that the dissolution of these elements is possible. These elements have a strong affinity for phosphorus; therefore their release will improve P retention through precipitation (Cucarella and Renman, 2009). However, excessive leaching can result in

a high initial performance which is short-lived for 5 years and followed by performance decline, hence a shorter longevity of the system. A similar scenario was reported in New Zealand for active slag filter treating pond effluent at a full scale level (Shilton et al., 2006).

5.3.3 Effect of competing ions

The maximum retention capacities during single and multisolute experiments for PhosphateTM were similar at 0.34 ± 0.001 and 0.32 ± 0.001 mg TP L⁻¹, respectively (Table 5.4). The presence of bicarbonates (HCO₃⁻) and sulphates (SO₄²⁻) had no impact on P retention capacity, consistent with a precipitation mechanism dominating over an adsorption pathway. The retention capacity of steel slag was 0.55 ± 0.001 mg TP g⁻¹ media during a single solute isotherm and reduced to 0.35 ± 0.001 mg TP g⁻¹ media during multisolute isotherm, which was a 36% reduction (Table 5.4). Either or both carbonates and sulphates compete with P during the precipitation phase. Differentiation is provided by Lee et al., (2012), who reported that sulphates had no effect on P retention by slag micropores, but instead carbonates reduced capacity by 21% when a 100 mM solution was used. The results show that PhosphateTM was increasing both sulphates and alkalinity into the solution (Table 5.4). Even during single solute, when only P was present in the solution, sulphates and alkalinity were detected during analysis indicating that the media released ions into the solution. The maximum, minimum and median values were 85.5, 12.5 ± 0.7 and 53.5 mg SO₄²⁻ L⁻¹, respectively. The same was observed during multisolute experiments as from an initial concentration of 70 mg SO₄²⁻ L⁻¹, the maximum, minimum and median concentrations in the filtrate were 180 ± 0.0 , 100 ± 0.0 and 150 ± 0.0 mg SO₄²⁻ L⁻¹. It has been reported that in soil, phosphates are preferred to sulphates, making sulphates susceptible to leaching (Geelhoed et al., 1997). Sulphur content decreased from $0.3 \pm 0.0\%$ by weight in fresh media to $0.17 \pm 0.1\%$ in exhausted media representing 43.3% of the observed difference. Pyrite mineral was present in the media (results not shown); the mineral is in most cases present in acid mine drainage sludge (Saria et al., 2006). The dissolution of the mineral occurs as described by Heal et al., (2004).

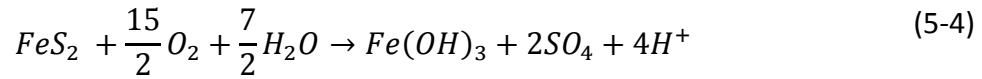


Table 5.4: Single solute and multisolute batch equilibrium experiments results

| | Phosphate TM | Steel slag |
|--|-------------------------|------------|
| P retention capacities (mg TP g⁻¹ media) | | |
| Single solute | 0.34±0.0 | 0.55±0.0 |
| Multisolute | 0.32±0.0 | 0.35±0.0 |
| Background sulphates (mg L⁻¹) | | |
| Maximum | 85.5 | 0.0 |
| Minimum | 42.5 | 0.0 |
| Median | 69.5 | 0.0 |
| Sulphates concentration in multisolute systems (mg L⁻¹) | | |
| Maximum | 180 | 69 |
| Minimum | 60 | 51.5 |
| Median | 156 | 62 |
| Background alkalinity (mg L⁻¹ as CaCO₃) | | |
| Maximum | 78 | 186 |
| Minimum | 42.5 | 46 |
| Median | 69.5 | 170 |
| Alkalinity in multisolute systems (mg L⁻¹ as CaCO₃) | | |
| Maximum | 165 | 263 |
| Minimum | 88 | 187 |
| Median | 125.5 | 212 |

In the case of steel slag, alkalinity increased with media dosage during single and multisolute experiments. When a phosphate only solution was used, the maximum, minimum and median values were 186, 46 and 170 mg L⁻¹ as CaCO₃, respectively. The same was observed during the multisolute experiment, as from an initial concentration of 100 mg L⁻¹, the maximum, minimum and median values were 263, 187 and 212 mg L⁻¹ as CaCO₃. These results agree with the report by Penn and McGrath (2011) that EAF slag removes background alkalinity as the material contains 766 mg CaCO₃ kg⁻¹.

It was found during dissolution of steel slag under different alkalinities that increasing alkalinity decreases Ca²⁺ ions released from the media, which will, in turn, reduce P

removal through CaP precipitation. The released calcium ions were, in turn, consumed by CO₃²⁻ ions to precipitate CaCO₃ thereby limiting CaP precipitation. This was supported by Korkusuz et al., (2007), who reported that materials containing calcium can retain low phosphorus when alkalinities are high.

5.3.4 Detailed batch experiments

5.3.4.1 Influence of initial concentration and pH on P removal

The capacity to remove P was similar in all trials irrespective of the initial pH, however varied with influent P levels (Table 5.5). For instance, the retention capacity was 0.02, 0.05 and 0.1 mg TP g⁻¹ media for initial P concentrations of 2.0, 5.0 and 10.0 mg TP L⁻¹, respectively. This is in agreement with the findings by Korkusuz et al., (2007) on blast furnace slag, where higher capacities were obtained when initial P concentrations were higher due to a greater driving force for mass transfer (Korkusuz et al., 2007). Results differ from previous observations (as seen in Chapter 3) where retention capacities of 0.51 and 0.47 mg TP g⁻¹ were observed for steel slag and PhosphateTM respectively with an initial P concentration of 5.6 mg TP L⁻¹. The difference can be attributed to media size which was 0.5 - 1.0 mm compared to 5.0 – 12.5 mm in the current test.

Table 5.5: Impact of initial concentration and pH on phosphorus retention

| Media | pH | Concentration (mg TP L ⁻¹) | | | | | |
|-------------------------|----|--|----------|----------|----------|----------|----------|
| | | 2 | | 5 | | 10 | |
| | | Capacity | Final pH | Capacity | Final pH | Capacity | Final pH |
| phosphate TM | 6 | 0.02 | 11.8 | 0.05 | 9.7 | 0.1 | 9.4 |
| | 8 | 0.02 | 11.8 | 0.05 | 9.9 | 0.1 | 9.9 |
| | 10 | 0.02 | 11.9 | 0.05 | 10.4 | 0.1 | 9.1 |
| | 12 | 0.02 | 12.2 | 0.05 | 10.6 | 0.1 | 11.0 |
| Steel slag | 6 | 0.02 | 9.9 | 0.05 | 11 | 0.1 | 10.9 |
| | 8 | 0.02 | 10.6 | 0.05 | 10.7 | 0.1 | 9.5 |
| | 10 | 0.02 | 12 | 0.05 | 9.9 | 0.1 | 10.1 |
| | 12 | 0.02 | 12.9 | 0.05 | 12.1 | 0.1 | 12.1 |

All effluent pH values had elevated by the time the experiments were ceased (Table 5.5). As P retention onto metal oxide surfaces decreases with pH increase (Bowden et al., 2009), precipitation is the most likely removal mechanism. The effect of pH on P

retention capacity of PhosphateTM is in agreement with the findings of Heal et al., (2004) who reported no significant effect of pH on P removal by ochre (initial pH levels studied were 4, 5, 7, 8.5 and 10) as a result of buffering capacity of the material.

It has been previously reported that high final pH is an indication that the phosphorus retention capacity has not been exhausted (Chazarenc et al., 2007). This was the case in this experiment, hence indicating that the materials were still releasing Ca²⁺ ions to precipitate phosphorus at the same time the OH⁻ ions released, elevating the pH.

5.3.5 Fixed bed column studies

Results from the column experiments using PhosphateTM revealed a removal efficiency of 98.0±0.7% in the first 9 bed volumes, which then decreased after 12 bed volumes (Figure 5.2). Subsequent samples were further analysed by filtering the effluent through a 0.45 µm filter, revealing effluent levels of 0.18 mg TP L⁻¹ compared to an unfiltered level of 2.7 mg TP L⁻¹. The phosphorus removal rate seemed not to be affected by the number of bed volumes treated at this stage due to the fluctuations in the influent observed as the soluble reactive phosphorus (SRP) remained below 0.1 mg L⁻¹. Particulate P can be removed through filtration and adsorption onto media (Babatunde et al., 2009). During initial media screening, through rapid small scale columns, it was observed that PhosphateTM breakthrough was reached after a few bed volumes despite higher capacity during batch tests. The samples were not filtered such that P was escaping as colloids in the effluent. The bed was acting as a sand filter and retaining P as particulate phosphorus (Chazarenc et al., 2007). Heal et al., (2004) reported that the form in which P occurs in wastewater can affect its removal through ochre as most researches have used synthetic solutions (soluble inorganic phosphorus). Reactive phosphorus occurs in particles > 0.45 µm in unfiltered soil media (Heal et al., 2004). This is in agreement with this study. In contrast, Dobbie et al., (2009) reported TP removal which was 85% initially and decreased with time when ochre was used for phosphorus removal from wastewater. No colloidal TP in the effluent was reported which could have been due to the lack of filtration carried out to compare filtered and unfiltered samples. However, it was suggested that a reduction in TP removal could have been due to the release of inorganic P associated with Fe³⁺

compounds (Dobbie et al., 2009). However these results are comparable to this study even though in this study it was observed that after 70 bed volumes, the efficiency of the bed increased even when filtering the samples was not carried out. During a bed volume of 70, media samples were collected from the bed for sequential P extraction. Phosphorus retained in the bed after 70 bed volumes (140 days) was 9613 mg or 69 mg d⁻¹. Phosphorus escaping in the outflow was 2730 mg TP or 19.5 mg TP d⁻¹. The mass extracted from media was 0.08 mg TP g⁻¹ media and from a total mass of 24.4 kg, 1952 mg TP could be extracted which is 20.3%. The amount of P that remains in the bed will then be 7661 mg TP in the form of loose colloids.

The steel slag bed was operated 92 days (46 bed volume) earlier than Phosphate™ bed during which time the influent phosphorus concentration was lower (Figure 5.2). The efficiency was initially high as 97% was removed after 1 bed volume but decreased with wastewater treated reducing to 89% as observed at bed volume 9. This trend continued such that removal was 78% after 36 bed volumes. A breakthrough (2.0 mg TP L⁻¹) was reached after 57 bed volumes (104 days).

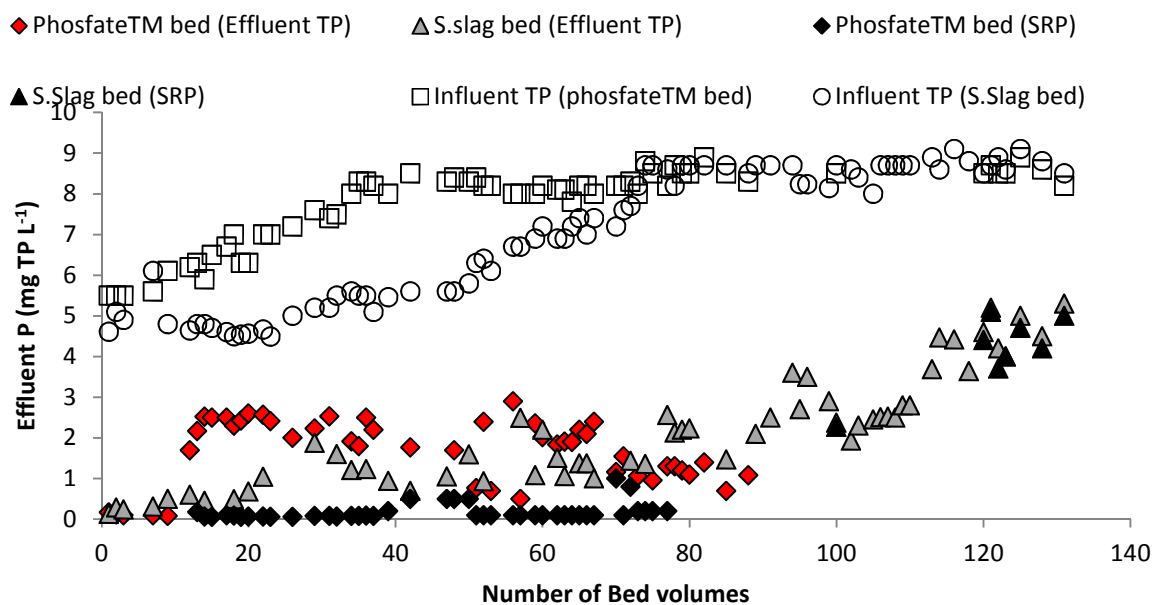


Figure 5.2: Influent and effluent TP, SRP from steel slag and phosphate™ beds

Phosphorus was not escaping as colloids as the amount of filtered and unfiltered effluents were similar. For instance, unfiltered concentration was 2.37 compared to 2.27 mg TP L⁻¹ for filtered effluent. There was fluctuating of effluent concentrations observed during the study period which was indicative of a slow release of ions (Ca²⁺, Fe³⁺ and Al³⁺) which precipitated phosphorus, and also slow reactions taking place during the processes. The fluctuation of effluent with bed volumes of wastewater treated observed in steel slag bed was comparable to the results of Drizo et al., (2008), when phosphorus retention capacity of EAF slag was investigated for treating dairy farm effluent. However, in general, the retention capacity decreased with time as observed in this study despite fluctuations of effluent concentrations. Similar trends were observed by Korkusuz et al., (2007) on phosphorus removal by blast furnace granulated slag, with influent and effluent averaging 6.61±1.78 and 3.18±1.82 mg TP L⁻¹ and the lower removal efficiency was attributed to the dilution of influent and flushing effect by the precipitation or rainfall. However, in general, the removal efficiency was observed to fluctuate with time as well. A subsequent decrease in P removal efficiency during rainfall was attributed to dilution and flushing effects in the bed, hence fluctuations. Subsequent concentrations were 5.1 and 5.2 mg L⁻¹ at bed volume 121 and 5.0 and 5.3 mg L⁻¹ at 131 bed volumes. The total phosphorus retained in the bed was 15932 mg, making a bed capacity of 637.3 g TP m⁻³ (2.4 g TP m⁻³ d⁻¹) or 0.34 g TP kg⁻¹ media retention. During the same period, the amount of phosphorus that escaped with the effluent was 11280 mg TP, 451.2 g TP m⁻³ (1.7 g TP m⁻³ d⁻¹). In terms of mass, the retention capacity of the bed was 0.34 mg TP g⁻¹ media and less than 0.51 mg TP g⁻¹ media determined during the batch experiment. Smaller diameter media (0.5-1.0 mm) were used during the batch experiment, which contributed to this difference. Phosphorus retention in steel slag bed (75%±14.0%) was closer to that reported by Shilton et al., (2006), which was 72% over 6 months of pilot studies. The difference was in influent TP concentration where Shilton et al., (2006) used an average of 8.4 mg TP L⁻¹, and in this study 6.9±1.6 mg TP L⁻¹ was used.

The amount of phosphorus retained in the bed after 113 bed volumes was 14420 mg or 64 mg TP d⁻¹. The amount of phosphorus that escaped in the effluent was 9266 or

41 mg TP d⁻¹. Phosphorus sequentially extracted was 0.27 mg TP g⁻¹ media. Given that the mass of media in the bed was 47.0 kg, and 12690 mg P (88.0%) could be extracted from the bed, 1730 mg could still be retained. In addition, the background P was 0.6 w/w% remaining in the bed and totalling 282 g. This makes a total of 283.7 g P in the bed, however the background could have been leached during low concentrated flows.

Comparing these two materials, PhosphateTM retained more phosphorus than steel slag. It was found that the ratio of PhosphateTM to steel slag capacity at any bed volume was between 1.2 and 1.4.

Effect of effluent pH

The influent pH into the PhosphateTM bed averaged 7.5±0.2 with the effluent pH reached 11.0 and was 11.75 by bed volume 29 (Figure 5.3). Wei et al., (2008) reported a decrease in P removal as pH increased using acid mine drainage (AMD) sludge from which PhosphateTM is made. The effluent pH during this study was very high making it favourable for CaP precipitation and HAP formation. It has been reported that near neutral pH is favourable for P removal using AMD (Wei et al., 2008). As mentioned earlier, elevated pH from the material is a result of mixing during pelletising the media, as Portland cement and lime were mixed with the materials. These two materials have basic or high pH.

From steel slag bed, the effluent pH was high during the first 4 bed volumes averaging 11.2±0.1, and then stabilised to 9.0. The initial pH elevation was due to the dissolution of minerals present in steel slag. Wu et al., (2011) reported effluent pH of 11.40 from steel slag bed due to dissolution of the calcium phase. High effluent pH indicates that P retention limit has not been reached (Chazarenc et al., 2007). There was no significance between effluent pH and effluent phosphorus (P = 0.6). It was observed that, in general, high pH suggested a likelihood of high phosphorus retained. The reduction in pH was due to the media not releasing enough OH⁻ ions to elevate pH, as well as the released ions being consumed during HAP precipitation (Joko, 1984).

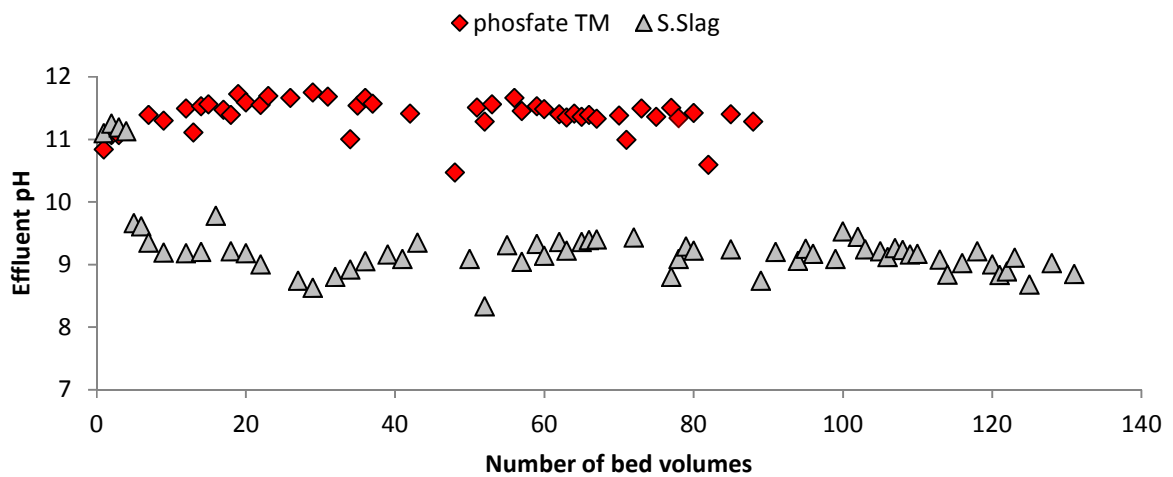


Figure 5.3: Change of pH with number of bed volumes treated by steel slag and phosphate™ beds.

The relationship between pH and P removed

The retention of phosphorus in the Phosphate™ bed occurred at elevated pH levels of between 10.5 and 11.75 (Figure 5.4). Heal et al., (2004) reported that pH has no significant effect on phosphorus removal when ochre was investigated for P removal, and this agrees with this study’s finding. In the case of steel slag, phosphorus removal was between pH 8.5 and 9.78 however initially removal was higher at pH 11 in the first four bed volumes before lowering to around 9.0 (Figure 5.4). After stabilising the highest removal rates were dominated by pH of above 9.0, with those below indicating a reduction in removal.

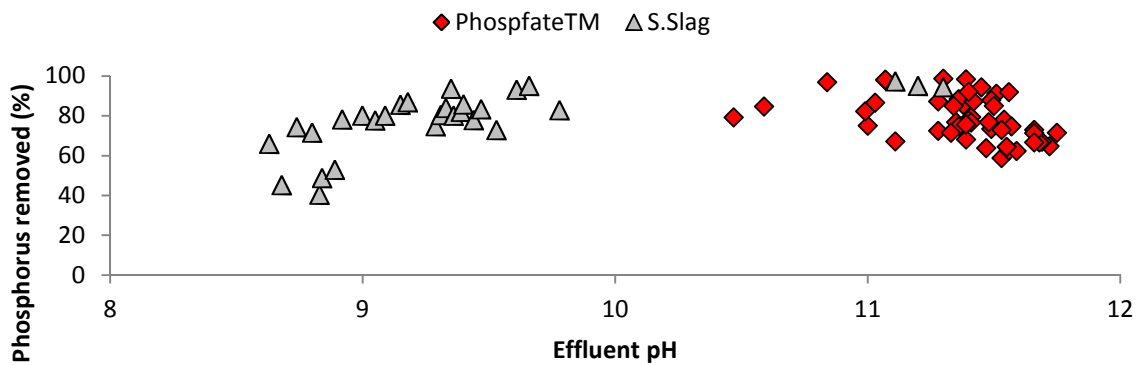


Figure 5.4: Impact of effluent pH on P retention onto Phosphate™ and steel slag beds

Influence of leaching metals on media performance

The release of metals such as Al, Ca, Fe and Mg from reactive media demonstrates that the dissolution of these elements is possible. These metals have a strong affinity for phosphorus; therefore their release will improve P retention through precipitation (Cucarella and Renman, 2009). However, excessive leaching can result in a high initial performance which is short-lived followed by decline in performance, hence shorter longevity of the system. Such a scenario was reported in New Zealand for an active slag filter treating pond effluent (Shilton et al., 2006).

The influent Al concentration into steel slag bed averaged 5.0 mg L^{-1} during the first 16 bed volumes and then fluctuated around 1.5 mg L^{-1} up to 72 bed volumes and then rose to 2.0 mg L^{-1} at 74 bed volume (Figure 5.5). The effluent concentrations were also observed to fluctuate, averaging 16.4 during the first 16 bed volumes and then 0.86 mg L^{-1} thereafter. Comparison of aluminium from fresh and exhausted media revealed an increase by 0.1 mg L^{-1} in the exhausted media (Table 5.6). AlPO_4 was detected in exhausted media, showing that aluminium was involved in the removal of phosphorus (Table 5.7). This indicates that the level of aluminum in the incoming flow was accumulating in the bed because of dead zones created from solid accumulations and then subsequently released through other pathways. In the case of calcium, influent and effluent average concentrations were 53.9 ± 21.4 and $46.5 \pm 16.8 \text{ mg L}^{-1}$, respectively which were in the range of 40 to 60 mg L^{-1} required for HAP formation (Joko, 1984). The levels of calcium in the fresh and exhausted steel slag were 4.6 and 4.8 mg L^{-1} , revealing a slight increase by 4.3%, indicating the role played by the presence of calcium in the influent which contributes to the efficiency of the system with regards to phosphorus precipitation. The exhausted media contained $10\text{CaO} \cdot 3\text{P}_2\text{O}_3 \cdot \text{H}_2\text{O}$ mineral, which indicates that calcium was involved in the removal of phosphorus. The presence of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ in both fresh and exhausted media suggests that this mineral was a seed for P during its own crystallisation process (Table 5.7). Comparing the influent and effluent Fe concentrations, it was observed that for up to 16 bed

volumes, the levels in the influent were higher than those in the effluent, with the difference averaging 1.0 mg L^{-1} in most cases. However, when monitoring of the metals was resumed after 45 bed volumes, it was observed that influent and effluent Fe concentrations were fluctuating with neither of the two higher than the other. A comparison of the levels of Fe in fresh and exhausted media indicated an increase by 1.0 mg L^{-1} in the exhausted media, which shows that there was accumulation from influent concentration. A new mineral, $(\text{Na, K, Ca})_2(\text{Fe, Mn})_5(\text{PO}_4)_4$, was found in the exhausted media indicating that Fe played a role in P removal through ligand exchange on the media surface as the level of Fe increased in the exhausted media.

The influent concentration of magnesium was stable, ranging between 8.6 and 9.5 mg L^{-1} throughout the monitored period. The effluent concentration was lower, ranging between 0.4 and 7.0 during the first 16 bed volumes and then rose to 8.1 and 8.5 mg L^{-1} between 45 and 74 bed volumes, suggesting that magnesium was either accumulating in the bed or involved in some reactions. However, fresh and exhausted media revealed similar concentrations of 0.3 mg L^{-1} , suggesting no release of magnesium. The X-ray diffraction results indicated the presence of $\text{NH}_4\text{Mg}(\text{PO}_3)_3$ which indicated that magnesium present in the influent was precipitating phosphorus.

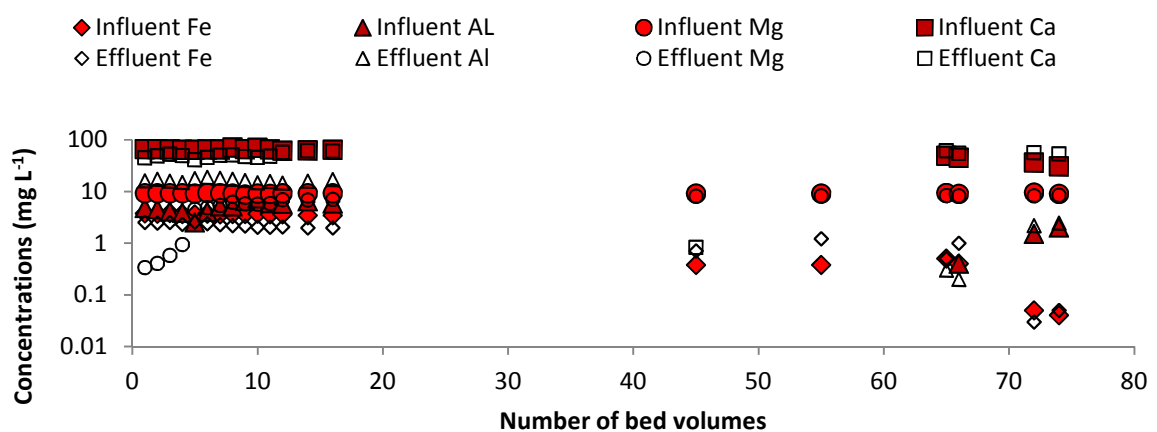


Figure 5.5: Correlations of metals in steel slag influent and effluent with bed volumes of wastewater treated

Table 5.6: Elemental composition of fresh and exhausted media from PhosphateTM and steel slag beds (n =3).

| Element | Fresh Steel slag mg L ⁻¹ | Exhausted steel slag mg L ⁻¹ | Δ S. slag bed mg L ⁻¹ | Fresh Phosphate TM | Exhausted Phosphate TM mg L ⁻¹ | Δ Phosphate TM bed mg L ⁻¹ |
|---------|--|--|-------------------------------------|-------------------------------|---|---|
| C | 1.6 | 0.0 | -1.6 | 0.9 | 4.6 | 3.7 |
| O | 6.7 | 6.7 | 0.0 | 5.4 | 4.8 | -0.6 |
| Mg | 0.3 | 0.3 | 0.0 | 0.1 | 0.05 | -0.05 |
| Al | 0.2 | 0.3 | 0.1 | 0.2 | 0.2 | 0.0 |
| Si | 0.8 | 0.8 | 0.0 | 0.5 | 0.3 | -0.2 |
| Ti | 0.07 | 0.1 | 0.03 | | | |
| P | 0.1 | 0.1 | 0.0 | | 0.01 | 0.01 |
| S | | 0.3 | 0.3 | 0.04 | 0.02 | -0.02 |
| Ca | 4.6 | 4.8 | 0.2 | 1.0 | 0.5 | -0.5 |
| Fe | 2.2 | 3.2 | 1.0 | 5.8 | 3.4 | -2.4 |
| Mn | 0.3 | 0.4 | 0.1 | | | 0.06 |
| K | | | | | 0.0 | |

The influent Fe concentration into PhosphateTM bed was higher than the effluent concentration (Figure 5.6). The concentrations in fresh and exhausted media were 5.8 and 3.4 mg L⁻¹, respectively revealing a decrease of 2.4 mg L⁻¹. These results indicate that Fe in the influent was precipitating phosphorus, which was also confirmed by the analysis of the media showing signs of Fe release. An analysis of the mineralogy in the exhausted media revealed the formation of FePO₄.2H₂O which was not present in the fresh media (Table 5.7). In the case of Al, the influent concentration ranged between 0.0 and 2.0 mg L⁻¹ compared to effluent concentration range between 0.2 and 3.6 mg L⁻¹. Fresh and exhausted media had the same concentrations of 0.2 mg L⁻¹. These results suggest that ligand exchange where OH⁻ ions are released and replaced by phosphate ions was the main P removal mechanism in the aluminum fraction of the media, and confirmed by the presence of AlPO₄ and Al₂₀P₂₀O minerals in exhausted media.

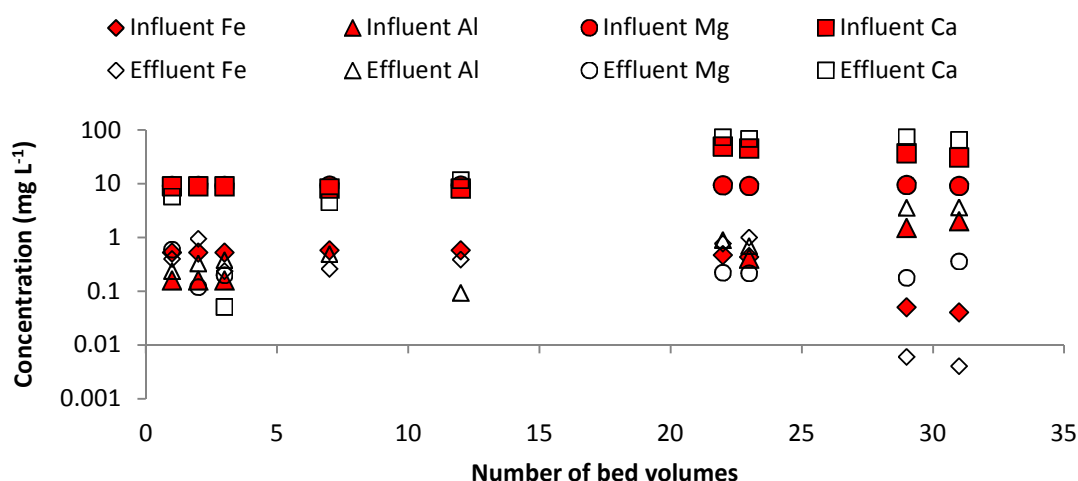


Figure 5.6: Correlations of metals in PhosphateTM influent and effluent with bed volumes of wastewater treated

The level of magnesium in the influent averaged 9.0 mg L^{-1} during the monitored period and the effluent levels were very low with a maximum value of 0.4 mg L^{-1} . In the case of calcium, the highest influent level was 49.2 mg L^{-1} at 22 bed volume. The corresponding effluent concentration was 73.04 mg L^{-1} . The concentration of calcium decreased from 1.0 mg L^{-1} observed in the fresh media compared to 0.5 mg L^{-1} in the exhausted media. Magnesium was involved in the retention of phosphorus as confirmed by the formation of $\text{Mg}_2\text{P}_2\text{O}_7$, $\text{MgP}_4\text{O}_{13}$, and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ in the exhausted media that was not detected in the fresh media (Table 5.7). This was an indication that magnesium ions present in the influent were used for precipitating phosphorus. The same was observed in the case of calcium where $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $2\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ were formed in the exhausted media. These results indicate that the metals present in the influent and those released from the media are all involved in the precipitation or retention of P in the bed

Overall, the findings suggest that P was retained through a combination of ligand exchange and precipitation consistent with the presence of these metals in both influents, and media is important for the removal of phosphorus from wastewater (Joko, 1984). Wei et al., (2008) reported 0.3 mg L^{-1} of Al leaching from AMD at pH 9, which was within the range observed in the current study. Fenton et al., (2009)

reported that the concentrations of some metals released from ochre exceeded EU (75/440/EEC, 1975) limits for surface water intended for the abstraction of drinking, as Fe was 44 g kg⁻¹. This agrees with this study for the leachability of aluminum and iron.

Table 5.7: X-ray diffraction results showing mineralogy of fresh and exhausted media.

| Fresh steel slag | Phosphate minerals from Exhausted steel slag Site A | Fresh phosphate TM | Exhausted phosphate TM |
|--|--|--|---|
| CaCO ₃ | Ca ₁₀ (PO ₄) ₆ (OH) ₂ | FeO ₄ | Mg ₂ P ₂ O ₇ |
| FeO | 10CaO.3P ₂ O ₃ .H ₂ O | Fe ₂ O ₃ | MgP ₄ O |
| MgP ₂ O ₇ | AlPO ₄ | FeO | AlPO ₄ |
| CaO ₂ .8H ₂ O | NH ₄ Mg(PO ₃) ₃ | FeO(OH) | Al ₂₀ P ₂₀ O |
| Ca ₁₀ (PO ₄) ₆ (OH) ₂ | FeO | Fe ₂ O ₃ .H ₂ O | FePO ₄ .2H ₂ O |
| CaSi ₂ | CaO | CaCO ₃ | CaHPO ₄ .2H ₂ O |
| CaMg ₂ | CaSi ₂ | CaO | 2CaO.P ₂ O ₅ .5H ₂ O |
| | Al ₈ Si ₇ /2Al ₄ C ₃ .SiC | CaO ₂ | MgNH ₄ PO ₄ .6H ₂ O |
| | MgP ₂ O ₇ | CaSO ₄ | Ca ₃ Al ₂ O ₆ |
| | (Na, K, Ca) ₂ (Fe, Mn) ₅ (PO ₄) ₄ | FeS | FeO ₃ .H ₂ O |
| | Ca ₃ (AlO ₃) ₂ | FeS ₂ | Fe(Al,Cr) ₂ O ₄ |
| | | Al ₂ O ₃ | |
| | | Fe ₂ O ₃ .H ₂ O | |

Retention of other ions in the bed

The maximum concentrations of sulphates in the influent and effluent of PhosphateTM bed were 72 and 233 mg SO₄²⁻ L⁻¹, respectively (Table 5.8). Alkalinity also showed an increase in the effluent as it increased from a maximum of 118 to 156 mg L⁻¹ as CaCO₃. In contrast, nitrate levels, reduced from a maximum concentration of 33.6 mg NO₃-N L⁻¹ in the influent to 26.3 mg NO₃-N L⁻¹ in the effluent, a 21.7% reduction.

Table 5.8: Influent and effluent concentrations of ions in PhosphateTM and steel slag beds (n = 20 for steel slag and 10 PhosphateTM leachability, n = 10 for both beds for competitive retention)

| Ion | Steel slag (mg L ⁻¹) | | | Phosphate TM (mg L ⁻¹) | | |
|-----|----------------------------------|-----------------|------|---|---------------|------|
| | Influent | Effluent | Δ | Influent | Effluent | Δ |
| Al | 4.5(0.0-7.3) | 15.8(0.0-18.9) | 3.1 | 0.2(0.0-2.0) | 0.44(0.1-3.6) | 1.6 |
| Fe | 3.6(0.0-3.8) | 2.1(0.6-2.6) | -1.2 | 0.5(0.0-0.6) | 0.4(0.0-1.0) | 0.6 |
| Ca | 64.5(0.0-70.5) | 48.9(0.0-61.60) | -8.9 | 8.9(8.2-49.2) | 8.7(0.0-73) | 23.8 |
| Mg | 9.2(0.7-9.5) | 5.8(0.0-8.5) | -1.0 | 9.1(9.0-9.5) | 0.2(0.0-0.6) | -8.9 |

| | | | | | | |
|-------------------------------|---------------|-----------------|-------|-----------------|----------------|-----|
| NH ₄ -N | 4.5(1.1-5.8) | 4.9(1.4-5.5) | -0.3 | 3.7(1.1-3.7) | 3.2(0.7-4.0) | 0.3 |
| NO ₃ -N | 26.6(20-55.3) | 21.5(15.2-28.5) | -26.8 | 27.2(18.5-33.6) | 17.1(8.6-26.3) | 7.3 |
| SO ₄ ²⁻ | 75(67-79) | 72.5(45-80) | 1.0 | 67(60-72) | 101.5(77-233) | 161 |
| Alkalinity | 94(60-104) | 102(88-117) | 13 | 86(60-118) | 102(80-156) | 38 |

N.B. - decrease

Almost similar results were observed from steel slag bed with an increase of maximum alkalinity observed as the influent and effluent concentrations were 104 and 117 mg L⁻¹ as CaCO₃, respectively. Maximum concentration of nitrates reduced by 48%, from influent concentration of 55.3 mg NO₃-N L⁻¹ to effluent concentration of 28.6 mg NO₃-N L⁻¹. Sulphates remained unchanged as the influent and effluent concentrations were 79 and 80 mg SO₄²⁻L⁻¹, respectively suggesting no retention in the bed.

5.3.6 Tracer studies

Actual flow conditions in the bed can be approximately defined by measuring residence time distribution obtained through experimental tracer studies and provides insights in relation to longitudinal dispersion, short circuiting of flow and dead zones (Tescano et al., 2009).

The two beds had similar residence time profiles (Figure 5.7) with lag times of 4.0 hours, and detected peak concentration at 28 and 32 hours in PhosphateTM and steel slag bed, respectively. The mean residence time in PhosphateTM bed was 48 hours compared to 38 hours in the case of steel slag bed; a 21% reduction. The presence of time lags is explained as being due to long inlet pipes between the tracer injection point and bed (Levenspiel, 1999). The difference in the mean residence time of the two beds suggests steel slag was experiencing channelling. This was confirmed as the indices of average retention time was less than 1.0 which is attributed to the angular structure of the media generally leading to different velocity profiles (MWH, 2005).

Velocity profiles in the vertical flow beds are assumed to be homogeneous; however this never occurs (Langergraber et al., 2009). This is due to the presence of stagnant waters, biofilm accumulation changing porosity of the bed (Langergraber et al., 2009).

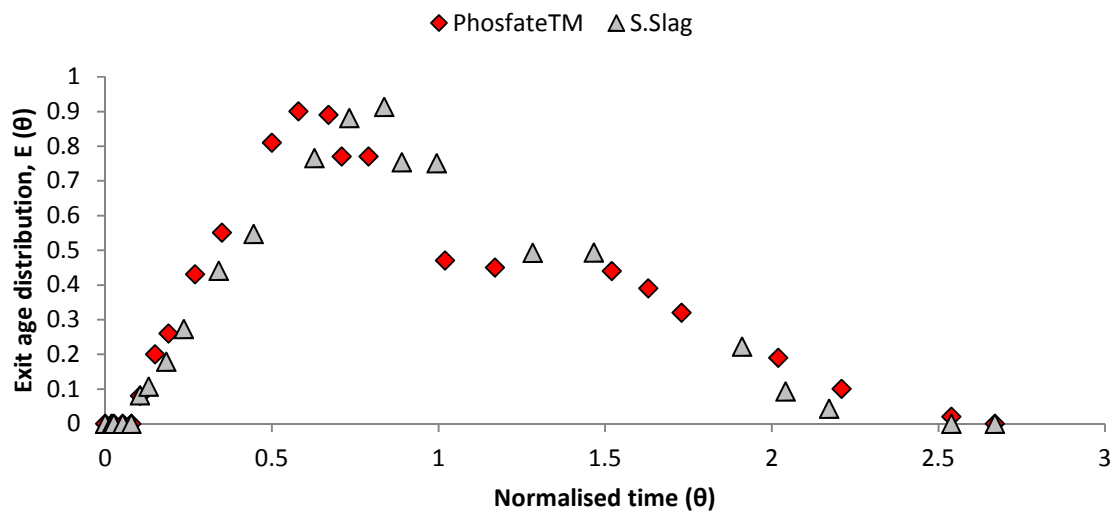


Figure 5.7: Exit age distribution curve of steel slag and Phosphate™ beds (EBCT = 48 hours)

The use of sodium chloride as a tracer resulted in a mass recovery of 53 and 56% respectively in Phosphate™ and steel slag beds. This was less than the 80-120% required for providing high levels of confidence (Bodin et al., 2012). Compared to other studies, Chazarenc et al., (2003) reported a 20% loss when using sodium chloride as a tracer for hydrodynamics of horizontal subsurface flow constructed wetlands. The results are comparable to some of the tracer studies by Giraldi et al., (2009) on the hydrodynamics of vertical flow constructed wetlands using a rhodamine WT tracer where recoveries between 58 and 88% were found. Lin et al., (2003) recovered 59% mass using rhodamine WT as a tracer on hydraulic characteristic of Prado Wetlands, California, USA, which was comparable to this study. Possible losses of tracer mass are retention in the bed, absorption and biological assimilation (Chazarenc et al., 2003). Since the tracer studies were conducted after the beds have been in operation for at least 40 bed volumes (80) days and biological growth were visible in the bed, biological assimilation was possible. The results from the two media beds indicate that the mean residence time from Phosphate™ bed was identical to nominal residence time (48 hours), indicating minimal short circuiting. In contrast, the lower mean residence time in steel slag bed suggests a potential short circuiting of flow in the bed. This will reduce treatment efficacy as the effective EBCT will be lower than designed. Such findings are

congruent with the fact that steel slag is known to be vulnerable to channelling due to its angular shape.

5.3.7 Phosphorus sequential extraction

Sequential phosphorus extracted from Phosfate™ was 61.7, 30.1, 6.4, 1.0 and 0.7%, respectively from iron bound, aluminum bound, loosely bound, stable residual pools bound and calcium bound fractions (Figure 5.8). In comparison, the amounts extracted from steel slag bed were 59.2, 18.8, 10.7, 9.1, and 2.1% from stable residual pools, loosely bound, aluminum bound, iron bound and calcium bound fractions, respectively.

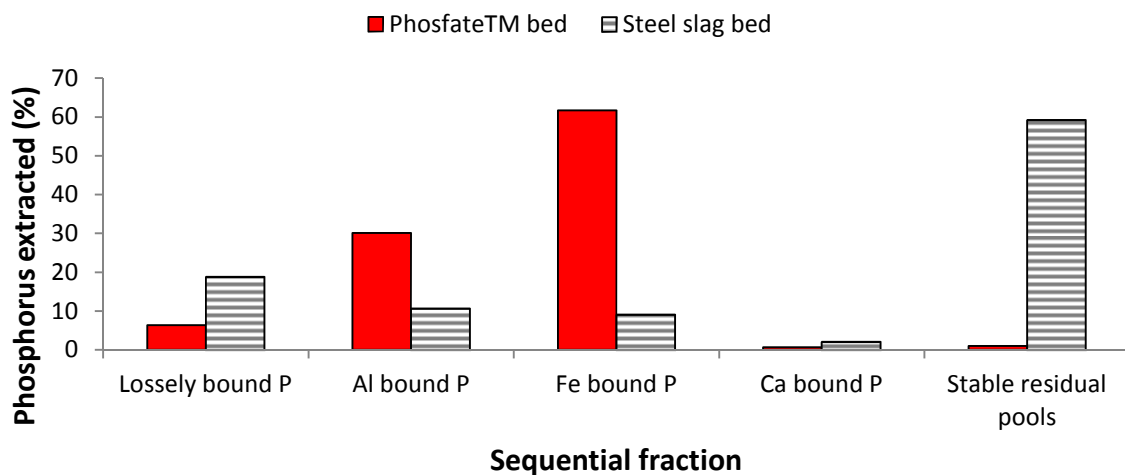


Figure 5.8: Phosphorus sequential extraction results from steel slag and Phosfate™ media (EBCT = 48 hours)

Phosphorus removal mechanism by Phosfate™ was through retention onto the iron fraction, however in steel slag bed precipitation through calcium (stable residual pool and Ca bound P) was the dominant removal mechanism. Retention onto the aluminium fraction was the second highest removal mechanism by Phosfate™, whereas a loosely bound fraction was the second highest in the case of steel slag. Heal et al., (2004) reported that the predominant removal mechanism by ochre is sorption onto iron and aluminum oxides/hydroxides and calcium carbonate. This is in agreement with the findings of this study, except that calcium fraction did not show any significant removal. In the case of steel slag bed, previous studies have suggested

the main removal mechanism being through CaP precipitation. This is in agreement with the findings by Drizo et al., (2008), however differs in this study only in that a loosely bound fraction had more P bound than Fe fraction.

These results have shown that the predominant P removal mechanism is calcium precipitation in steel slag whereas in the case of PhosphateTM, P is mainly bound to iron fraction. In addition, phosphorus mainly formed stable residual pools in steel slag. The fact that a higher amount of loosely bound P was extracted from steel slag than PhosphateTM can be attributed to colloidal P which was observed leaching from the bed compared to a lower value from steel slag bed.

The loosely bound P has been described as the material which can contain pore water P released from calcium carbonate associated phosphorus or due to leachability from biomass (Kaiserli et al., 2002). It has been explained by Kaiserli et al., (2002) that P extracted by NaOH represents the phosphorus bound to metal Al and Fe metal oxides, and this type is exchanged with OH⁻ ions and can be used to estimate short term and long term P in sediments. Calcium bound P has been described as the form sensitive to low pH which is mainly apatite and can be bound to carbonates. This P is stable and contributes to permanent burial in media (Kaiserli et al., 2002). From these descriptions, steel slag was found to retain P in a form that was stable and permanently bound (calcium fractions) and the formation of hydroxyapatite was the most likely formation of P. In the case of PhosphateTM, P was mainly removed through exchanging OH⁻ ions on the media surface with phosphate ions. This was the reason why the effluent pH was elevated throughout the experiment as OH⁻ ions were released.

The amount of phosphorus sequential extracted represent the material retained on the media which is an inorganic pool. It was reported earlier that PhosphateTM bed was releasing phosphorus in the colloidal form with the effluent leaving the bed. This form of P is colloidal and is the filtratable portion which can be retained by 0.45 µm filter papers. The organic P was very less noticeable from steel slag bed. The other form of P was trapped between void spaces of the media in the bed.

5.4 Conclusion

In this study, Phosfate™ and steel slag were evaluated as potential media for P removal from wastewater. Media properties were evaluated at batch scale and later at a pilot scale in order to assess properties which were not evaluated during the initial screening as well as performance when treating real wastewater.

- The two media are basic with elevated pH values which could lead to high effluents pH needing lowering before discharge. This was further confirmed during pilot trials where effluent pH from steel slag bed was initially high initially but stabilised after 4 bed volumes. In the case of Phosfate™, the effluent pH was above 11.0 throughout. Such pH values can also favour CaP precipitation as the main removal mechanism.
- Both media released high calcium under a pH controlled environment which can contribute to water hardness or improve media performance through CaP precipitation. High concentrations of aluminium were only observed from steel slag at elevated pH values of 10 and 12; this was further observed during the pilot scale trial.
- However trials revealed that alkalinity and sulphate ions reduced P retention capacity of steel slag but had no impact on P removal capacity of Phosfate™.
- During batch trials, it was observed that the retention capacity of both media increased with increasing P concentration but pH had no impact on P retention capacity. However, during pilot trials, elevated pH values from steel slag bed correlated with higher removal efficiency most of the times.
- Colloidal phosphorus was observed escaping with effluent from Phosfate™ bed but was minimal in the later stages of the experiment.
- Steel slag is vulnerable to channelling due to angular shapes of the media and hence the possibility of reduced performance of the bed. In contrast, Phosfate™ bed revealed a lower possibility of channelling due to the rounded shapes.

- It was concluded that Phosphorus removal by phosphateTM was predominantly through retention on iron oxides where as in steel slag precipitation through calcium was dominant.

5.5 Acknowledgements

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**CHAPTER 6: PHOSPHORUS REMOVAL FROM LOW AND HIGH
CONCENTRATED PHOSPHORUS EFFLUENTS USING STEEL SLAG**

6 PHOSPHORUS REMOVAL FROM LOW AND HIGH CONCENTRATED PHOSPHORUS EFFLUENTS USING STEEL SLAG

6.1 Introduction

Detrimental effects of algal bloom (eutrophication) in surface waters as a result of phosphorus (P) are well documented (Shilton et al., 2005; Bellier et al., 2006; Barca et al., 2012). The problems associated with eutrophication include degradation of water quality in water bodies, such as lakes and rivers resulting in depletion of dissolved oxygen (Xue et al., 2009). Sedimentation of storage impoundments when algae settle reduces volume resulting in incurring costs during the treatment of water abstracted for domestic purposes. Stringent wastewater quality regulations worldwide for P discharges have resulted in consent limits necessitating the need for research into suitable treatment technologies (Lee et al., 2010). Conventional technologies such as enhanced biological phosphorus removal and chemical precipitation are very expensive due to energy, chemicals, sludge, and operation and maintenance costs (Siracusa and Rosa, 2006). Recently, there has been wide research into the use of passive systems such as constructed wetlands as an alternative for phosphorus removal utilising reactive media (Berg et al., 2005; Sovik and Klove, 2005; Babatunde et al., 2009). The studies conducted have identified steel slag as a potential medium for use in passive systems (Chazarenc et al., 2007; Drizo et al., 2008; Lee et al., 2010). Various studies have been conducted through laboratory batch and pilot trials (Table 6.1). The results have shown that steel slag (EAF slag, BOF slag) has a promising performance for P removal from tertiary effluents. During these experiments, synthetic P solutions, some with unrealistic concentrations (500 mg P L^{-1}) have been used as well as real wastewater. The performance of steel slag in removing phosphorus from high and low strength effluents has not been compared in most literature. Studies have suggested desorption of P when influent concentration is 0.1 mg P L^{-1} (Pant and Reddy, 2003; Bowden et al., 2009). As shown in Table 6.1, different experimental conditions results in discrepancies in the understanding of media performance.

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6

Table 6.1: Previous studies results on P removal using steel slag

| Media | Type of solution and concentration (mg P L ⁻¹) | Media size (mm) | Mode of test | Capacity (mg g ⁻¹ media) | Reference |
|------------|--|-----------------|-------------------------------------|---|-------------------------------|
| EAF slag | Synthetic (5,10,25,100) | 5-10 > 10 | Batch | 0.09 to 0.28 | Barca eat al., (2012) |
| | Spiked real wastewater (5,10,25, 100) | 5-10 > 10 | Batch | 0.12 to 0.63 | Barca eat al., (2012) |
| BOF slag | Synthetic (5,10,25,100) | 5-10,> 10 | Batch | 0.03 to 2.49 | Barca eat al., (2012) |
| | Spiked real wastewater(5,10,25, 100) | 5-10. 10 | Batch | 0.14 to 2.5 | Barca eat al., (2012) |
| EAF slag | Wastewater (10) | 5-10 | Bench scale columns (15 cm x 35 cm) | 0.3 g P kg ⁻¹ slag | Chazarenc et al., (2007) |
| EAF slag | Wastewater (10) | 5-10 | Pilot scale (30 cm x 100 cm) | 2.0 g kg ⁻¹ slag | Chazarenc et al., (2007) |
| FS slag | Synthetic (11-107) | 5-10 | Column | 8.3 | Claveau-Mallet et al., (2013) |
| EAF slag | Synthetic 1-320) | 2.5-10 | Batch tests and column | 0.31-3.93 and 1.35 g kg ⁻¹ media | Drizo et al.,(2002) |
| EAF Slag | Wastewater (24.3) | 5-10 | Column | 1.72 g DRP kg ⁻¹ media | Drizo et al., (2008) |
| EAF Slag | Synthetic solution (20) | 2.5-10 | Colum(15.2 x 43.4-48.4 cm) | 2.3 g P kg ⁻¹ media | Drizo et al., (2006) |
| Steel slag | Wastewater (8.2) | 10-20 | Field trials | 1.23 g P kg ⁻¹ | Pratt and Shilton, (2010) |

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6

| | | | | | |
|-------------------------|---|--------------|------------------|--|-----------------------|
| Basic oxygen steel slag | Synthetic (1-300 mg P L ⁻¹) | >300 μm , >5 | Batch and column | 8.39 g P kg ⁻¹ | Bowden et al., (2009) |
| BOF slag | 10-500 mg P L ⁻¹ | 0.6 | Batch | 0.99-43.1, 0.98-41.6, 0.82-37.6 mg P g ⁻¹ | Xue et al., (2009) |

The purpose of this study was, therefore, to further investigate the use of steel slag as a retention media for phosphorus removal from high and low strength wastewater effluents. The main objective of this study was to evaluate the appropriate design and operating limits of fixed bed columns based on chosen media to establish the performance of passive systems. The second objective was to investigate the influence of P strength on steel slag performance. The average performance was compared by conducting experiments at three different sites through P concentration and empty bed contact time. Key parameters such as media retention capacity, leachability of media, effluent pH elevation, and competing effect of other anions in wastewater, P removal mechanisms and tracer studies were conducted for comparison. The study was conducted through pilot scale fixed bed columns.

6.2 Materials and methods

Three sites were chosen for conducting the experiments and these have been assigned the codes A, B and C at the request of the participating water companies. Sites A and C were treating higher strength P effluents and site B a low P effluent. Pilot scale experiments were conducted at all the sites. Steel slag was sourced from the steel works at Tarmac and size graded to 5 – 12.5 mm in line with standard constructed wetland practice (Walters et al., 2014). The media was washed in DI water and left to dry before use.

For sites A and B, fixed bed column experiments were conducted in 250 mm diameter Perspex columns operated in a downward flow with a constant head of 0.3 m. 500 mm of media (0.025 m³) was placed in the columns in 50 mm batches and compacted to ensure even porosity. The total mass in each column was 47.0 kg. The columns were

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag

Chapter 6

then washed with DI water to remove dust. Site A and B were fed with high and low P strength effluent, respectively in a downward flow motion using Watson Marlow 520S peristaltic pumps. Flow rates were checked on a daily basis using a stop watch and measuring cylinder (measuring flow rate and adjusted accordingly) to make sure that EBCT had not changed. After exhaustion, the media was removed and placed in different plastic containers and the procedure repeated for a different EBCT.

For site C, Polyvinyl chloride (PVC) cylinders of 16 cm diameter and 1000 mm height were used as fixed bed columns. Media diameters of between 5 and 7 mm were prepared in the same procedure described for site A and C. Media was placed into the columns to heights suitable for EBCT investigation and fed directly from a storage tank in downward motion using the same pumps described earlier. The experiments were conducted by another research student based at the site.

Sampling

Influent and effluent samples were collected at regular bed volumes. During effluent sampling, valves were opened to flush stagnant wastewater before filling sampling bottles. Analyses were conducted at Cranfield University wastewater laboratory. Samples for metal analysis were filtered using 0.45 µm filter papers and preserved by adding pH 4.0 nitric acid, and stored at 4°C ready for analysis.

Tracer studies

The protocol adopted was the same as that used by Chazarenc et al., (2003). A known mass of sodium chloride was dissolved in wastewater and conductivity was determined. The background conductivity of the wastewater was determined as well. A known volume of solution was fed (via a pulse injection) into the beds. Samples were immediately taken at the outlet. The normalised tracer curve and all other parameters were determined as per MWH (2005); Headley and Kadlec (2007); Bodin et al., (2012).

Media characterisation

Elemental composition and mineralogy were determined using scanning electron microscopy (SEM and X-Ray diffraction, respectively).

Phosphorus sequential extraction

Samples of exhausted media were collected from site A and B after 226 and 82 days of operation, respectively from 48 hours EBCT beds. The experiment was conducted in triplicates using 20 g of media. The media was placed in 250 mL Erlenmeyer flasks, appropriate chemicals (Table 6.2) added, and shaken for 24 hours on an orbital shaker. Flasks were removed and mixtures filtered through 0.45 µm.

Table 6.2: Protocol for P sequential extraction (adopted from Korkusuz et al., 2007 and Drizo et al., 2008)

| Fraction | Extractant | Procedure |
|-------------------|--------------------------|--|
| Loosely bound P | 1M NH ₄ Cl | 50mL of extractant and shaken for 24 hours |
| Al bound P | 0.1 M NaOH | 50mL of extractant and shaken for 24 hours |
| Fe bound P | 0.5 M NaHCO ₃ | 50mL of extractant and shaken for 24 hours |
| Ca bound P | 1 HCl | 50mL of extractant and shaken for 24 hours |
| Stable residual P | Concentrated HCl | 50mL of extractant and shaken for 24 hours |

Each media sample was washed twice with 25 mL supersaturated sodium chloride solution between each step to remove P that could have been retained by media, and filtrates placed into relevant bottles to make 100 mL solutions. Mixtures were filtered through 0.45 µm filter papers and solutions placed into separate bottles. The amount of total P (TP) extracted was calculated from the equation described below:

$$TP = \frac{Ce \times V}{M} \quad (6 - 1)$$

Where TP is in mg g⁻¹ media, Ce is the effluent concentration in mg TP L⁻¹, V is the volume in litres and M is the media mass (g).

For media regeneration, 0.5 – 1.0 mm media was placed in 25 mm diameter Perspex columns in the same procedure previously described. The columns were fed with 15 mg TP L⁻¹ solution at 10 minutes EBCT until saturation using the same pumps. The solution was drained from the column and left for 5 hours. A 0.1 M sodium hydroxide

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag

Chapter 6

(NaOH) (pH 13) solution was fed into the columns at 60 minutes EBCT until no P was stripped. Phosphorus was recovered from the spent regenerant by precipitating with calcium nitrate hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) at different pH values and times until optimum values were identified.

Sample and data analysis

The pH was measured using a Jenway pH and conductivity meter, 3540, after calibration. Total phosphorus was determined through the phosphomolybdenum blue method, photometrically using NOVA 60 photometer. The method is analogous to EPA 365.2+3, American Public Health Association (APHA) 4500-PE, and DIN EN ISO 6878. Ammonium nitrogen ($\text{NH}_4\text{-N}$) was determined photometrically according to EPA 350.1, APHA-NH₃ D, and ISO 7150/1 and DIN 38406 E 5, method. Nitrates (NO_3^- -N) were analysed through 4-nitro-2, 6-dimethylphenol method and determined photometrically. Sulphates (SO_4^{2-}) were determined photometrically according to EPA 375.4 and APHA 4500 - SO_4^{2-} E method. Nitrites (NO_2^-) were determined according to EPA 354.1, APHA 4500- NO_2^- B, and DIN EN 26777 D 10 method. Samples for metal analysis were filtered using 0.45 μm filter papers and preserved by adding nitric acid, and stored at 4°C for later analysis. Alkalinity was determined through the titration method as per Standard Methods of Water and Wastewater, 1998. Metal analysis was carried out as previously described (Chapter 5).

Data was analysed using IBM Statistical Product and Service Solutions (SPSS) statistics software. Mean, standard deviation, minimum and maximum values of descriptive statistics were calculated.

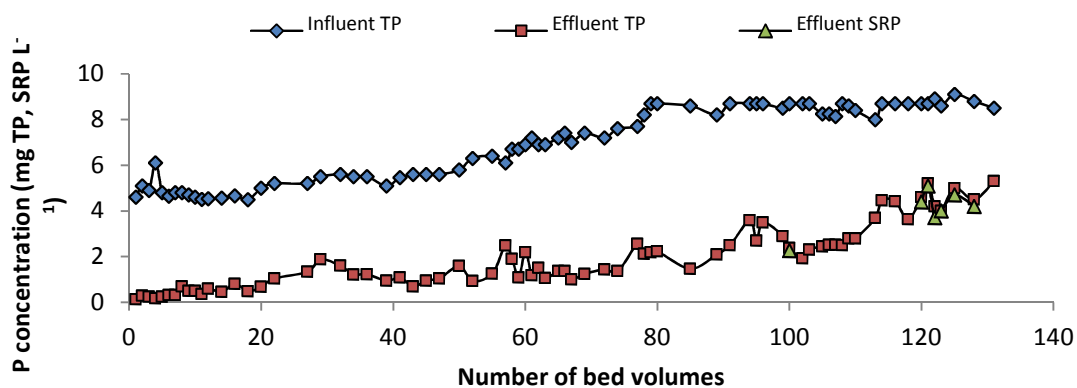
6.3 Results and discussion

6.3.1 Phosphorus removal from tertiary effluents

The effluent concentrations for all three sites were initially fluctuating with increasing bed volume (Figure 6.1). To illustrate, the effluent concentrations during the first four bed volumes were 0.13, 0.29, 0.24 and 0.18 mg TP L⁻¹ for site A (Figure 6.1 A), compared to 0.71, 0.66, 0.55 and 0.66 mg TP L⁻¹ in the case of site B (Figure 6.1 B) whereas for site C the concentrations were 0.51, 0.36, 0.35 and 0.39 mg TP L⁻¹ for the

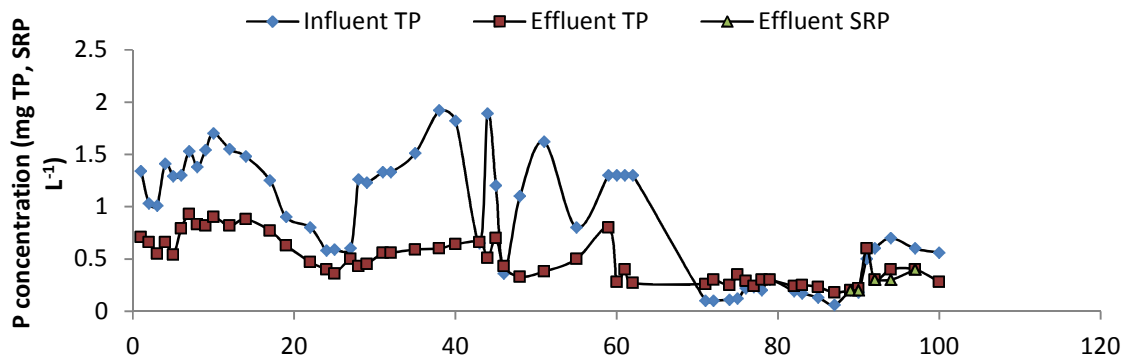
Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6

same duration (Figure 6.1 C). This trend was similar for most of the experiment. Site C was very efficient in the first 10 bed volumes compared to the other two. To illustrate, the performances were 95 ± 2.8 , 92.9 ± 3.8 and $45.2\pm 6.9\%$, respectively for sites C, A and B. However when site C was stopped after 55 bed volumes, its performance was similar to site A at 85.5 ± 8.5 and $84.3\pm 10.4\%$, respectively compared to $45.4\pm 20.4\%$ for site B. The performances of the other two beds remained similar, with fluctuations observed. After 109 bed volumes, the efficiency of site A was observed to decrease with any further influent treated. The efficiency ranged between 40 and 67%. The removal decreased significantly after 100 bed volumes, which is an indication that the bed was nearing exhaustion. The highest efficiencies observed for B were 73, 76.5, 78.5 and 79.2% corresponding to influent P concentrations of 1.89, 1.62, 1.3 and 1.3 mg TP L⁻¹, respectively. An interesting observation was made at site B between bed volumes of 71 and 90. The feed P concentration had dropped to 0.2 ± 0.1 mg TP L⁻¹ and the effluent concentration exceeded the influent at 0.3 ± 0.1 mg TP L⁻¹. After a bed volume of 91, the feed concentration increased to 0.6 mg TP L⁻¹ and effluent concentration remained at 0.3 mg TP L⁻¹, 50% retention. This observation is in agreement with Pant and Reddy (2003), who reported that P could be released from media during initial periods or when influent concentration is low.

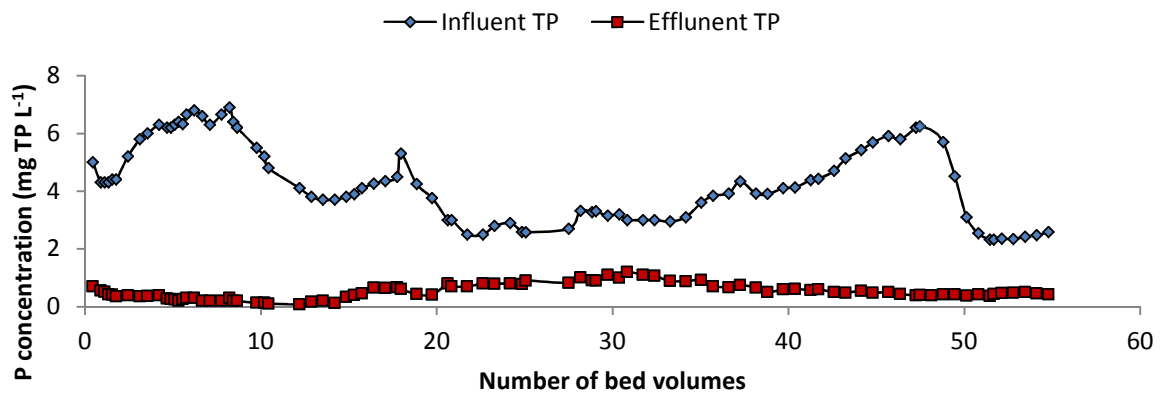


Site A

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6



Site B



Site C

Figure 6.1: Results of P removal from tertiary effluent at three different sites (A, B and C).

This concurs with Bowden et al., (2009), who reported that at low initial P concentrations (0.1 mg TP L^{-1}), desorption of phosphorus present in media is likely to take place. Sovik and Klove, (2005) observed that phosphorus in raw shell sand desorbed in distilled water, further confirming that the background P in media will be released when very dilute wastewater is passed through the bed. It was observed from the results that influent load influences performance as site B, treating low strength feed, had a lower efficiency compared to the sites treating higher strength feeds. The P retention capacities of the three sites increased with each bed volume treated. The media had not reached its maximum capacity when all three beds were stopped due to

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag Chapter 6

time constraints. The same findings were reported by Drizo et al., (2006) when determining the retention capacity of EAF slag for P removal in columns. The capacity was observed increasing with each P load added.

No documentation of previous studies comparing the removal of phosphorus from low and high phosphorus wastewater has been found in literature. This makes comparison with other studies difficult, though it has been reported in some literature that when phosphorus concentration in the influent is very low, the retained phosphorus is flushed out (Pant and Reddy, 2003, Bowden et al., 2009). However, the results revealed that steel slag can remove phosphorus from both influents with low and high phosphorus concentration, though efficiency is low in low concentrated influent. This was expected as the driving force is low during such cases.

The experiments were stopped at 55, 100 and 131 bed volumes for sites C, B and A, respectively. The corresponding removal efficiencies at the times were 84.3 ± 10.4 , 13.4 ± 70 and $75.3 \pm 13.9\%$, respectively. The initial high removal efficiency is consistent with an excess of calcium ions being released by the media (bed volume 1 to 85 for site A and 1 to 55 for site C). In the case of site B, it was difficult to explain due to efficiency dependence on influent P concentration in addition. As the process continues precipitation products coat the surfaces of the media restricting further release of calcium resulting in reduced P removal, (Bowden et al., 2009) (bed volume 86 – 131 for site A). The calcium ions in the feed were the most important for precipitating P (Bowden et al., 2009).

The capacity of the media at site A at the end of the run was $0.34 \text{ g TP kg}^{-1}$. The amount of P retained in the bed at 113 bed volumes (when media was sampled) was 14420 mg (64 mg TP d^{-1}) and the corresponding amount that escaped with the effluent was 9266 (41 mg TP d^{-1}). The amount extracted from the media after 113 bed volumes was $0.27 \text{ mg TP g}^{-1}$ media, and 12690 mg TP (88.0%) can be extracted from the entire bed (47 kg) such that 1730 mg is still retained in the bed.

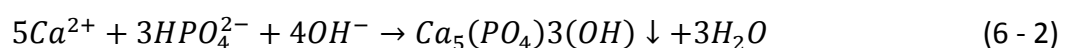
In the case of low strength feed (site B), the capacity remained the same at $0.03 \text{ g TP kg}^{-1}$ at bed volume 82 until the end of the run at 100 bed volume. The amount of P

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag Chapter 6

retained in the bed was 893 mg (5.45 mg TP d⁻¹) and 1460 (8.9 mg TP d⁻¹) escaped from the bed in the effluent, indicating that more P escaped than was retained. SEM results have indicated that steel slag used in this study contained background P of 0.6 w/w%, hence a total of 282 g P in the bed. Therefore part of the leaching P was the fraction that was already in the media. A total of 0.11 mg TP g⁻¹ media was extracted from the used sampled, hence 5170 mg TP can be extracted from the entire bed making a deficit of 4277 mg TP which could be extracted from background P in the media.

The corresponding capacity for site C was 0.09 g TP kg⁻¹ at the end of the run (55 bed volumes). The higher strength trials are in line with previous bench scale column data (0.3 g TP kg⁻¹), however are substantially lower than 2 g TP kg⁻¹ reported during pilot scale trials on a horizontal flow column treating effluent from a saturated horizontal flow constructed wetland treating fish farm wastewater (Chazarenc et al., 2007). The differences reflect variation in the P load and the total load applied which was 1.5, 2.0 and 15.9 g TP for sites B, C and A, respectively compared to an estimated total load of 216 g TP (after 6 months) in the case of the published study.

The average feed pH values of the three sites were 7.2±0.3, 8.5±0.7 and 7.5±0.6 for A, B, and C, respectively. During the first 4 bed volumes, the influent pH values were 7.3, 7.3 and 7.5±0.6 for A, B, and C, respectively. The effluent values increased to 11.1±0.1, 8.2±0.1 and 8.7±0.1, respectively (Figure 6.2). The efficiency corresponding to these pH values were 97.0, 53.2 and 93.8%, respectively. However, during a bed volume of 10, the effluent pH of site A decreased to 9.2 and efficiency dropped to 89.1%. The consumption of OH⁻ by HAP precipitation is believed to lower the effluent pH from steel slag columns (Joko, 1984) and the critical pH range was shown to be between 8 and 11.0. However as Ca²⁺ concentration increases, the critical pH for P precipitation is lowered (Joko, 1984). Therefore the observed pH decrease after 4 bed volumes was an indication of OH⁻ consumed during HAP formation.



Phosphorus removal from low and high concentrated phosphorus effluents using steel slag Chapter 6

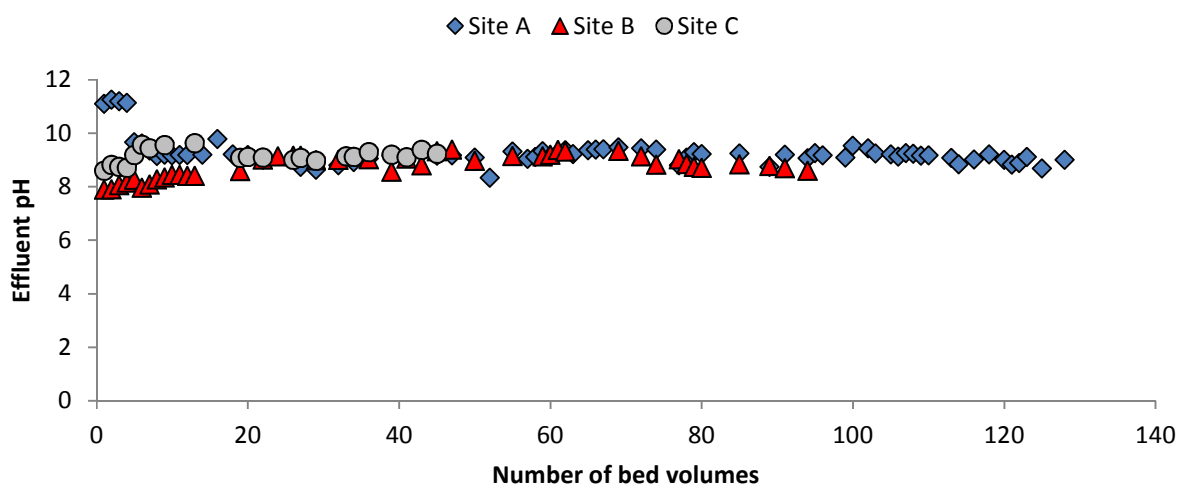


Figure 6.2: Change of pH with number of bed volumes treated at sites A, B and C.

Generally, pH was observed to fluctuate throughout the study especially for sites A and C. This was an indication of the slow release of Ca^{2+} and OH^- ions and the consumption of OH^- ions during HAP formation. It was also observed that in most cases pH elevation correlated positively with bed efficiencies, although were not consistent throughout the study period. To illustrate, high efficiencies were observed at pH 11.1, 11.13, 11.2 and 11.3 corresponding to efficiencies 97.2, 97, 95 and 94.3%. Lower efficiencies of 38, 45.1 and 48.6% corresponded to pH values of 8.89, 8.7 and 8.84, respectively for site A. The results show that although effluent pH values fluctuated at all the three sites, they remained between 8.0 and 9.0 which favoured CaP precipitation. Effluent pH values from sites A and C followed the same trend reported by Webber et al., (2007) from vertical flow pilot columns, using EAF steel slag, treating effluent from CW treating dairy farm wastewater. There was an initially elevated pH averaging 11.0 during the first 3 weeks of the experiment which gradually decreased and stabilised to between 8.5 and 9.0, the same as in this study. However, the results are in contrast to the findings of Lee et al., (2010) from steel slag bed treating dairy farm wastewater, which ranged between 10 and 12. Lower effluent pH was associated with shorter retention times (Lee et al., 2010). The effluent pH values > 8.0 observed at the three sites favour P removal through HAP precipitation (Sovik and Klove, 2005). The lower effluent pH observed from site B was due to high alkalinity in the wastewater which

suppressed the dissolution of steel slag to release Ca^{2+} and OH^- ions. In contrast, in this study, pH values are higher than those reported by Drizo et al., (2008) which stabilised to near neutral levels after two weeks and were below 9.0 for most of the 2.5 years of the experiment on Investigation of P retention and rejuvenation in EAF steel slag fed with dairy farm effluent. Previous studies on steel slag (Chazarenc et al., 2007; Webber et al., 2007) have raised a concern of the elevated effluent pH values. The effluent pH values observed during this study are within the limits of 5.0 to 9.0, except during initial phases. The elevated pH will need to be lowered before disposal into the environment, although such additional facilities will increase both capital and operational costs. Post treatment by passing effluent through gravel and peat moss beds has been suggested (Webber et al., 2007).

6.3.2 Effect of empty bed contact time on steel slag efficiency

Removal efficiency was observed to positively correlate with increasing EBCT (Figure 6.3). To illustrate, the combined results of sites A and C revealed increasing efficiencies of 47.3 ± 14.8 , 62.5 ± 8.1 , 65 ± 12.4 , 68 ± 20.6 , 74 ± 13.8 and $83.4 \pm 8.4\%$ as EBCT increased to 2, 6, 12, 24, 30 and 48 hours, respectively. The same trend was observed for site B, as efficiencies of 29 ± 7 and $34.6 \pm 8.0\%$ were observed corresponding to EBCT values of 12 and 48 hours, respectively.

Similarly, Webber et al., (2007) and Drizo et al., (2006) (named as others in the graph), reported the same observations. Removal efficiency from the study by Webber et al., (2007) was 74% for vertical flow columns (EBCT, 24 hours, media size 5-14 mm) treating wastewater from a horizontal flow constructed wetland system. This efficiency was similar to this study, where efficiency for 24 hours EBCT was $68 \pm 20.6\%$. The removal efficiency reported by Drizo et al., (2006) was 100% when EBCT was 55 hours for vertical flow columns, 152 mm diameter and media size 2.5-10 mm treating a synthetic solution of 20 mg P L^{-1} . The same observation was reported by Shilton et al., (2005), where efficiency increased as 5, 27, 35 and 50% when residence time increased to 3, 12, 48 and 96 hours for 150 mm diameter x 1000 mm column treating 10 mg P L^{-1} synthetic solution.

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag Chapter 6

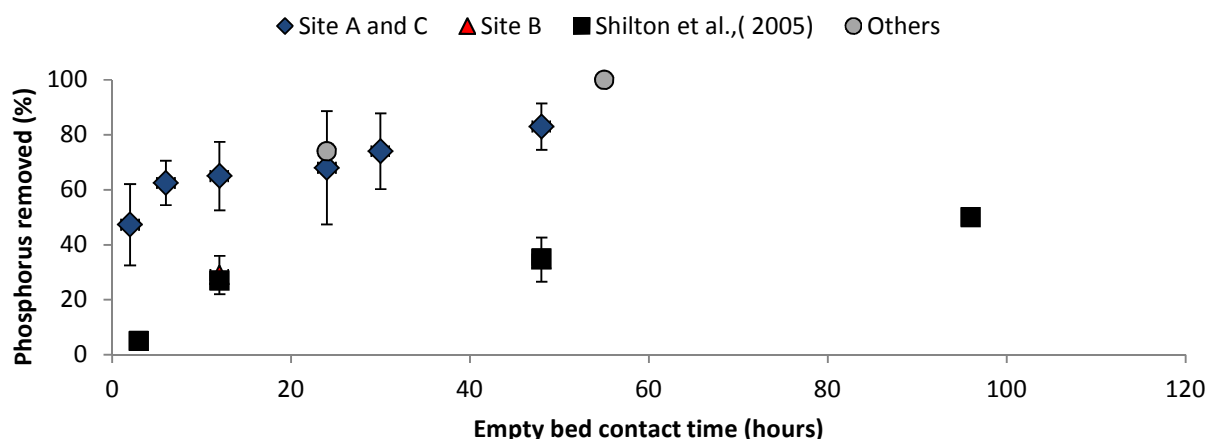


Figure 6.3: Impact of EBCT on P removal from wastewater using steel slag (Site A = 12, 30 and 48 hours EBCT, site C = 2, 6 and 24 hours EBCT, Others = Drizo et al., (2006) and Webber et al., (2007)).

These results show that contact time is crucial for the performance of passive systems utilising steel slag as a reactive media. This is in agreement with previous results (Chapter 4), where it was found that the dissolution of steel slag into Ca^{2+} in both DI water and sewage effluent was time dependent. The capacity of steel slag was also observed to increase with increasing contact time when treating high strength P effluent.

Effect of pH on removal efficiency

The results show that the operating range of steel slag in sites A and C was between pH 8.5 and 10.0, with only a few cases where the pH exceeded this level and this was at the beginning of the experiment (Figure 6.4). For site B, the operating range was between pH 8.0 and 9.0, with only a few cases below pH 8.0 or above 9.0. The effluent pH was not influential in P removal at the site B.

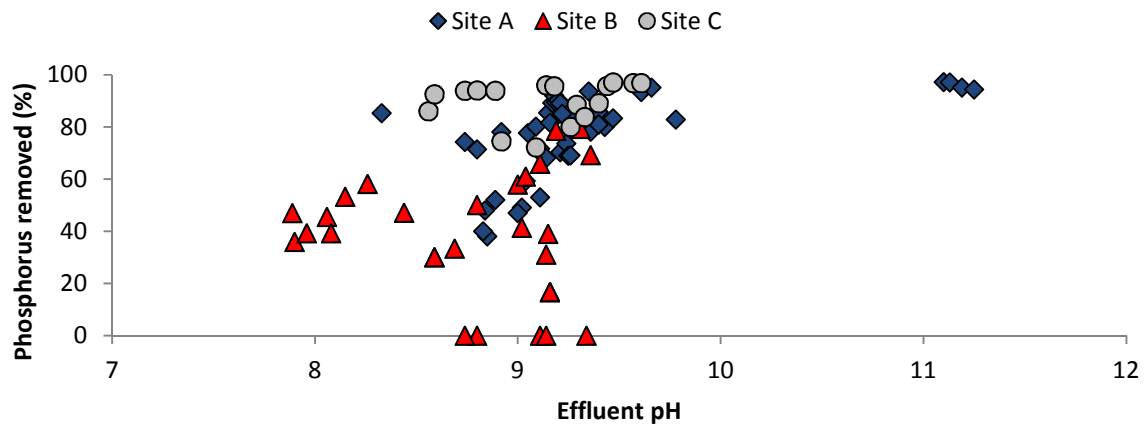


Figure 6.4: Impact of pH on P removal using steel slag

It was observed that influent concentration played a major role as well, since negative removal rates were observed at pH values greater than 9.0 when influent concentrations were very low. The lowest efficiency observed at site C was 74.4% corresponding to pH 8.92. This was expected since the site was stopped at bed volume 55 when the media was still releasing more Ca^{2+} ions. The observed highest efficiencies for sites B, A and C were 79.2, 97.2 and 97.0% corresponding to pH values 9.3, 11.0 and 9.5. Some studies have reported that high pH values in steel slag beds associate with high P removal. Webber et al., (2007) reported an effluent pH range for steel slag as high as 10.0 during the first 30 days and stabilising to 9.0 during the next 31 to 65 days and dropping to 8.5 thereafter. The effluent pH values reported by Drizo et al., (2006) for steel slag treating 20 mg P L^{-1} synthetic solution ranged between 10.6 and 11.4 from an initial value of 6.0. The reported removal efficiency was 100%. Except for low strength effluents, the findings suggest that high effluent pH values are associated with higher P removal. This concurs with the report by Bowden et al., (2009), who observed the highest P removal by steel slag when equilibrium pH was high during batch experiments.

6.3.3 Influence of leaching metals on media performance

Throughout this study, phosphorus is reported as total phosphorus by photometrically measurement after digestion for 30 minutes at $120 \text{ }^\circ\text{C}$. The detection limit ranged

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag Chapter 6

between 0.05 – 5.00 mg L⁻¹ and the samples were diluted with DI water, where accordingly any reference to phosphorus in the thesis refers to TP.

The level of Al in the influent into high phosphorus bed averaged 5.0 mg L⁻¹ during the first 16 bed volumes and then fluctuated as 1.5 mg L⁻¹ was detected at 72 bed volumes and then rose to 2.0 mg L⁻¹ at 74 bed volume (Figure 6.5).

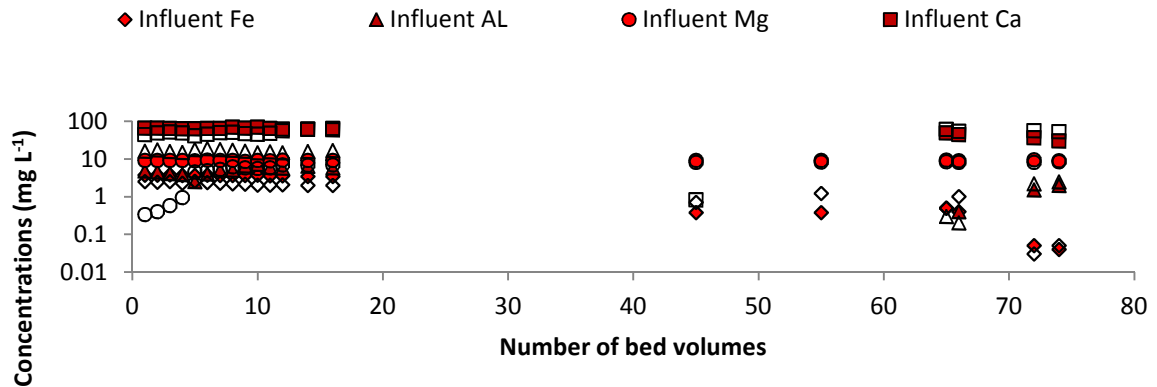


Figure 6.5: Correlations of metals in steel slag influent and effluent with bed volumes in high phosphorus wastewater

The effluent concentrations were also observed to fluctuate, averaging 16.4 during the first 16 bed volumes and then 0.86 mg L⁻¹ thereafter. A comparison of aluminium from fresh and exhausted media revealed an increase by 0.1 mg L⁻¹ in the exhausted media (Table 6.3). This was an indication that the level of aluminium in the incoming flow was accumulating in the bed because of dead zones created from solid build ups, and later on released through preferential pathways. AlPO₄ mineral was detected in exhausted media showing that Al was involved in the removal of phosphorus (Table 6.4). In the case of calcium, influent and effluent average concentrations were 53.9±21.4 and 46.5±16.8 mg L⁻¹, respectively which were in the range of 40 to 60 mg L⁻¹ required for HAP formation (Joko, 1984). Similar results were reported by Barca et al., (2012), where increased P retention capacities of EAF steel slag and BOF slag were observed when removing phosphorus from wastewater which had background Ca²⁺ concentrations between 40.9 to 48.6 mg L⁻¹ compared to removing P from synthetic solution without background Ca²⁺ ions. The levels of the same in the fresh and

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6

exhausted steel slag were 4.6 and 4.8 mg L⁻¹ revealing a slight increase by 4.3%, indicating the role played by the presence of calcium in the influent which contributes to efficiency of the system through phosphorus precipitation.

Table 6.3: Elemental composition of fresh and exhausted steel slag treating low and high P wastewater

| | Fresh Steel slag (Site A) | Exhausted steel slag (Site A) | Δ Site A | Fresh Steel slag (Site B) | Exhausted Steel slag (site B) | Δ Site B |
|---------|---------------------------|-------------------------------|--------------------|---------------------------|-------------------------------|--------------------|
| Element | mg L ⁻¹ | mg L ⁻¹ | mg L ⁻¹ | mg L ⁻¹ | mg L ⁻¹ | mg L ⁻¹ |
| C | 1.6 | 0.0 | -1.6 | 1.6 | 2.2 | 0.6 |
| O | 6.7 | 6.7 | 0.0 | 6.7 | 6.8 | 0.1 |
| Mg | 0.3 | 0.3 | 0.0 | 0.3 | 0.3 | 0.0 |
| Al | 0.2 | 0.3 | 0.1 | 0.2 | 0.2 | 0.0 |
| Si | 0.8 | 0.8 | 0.0 | 0.8 | 0.9 | 0.1 |
| Ti | 0.07 | 0.1 | 0.03 | 0.07 | 0.1 | 0.03 |
| P | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 |
| S | | 0.3 | 0.3 | | 0.02 | 0.02 |
| Ca | 4.6 | 4.8 | 0.2 | 4.6 | 4.8 | 0.2 |
| Fe | 2.2 | 3.2 | 1.0 | 2.2 | 2.9 | 0.7 |
| Mn | 0.3 | 0.4 | 0.1 | 0.3 | 0.4 | 0.1 |
| K | | | | | | |

There was 10CaO.3P₂O₃.H₂O mineral in the exhausted media indicating that calcium was involved in the removal of phosphorus. The presence of Ca₁₀(PO₄)₆(OH)₂ in both fresh and exhausted media suggests that this mineral was a seed for P its own crystallisation process. Comparing the influent and effluent Fe concentrations, it was observed that up to 16 bed volumes, the levels in the influent were higher than those in the effluent, with the difference averaging 1.0 mg L⁻¹ most of the time. However, at 45 bed volumes, it was observed that influent and effluent concentrations were fluctuating with neither of the two higher than the other. A comparison of the levels of Fe in fresh and exhausted media indicated an increase by 1.0 mg L⁻¹ in the exhausted media, indicating that there was accumulation from influent concentration. A new mineral, (Na, K, Ca)₂(Fe, Mn)₅(PO₄)₄, was found in the exhausted media indicating that Fe also played a role in P removal through ligand exchange on the media surface as the level of Fe increased in the exhausted media.

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6

The influent concentration of magnesium was stable, ranging between 8.6 and 9.5 mg L⁻¹ throughout monitoring period. The effluent concentration was lower, ranging between 0.4 and 7.0 during the first 16 bed volumes, and then rose to 8.1 and 8.5 mg L⁻¹ between 45 and 74 bed volumes, suggesting that magnesium was either accumulating in the bed or involved in some reactions. However, fresh and exhausted media revealed similar concentrations of 0.3 mg L⁻¹ suggesting no release of magnesium. X-ray diffraction results indicated the presence of NH₄Mg(PO₃)₃ which suggests that magnesium present in the influent was precipitating phosphorus (Table 6.4).

Table 6.4: X-ray diffraction results of fresh and exhausted steel slag treating low and high phosphorus influent.

| Fresh steel slag | Phosphate minerals from Exhausted steel slag Site A | Site B |
|--|--|--|
| CaCO ₃ | Ca ₁₀ (PO ₄) ₆ (OH) ₂ | Fe ₃ O ₄ |
| FeO | 10CaO.3P ₂ O ₃ .H ₂ O | Fe ₂ O ₃ |
| MgP ₂ O ₇ | AlPO ₄ | FeO |
| CaO ₂ .8H ₂ O | NH ₄ Mg(PO ₃) ₃ | CaCO ₃ |
| Ca ₁₀ (PO ₄) ₆ (OH) ₂ | FeO | MgP ₂ O ₇ |
| CaSi ₂ | CaO | SiO ₂ |
| CaMg ₂ | CaSi ₂ | AlFeO ₃ |
| | Al ₈ SiC ₇ /2Al ₄ C ₃ .SiC | Ca(H ₂ PO ₄) ₂ .H ₂ O |
| | MgP ₂ O ₇ | Ca ₅ Cl(PO ₄) ₃ |
| | (Na, K, Ca) ₂ (Fe, Mn) ₅ (PO ₄) ₄ | |
| | Ca ₃ (AlO ₃) ₂ | |

The concentration of calcium into the low phosphorus bed ranged between 53.0 and 85.0 mg L⁻¹ and the range in the effluent from the same bed was 0.6 to 57.0 mg L⁻¹ respectively (Figure 6.6). As for magnesium, the influent and effluent concentration ranges were 16.8 to 24.4 and 18.0 to 24.4 mg L⁻¹, respectively. Aluminium concentration in the influent was very low compared to the effluent level as ranges of between 0.0-2.8 and 0.0-9.0 mg L⁻¹ were observed, respectively. Iron was not detected in the influent in the first 22 bed volumes of wastewater treated (Figure 6.6). Between 31 and 40 bed volumes, iron decreased from 1.1 to 0.02 mg L⁻¹. Iron was not consistently detected in the effluent indicating that the media was not releasing the

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6

metal. Small levels were detected between bed volumes 3-6 and 22-40 and were attributed to iron in the influent with a slight contribution from media dissolution.

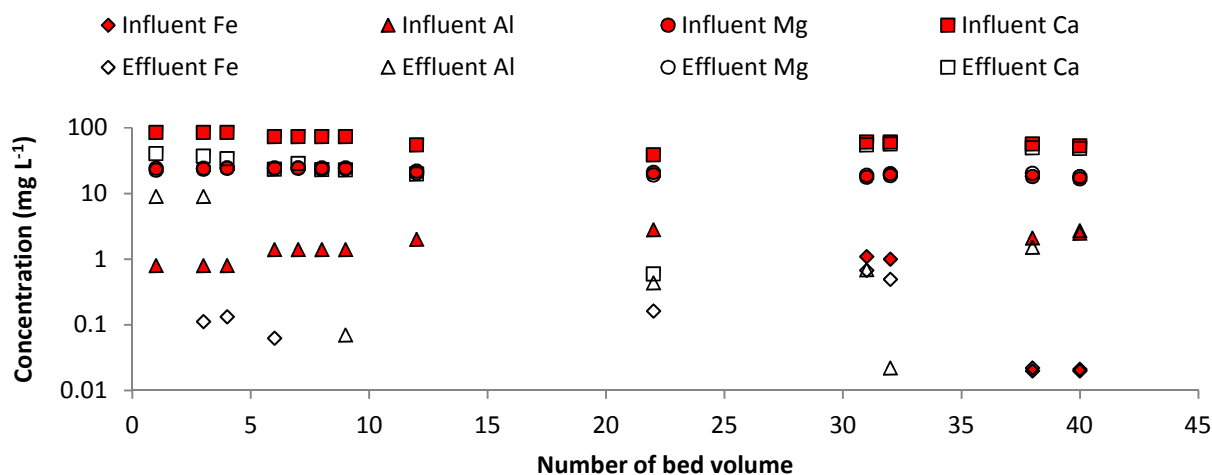


Figure 6.6: Correlation of concentrations of influent and effluent metal with bed volume in low phosphorus wastewater

The levels of Al and Mg in fresh and exhausted media were similar with no increase or decrease observed (Table 6.3). However, Ca and Fe increased by 4.3 and 31.8%, respectively suggesting that the increase was due to an accumulation from the influent.

The results suggest that only CaP precipitation was involved in the removal of phosphorus from low phosphorus wastewater as only $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Ca}_5\text{Cl}(\text{PO}_4)_3$ was formed (Table 6.4). The other metal phosphate present in both fresh and exhausted media was Mg_2PO_7 which could have been a seed for phosphorus removal. This metal phosphate was also present in both cases when high strength phosphorus wastewater was treated.

Some of the metals concentrations such as Al, Ca and Fe had increased in the exhausted media of both high and low phosphorus wastewaters. There was a suggestion that the presence of these metals in the influent resulted in the accumulation on the media surfaces. The same observation was reported by Pratt et al., (2007) after examining fresh and exhausted slag collected from ponds that had

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6

been removing P from wastewater for a long time in New Zealand. It was found that metals such as iron had increased in the exhausted media.

There were interesting results observed in the case of P in fresh and exhausted media from the two sites, as the concentrations were similar. The concentrations of phosphorus in fresh and exhausted media were the same, 0.1 mg TP L⁻¹. This was due to leaching of the element from the two beds. It was mentioned earlier that when feed P concentration into site B bed was below 0.2 mg TP L⁻¹, the effluent concentration was higher due to leaching of the retained phosphorus from the bed. Pant and Reddy, (2003) reported that P can be released from media during initial periods or when influent concentration is low, and Bowden et al., (2009) reported the same.

6.3.4 Retention of other anions by steel slag bed

The key points from the results show that the level of NO₃-N from site A decreased compared to the feed concentration (Table 6.5). To illustrate, the maximum, minimum and median levels in the feed were 55.3, 20 and 26.6 mg L⁻¹ compared to effluent concentrations of 28.5, 15.2 and 21.5 mg L⁻¹, respectively. The results indicate that the nitrates were utilised in the bed. Results from site B show similar levels in the feed and effluent leaving the bed, as influent maximum, minimum and median levels were 6.7, 0.5 and 1.7, and corresponding effluent levels were 6.7, 0.2 and 0.9 mg L⁻¹, respectively. It can be deduced from the results that steel slag bed only utilises nitrates when concentrations are higher; consistent, in general, with findings with biological denitrification (Vymazal, 2008).

Table 6.5: Influent and effluent concentrations of other anions

| Site A | Influent (mg L ⁻¹) | | | Effluent(mg L ⁻¹) | | |
|---|--------------------------------|---------|--------|-------------------------------|---------|--------|
| | Maximum | minimum | median | maximum | minimum | median |
| NH ₄ -N | 5.8 | 1.1 | 4.5 | 5.5 | 1.4 | 4.9 |
| NO ₃ -N | 55.3 | 20 | 26.6 | 28.5 | 15.2 | 21.5 |
| SO ₄ ²⁻ | 79 | 67 | 75 | 80 | 45 | 72.5 |
| Alkalinity (mg L ⁻¹ as CaCO ₃) | 104 | 60 | 94 | 117 | 88 | 102 |
| Site B | | | | | | |
| NH ₄ -N | 4.0 | 0.02 | 0.2 | 0.2 | 0.0 | 0.04 |
| NO ₃ -N | 6.7 | 0.5 | 1.7 | 6.7 | 0.2 | 0.9 |

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6

| | | | | | | |
|---|-----|-----|-----|-----|-----|-------|
| SO ₄ ²⁻ | 132 | 87 | 97 | 132 | 87 | 104.5 |
| Alkalinity (mg L ⁻¹ as CaCO ₃) | 216 | 150 | 182 | 216 | 150 | 180 |

6.3.5 Tracer studies

The purpose of conducting tracer studies was to define the actual flow conditions in the bed, which can be defined better by using residence time distribution obtained by experimental results of the study. The two sites exhibited similar residence time distribution profiles that fitted onto each other at 48 hours nominal residence time (Figure 6.7). The similarity was further expressed through lag times of 4 and 3 hours, respectively from sites A and B, and the peak concentrations were detected at 32 hours. The presence of time lags in both beds suggests a long inlet pipe (Levenspiel, 1999). The mean residence times were similar, being 38 and 36 hours for sites A and B, respectively which were 21 and 25% reductions. The lower mean residence times suggests channelling of flow or short circuiting, and were confirmed by indices of short-circuiting which were 0.08 and 0.06 at sites A and B, respectively. This confirms non ideal flows which can affect the efficiency of the bed (MWH, 2005). The cause of short circuiting was internal packing as the media was not evenly distributed according to particle sizes hence poor interlocking of particles. Solid build ups in the bed also contributed to this.

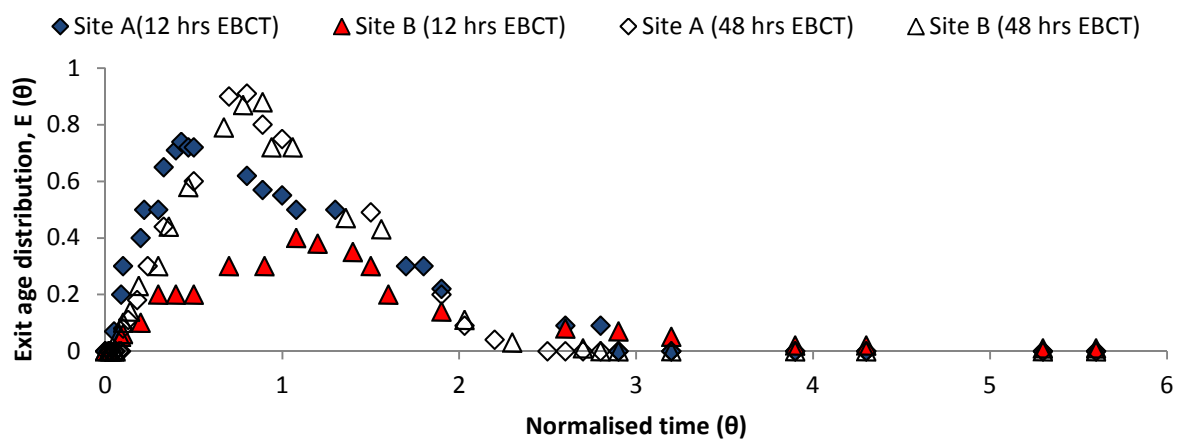


Figure 6.7: Exit age distribution curve for Site A and B for 12 and 48 hours residence times.

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag

Chapter 6

Mass recovery from sites A and B were 56 and 65%, respectively, showing that recovery was not successful and less than the 80-120% recovery which indicates successful recovery (Bodin et al., 2012). Low mass recovery expressed by both beds was due to dilution in the bed. The presence of dead zones contributed to low mass recovery as some of the tracer did not move to the exit point. Low mass recovery was due to retention in the bed, absorption and biological assimilation (Chazarenc et al., 2003). However, recovery was comparable to another study conducted by Giraldi et al., (2009) when using rhodamine WT as a tracer in constructed wetlands where 58% was recovered. The results were also similar to those reported by Lin et al., (2003) where 59% was recovered when using the same tracer at Prado Wetlands in California.

When nominal residence times were reduced to 12 hours, lag times were 1.5 hours however peak concentrations were detected at 12.5 and 19 hours, respectively in site A and B (Figure 6.7). The corresponding mean residence times were longer than nominal residence time, as 18 and 29 hours were observed which increased by 46 and 142%, respectively. The results are comparable to those reported by Seeger et al., (2013). The reported residence time increases were 52 and 34% as observed in horizontal subsurface flow wetland types for treating ground water contaminated with ammonia, BTEX and fuel additives (Seeger et al., 2013). It has been suggested that this is due to the presence of stagnant zones or tracer sorption by microbial biofilms (Seeger et al., 2013). The exit age distribution curves for 12 hours residence times were both asymmetrical and indicative of dispersion and dead zones in the bed (Bodin et al., 2012). Mass recovery was 85 and 87% for sites A and B, respectively and within an 80 – 120% confidence range indicating successful recovery (Bodin et al., 2012). Decreasing nominal residence time increased flow rate and this contributed to higher recovery as fluid was moving faster through the bed and reducing dead zones.

6.3.6 Phosphorus sequential extraction

The amount of P extracted from site A decreased as 59.2 ± 1.9 , 18.8 ± 2.4 , 10.7 ± 1.0 , 9.1 ± 1.0 and $2.1 \pm 0.5\%$, respectively from stable residual pool, loosely bound, Al bound, Fe bound and Ca bound P fractions (Figure 6.8). In the case of site B, the amount of phosphorus extracted were 56.6 ± 1.0 , 17.5 ± 1.1 , 11.6 ± 0.01 , 11.0 ± 0.5 and $3.3 \pm 0.4\%$,

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag Chapter 6

respectively from stable residual pool, Fe bound, loosely bound, Al bound and CaP bound fractions (Figure 6.8). This shows that more phosphorus was extracted from calcium fraction (stable residual and Ca bound). The results indicate that the dominant phosphorus removal mechanism in steel slag was through calcium precipitation. The retention of P through iron fraction was the next best removal mechanism in site B but from A loosely bound P was the second removal mechanism. The findings of this study are in agreement with Drizo et al., 2006) who reported that P removal mechanism in EAF steel slag is specific adsorption on metal hydroxides and calcium precipitation.

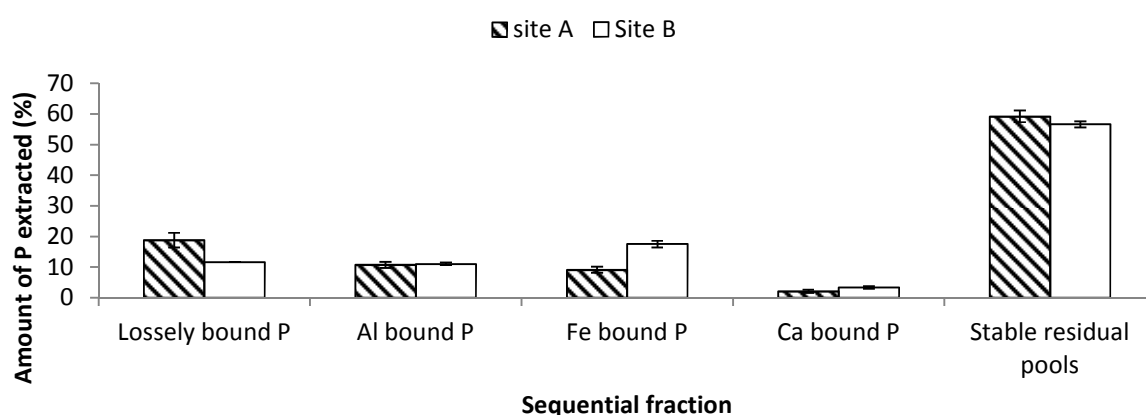


Figure 6.8: Phosphorus sequential extraction from Site A and B

6.3.7 Steel slag regeneration and P recovery

6.3.7.1 Regeneration trial

The impact of regeneration on performance was observed in terms of reduction in operation sequence for breakthrough of 2.0 mg TP L^{-1} to occur (Figure 6.9). For instance, during the first cycle, the breakthrough was reached after 114 bed volumes, however reduced to 5 and 3 bed volumes during the second and third cycles respectively. In contrast, the saturation points during the first and second cycles were identical at 470 bed volumes, however decreased to 114 bed volumes during the third cycle. The amount of P retained by the bed also decreased with increasing cycles. During the first run, 154.4 mg TP was retained by the bed which reduced by almost half to 88.7 mg TP during the second feeding.

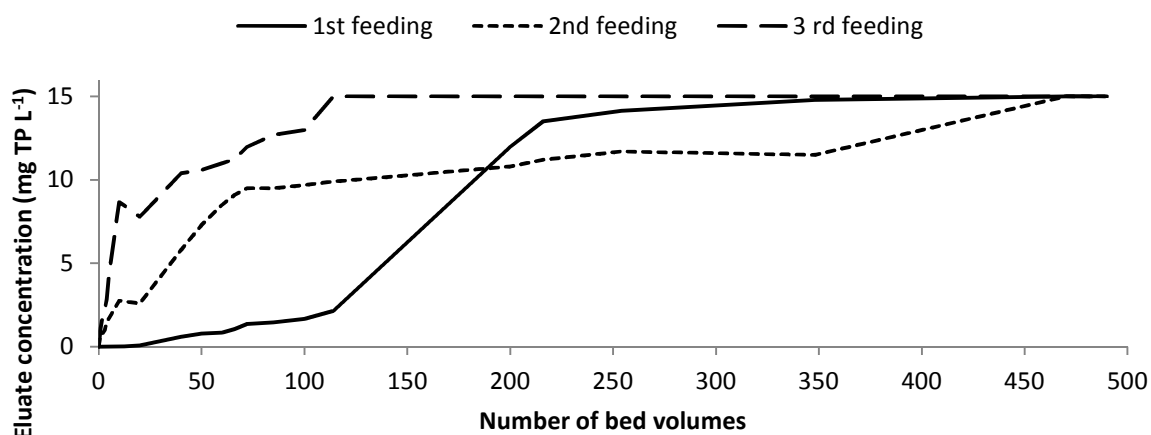


Figure 6.9 Impact of feeding cycles on steel slag bed using 0.1 M NaOH solution (EBCT = 60 minutes, $C_0 = 15 \text{ mg TP L}^{-1}$)

During the third cycle, retention was a quarter of the second cycle at 22.0 mg TP. With 85 g of the materials in the column, the media retention capacity decreased to 1.8, 1.0 and 0.3 mg TP g^{-1} . This indicates that not all active sites were regenerated, indicating a strong formation of bonds between metallic and phosphate ions such as CaP precipitation (Bowden et al., 2009). This capacity during the first cycle is similar to the findings of Drizo et al., (2008), who reported a capacity of 1.72 g TP kg^{-1} using a media size of 0-10 mm and influent concentration of $29 \pm 3.47 \text{ mg DRP L}^{-1}$, and the capacity increased to 3.18 g DRP kg^{-1} after resting for 5 weeks with feed concentration $33 \pm 5.21 \text{ mg DRP L}^{-1}$. The reason the capacity was even high though coarser media was used relates to the loading of P which was 2 fold that used in this study.

The maximum concentration of P removed from the saturated media decreased from 28 mg TP L^{-1} during the first regeneration trial to 22 mg TP L^{-1} during the second trial (Figure 6.10). The total amount of P released from the bed was 5.7 mg TP (3.7%) during the first regeneration cycle and decreased to 1.7 mg TP during the second cycle; a decrease by 3.4 times. This value is very low compared to results from sequential extraction where 88% P was extracted from media from different fractions. These results suggest that the OH^- ions from sodium hydroxide used (0.1 M NaOH) did not displace some of the phosphate ions in the media, hence retention sites decreased

Phosphorus removal from low and high concentrated phosphorus effluents using steel slag Chapter 6

with each feeding cycle. Another reason for low retention sites available is that NaOH as regenerant displaced phosphate ions were retained by Fe sites, however those precipitated by calcium were not freed. The regenerant used in this study was weak compared to those used in other studies. For example, Sengupta and Pandit, (2011) used 2.5% NaCl and 2.0% NaOH solution as a regenerant. Compared to findings by Pratt et al., (2011), 50% P was stripped from exhausted slags using 1 M HCl and 31% P striped using 1 M NaOH. This confirms that a concentrated NaOH solution is needed or HCl instead. Furthermore, work by Pratt et al., (2011) showed that P retention by exhausted slag treated with $\text{Na}_2\text{S}_2\text{O}_4$, 1M HCl and 1 M NaOH reached maximum capacities of 89, 50 and 25 mg P kg^{-1} media showing that NaOH as a reagent is weak compared to the other two. Midorikawa et al., (2008) used an 8 wt. % NaOH (80 g in 1000 mL) regenerant for desorbing P from exhausted media, which was a high strength solution.

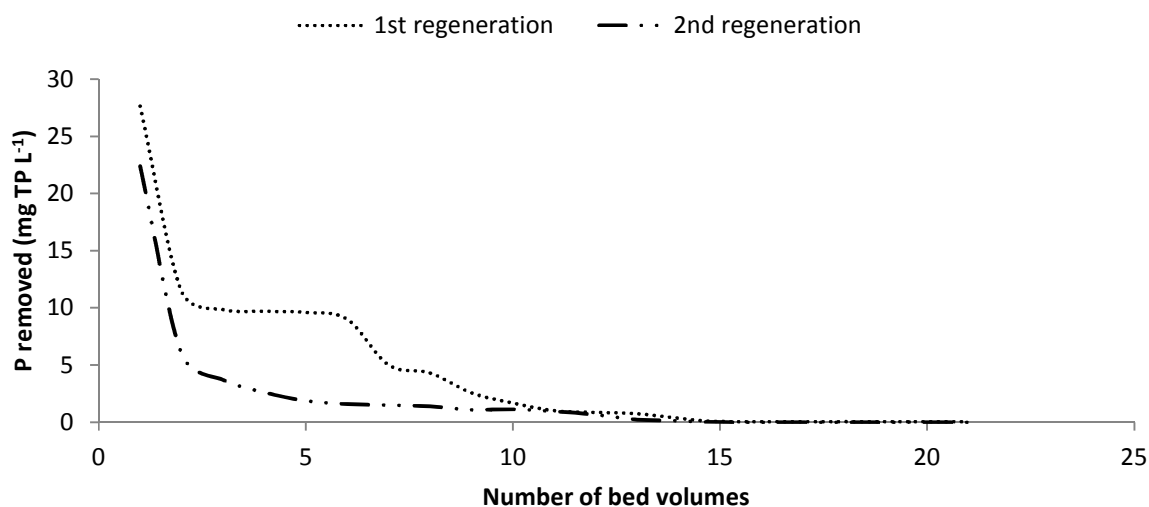


Figure 6.10: Impact of regeneration cycles on P recovery from steel slag bed using 0.1 M NaOH solution

These results show that the P retention capacity of steel slag decreases with regeneration cycles.

6.3.7.2 Phosphorus recovery

Determination of optimum pH and time

The amount of phosphorus recovered increased with increasing pH (Figure 6.11). Recovery was 23.5, 35.3, 94.1, 99.2, 99.8 and 99.8% as pH increased to 7, 8, 9, 10, 11 and 12, respectively. The optimum pH level was 9.0 where 99.2% phosphorus was recovered from the spent regenerant and any further increase thereafter did not yield any significant change.

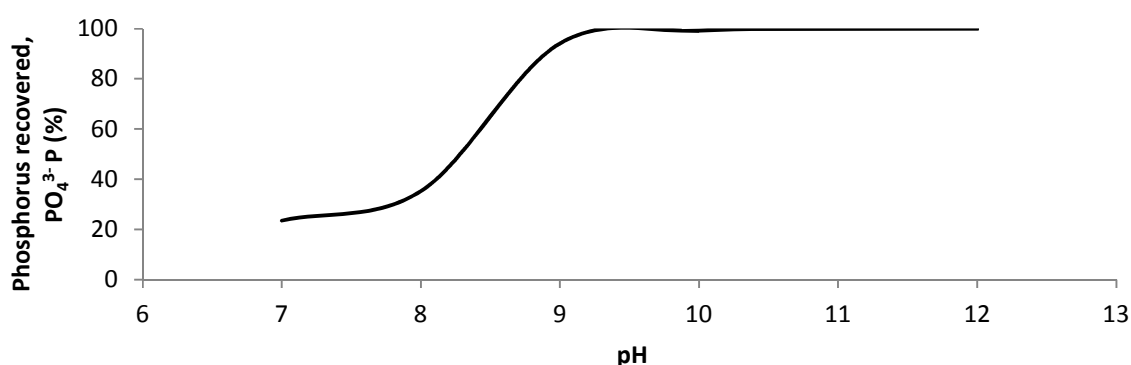


Figure 6.11: Impact of pH on P recovery from spent regenerant (Initial pH = 7, 8, 9, 10, 11 and 12, 0.5 g Ca (NO₃)₂.H₂O at 160 rpm for 1 hour).

After phosphorus was stripped from media in the bed using 0.1 M NaOH, the dissolved phosphorus in the solution was precipitated using calcium nitrate hydrate (Ca (NO₃)₂.H₂O) to form CaHPO₄, and 99% was removed within 5 minutes of the reaction time (Figure 6.12). This indicates that P can be recovered from the spent regenerant (0.1M NaOH solution). The same results for calcium phosphate precipitation were reported by Song et al., (2006) where P recovery occurred within 10 minutes when pH was ≥ 9.0 . The recovery was achieved using CaCl and K₂HPO₄ or KH₂PO₄ solutions. Similar results were reported by Qiu et al., (2011) where 99.5% recovery was achieved from fosfomicin pharmaceutical wastewater using wet air oxidation using CaCl, pH 9.0 \pm 0.1

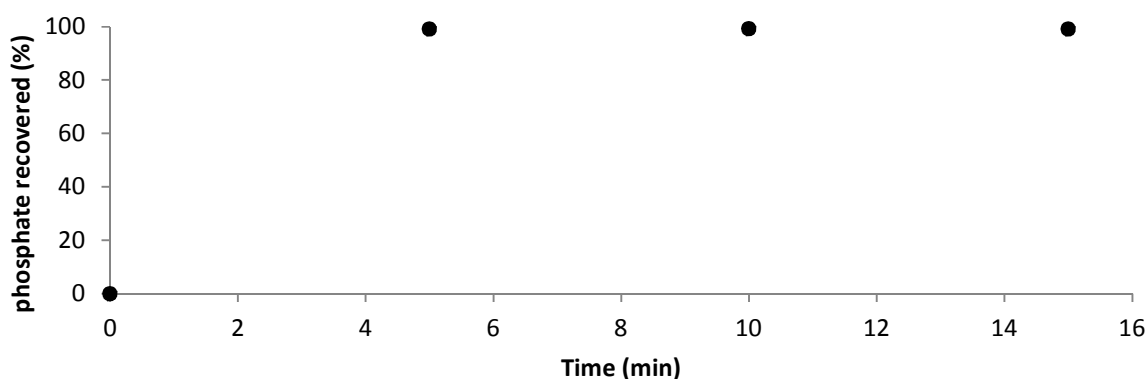


Figure 6.12: Impact of contact time on P recovery from regenerant

6.4 Toxicity effect of the two media

The leachability tests from different experiments (shown in Chapters 5 and 6) revealed that, in some cases, the levels of some of the metals exceeded the Environmental Agency threshold values. Such cases were observed during pH static tests conducted on the two media chosen for further studies and pilot trials conducted. To illustrate, the level of calcium during pH controlled tests was higher than the regulatory threshold value of 100 mg L^{-1} ranging between 121 and 445 mg L^{-1} in some instances. In the case of the PhosphateTM, the range was between 109 and 414 mg L^{-1} . Other observations made were that of aluminium, where at pH 10 and 12, leachability from steel slag was 0.3 and 2.1 mg L^{-1} , respectively exceeding the 0.2 mg L^{-1} regulatory discharge threshold. During continuous flow pilot experiments, it was found that iron and aluminium concentrations from both beds treating low and high P wastewater were escaping in high levels. Iron levels from high strength P wastewater was above the regulatory discharge threshold value, and ranged between 0.5 and 2.5 mg L^{-1} with aluminium ranging between 0.2 and 18.9 mg L^{-1} . In the case of the low strength phosphorus wastewater trials, iron and aluminium exceeded the threshold but with iron concentrations between 0.5 and 0.7 mg L^{-1} , whereas aluminium was very high in most cases reaching a maximum level of 9.0 mg L^{-1} .

In the case of PhosphateTM, the highest level of Fe in the effluent was 0.9 mg L^{-1} , however after 23 bed volumes levels reduced to below 0.2 mg L^{-1} . It was also observed

that, in most cases, aluminium levels were higher than 0.2 mg L^{-1} . From these results, the presence of aluminum and iron in the influent might contribute to the high levels observed. Since these metals were present in the incoming influent, there was accumulation in the bed attributed to the dead zones where preferential dissolution pathways were developed.

6.5 Conclusion

The performance of steel slag on removing phosphorus from low and high concentrated P effluents was investigated at different empty bed contact times in order to understand the design limits of the media and implications that can surface during full scale implementation.

- The efficiency of steel slag treating wastewater with high P concentration was high compared to that treating low phosphorus wastewater. This implies that there is a need to know the targeted effluent P concentration when such wastewaters are treated.
- The media released the retained phosphorus when influent concentration was lower than 0.2 mg TP L^{-1} implying that the bed can be the polluter during such scenarios.
- Initially, high effluent pH values were observed from steel slag bed treating high phosphorus wastewater, however stabilised after four bed volumes. In the case of PhosphateTM, pH values from a low phosphorus bed were always within regulatory limits.
- Both systems released high amounts of aluminum which were above the regulatory limits.
- The efficiency of steel slag correlated positively with empty bed contact time, as increasing contact time increased P removal efficiency.
- Tracer study results revealed that both beds experienced short circuiting.
- The phosphorus removal mechanism from both systems was predominantly CaP precipitation, although some of the phosphorus was loosely as well as Al and Fe bound.

- Steel slag has the potential for regeneration for further reuse and phosphorus can be recovered from the spent regenerant.

6.6 Acknowledgements

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Chapter 6

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Chapter 6

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Chapter 6

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Phosphorus removal from low and high concentrated phosphorus effluents using steel slag
Chapter 6

1

CHAPTER7: DISCUSSIONS

7 DISCUSSIONS

7.1 Which phosphorus removal pathways were involved in the two media?

Phosphorus removal through the use of reactive media in passive systems occurs through different complex reactions. The high phosphorus retention capacities of steel slag and Phosphate™ are influenced by physical and chemical properties of these media.

7.1.1 Media dissolution into Ca^{2+} and OH^- ions

The incoming sewage feed whose pH was near neutral conditions resulted in the dissolution of minerals such as CaO released free Ca^{2+} and OH^- ions (Figure 7-1). The release of OH^- ions elevated the pH in the bed. The contact time the media and influent spend is crucial for the success of the process. High efficiency correlates with longer residence time due to more Ca^{2+} and OH^- ions released as confirmed through kinetic experiments on dissolution of steel slag.

The elevated pH favours precipitation of phosphorus by calcium reactions which take place through a number of processes and steps.

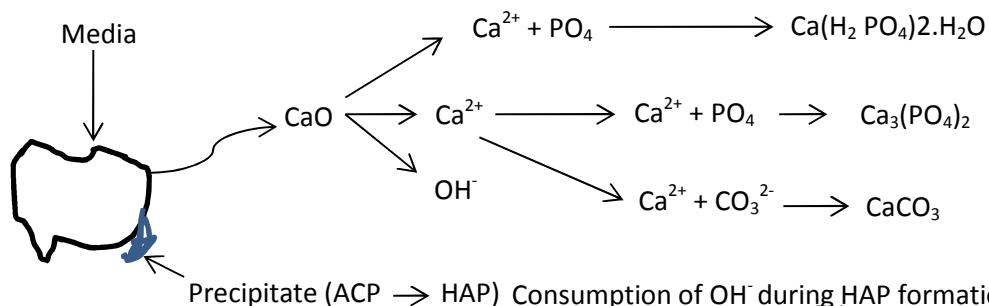


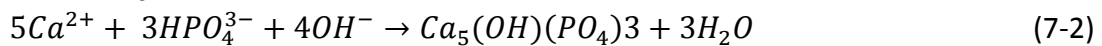
Figure 7-1: Typical reactions during of steel slag and Phosphate™ dissolution into Ca^{2+} ions and phosphorus precipitation

7.1.2 Formation of precursors (OCP and ACP)

Precursors formed are the intermediate phases of CaP minerals such as octacalcium phosphate (OCP) and amorphous calcium phosphate (ACP) formed before HAP (Manas et al., 2012). These two phases are unstable and therefore undergo hydrolysis very quickly. OCP is favoured at acidic conditions (Gao et al., 2010) and ACP is formed at a wider pH range and ionic strengths (Manas et al., 2012) even as high as 10.5 (Lu et al., 2010), and a range of 6.8 -10 has been reported by Montastruc et al., (2003).

7.1.2.1 ACP formation

ACP is an intermediate phase for the formation of many calcium phosphate precipitates (Combes and Rey, 2010). In the case of low strength effluent where pH elevation was not high, $Ca(H_2PO_4)_2 \cdot H_2O$ was one of the minerals formed.

7.1.2.2 HAP formation

Since HAP formation takes place at a slow reaction rate, precursors such as OCP and ACP are precipitated first in the bed (Lu et al., 2010). The formation of HAP is influenced by the conditions of reactions such as P concentration, Ca^{2+} concentration, bicarbonate ion and pH (Chen et al., 2009). In addition, OH^- ions should be present which are consumed and result in lowering of the pH during the process. The rapid initial pH increase observed in Site A (Chapter 6) meant that the saturation index of the solution with regard to calcium phosphate phases increased, and therefore increasing P removal through precipitation (Karapinar et al., 2006). The average influent and effluent pH values were 7.2 ± 0.3 and 9.3 ± 0.0 , respectively in steel slag bed treating high strength effluent from site A. The conditions favoured the formation of ACP as a precursor for HAP and at times the pH reached 11.0.

7.1.3 $CaCO_3$ Precipitation

Since the influent was observed to have an alkalinity of 82 and 200 $mg\ L^{-1}$ as $CaCO_3$ in high and low strength effluent, some of the released Ca^{2+} ions were precipitating $CaCO_3$ which also acts as a seed for HAP formation. In fact, high alkalinity in the low strength effluent meant that $CaCO_3$ precipitation predominated over the CaP pathway. The formation of $CaCO_3$ was more likely in PhosphateTM bed and sites A and C, where the pH was higher than 9.0 favouring the conversion of HCO_3^- ion to CO_3^{2-} ion, hence $CaCO_3$ formation which decreased Ca^{2+} ions (Chen et al., 2009). The formation of $CaCO_3$ negatively and positively affected P removal in the beds. The negative part was the consumption of Ca^{2+} ions, therefore reducing CaP precipitation and the positive

contribution being the precipitate being a seed for HAP formation. Such a scenario resulted in the formation of calcium deficient carbonated HAP ($\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)_3(\text{OH})_2$) instead of the normal $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Such cases resulted in larger molar ratios observed during dissolution experiments (Chapter 4).

This was a suggestion that P was bound to media surfaces and the other part was observed leaving as fine colloids in the effluent.

7.1.4 Other P removal pathways

In addition to P removal through calcium precipitation, another process involved was adsorption onto metal oxide surfaces. During the process, OH^- ions were replaced by PO_4^{3-} ions on the media surface and adsorption began (Figure 7-2). The released OH^- ions raised the pH as was the case with both media when treating high strength effluent using steel slag and PhosphateTM; however pH elevation was minimal in the case of low strength bed due to inhibition by high alkalinity.

Phosphorus is chemically retained onto Fe and Al oxides in acidic to near neutral conditions through ligand exchange (MHW, 2005). P Retention is rapid initially through precipitation on the media surface and the precipitates formed are not exchangeable and act as sorption sites for Fe or Al, which then remove P forming; for example, amorphous iron phosphate precipitates. In the same way as during Ca^{2+} dissolution, Fe^{2+} and Al^{3+} are released from the material and hydrolyse to form $\text{Al}(\text{OH})_3$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})_2^+$ which finally transforms into $\text{Al}(\text{OH})_3$. Fe^{3+} hydrolyses to $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3$ and finally to $\text{FeO}(\text{OH})$ crystalline (Oguz, 2004). The stable minerals formed during the precipitation of phosphorus by Al and Fe oxide/hydroxides are AlPO_4 (veriscite) and FePO_4 (strengite). These minerals are stable at pH values of less than 6.5 (Oguz, 2004). The formation of minerals such as AlPO_4 , $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was a further indication that other than CaP precipitation, other metal such as Al, Fe and Mg were involved in the removal of phosphorus.

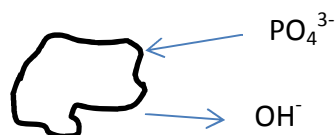


Figure 7-2: Other P removal pathway involved in steel slag and Phosphate™

The process was involved in both exhausted steel slag and Phosphate™ as confirmed through the formation of new phosphate minerals which were not present in fresh media. For example minerals such as $\text{Na, K, Ca}_2(\text{Fe, Mn})_5(\text{PO}_4)_4$ were present in exhausted steel slag indicating that other metals were involved in the removal of phosphorus. There were instances when the treated influent had a lower pH of between 6.5 and 7 which slightly favoured P removal through Al and Fe metals. In fact, AlPO_4 and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ were formed in the Phosphate™ bed in addition to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The average amount of dissolved oxygen in the beds also meant that removal through these other metals was possible. High and low strength effluents had average DO values of 4.1 ± 0.2 and 9.8 ± 1.0 , respectively, which favoured removal through Al and Fe before anaerobic conditions prevailed, favouring removal through calcium precipitation. The formation of biofilm and precipitates on the media surface affected P removal through adsorption as micropores were blocked. The other likely removal pathway was through biological metabolism by some different species present in the beds.

7.2 Key observations

7.2.1 Contact time influences performance

Steel slag dissolution experiments revealed that contact time is a crucial parameter for the success of the process. It was observed that dissolution of the material to release Ca^{2+} ions correlated positively with increasing contact time. This was confirmed through batch kinetic results where P retention capacity of steel slag increased with time when treating real effluent. This was expected, as more Ca^{2+} ions were released as contact time increased, hence precipitating P. Other removal mechanisms beside precipitation are favoured with longer contact time. It has been reported that adsorption takes longer to complete even months (Cooney, 1999). Further confirmation was revealed through pilot studies where P removal through vertical flow

fixed bed columns increased with increasing residence times (2, 6, 12, 24, 30 and 48 hours). The same results were reported by Shilton et al., (2013) on P removal using active slag filters.

7.2.2 Media regeneration and P recovery

Batch regeneration trials showed that both steel slag and Phosfate™ could be regenerated and be reused before replacement. However, it was observed that the P retention capacity of Phosfate™ diminished with each regeneration cycle compared to that of steel slag which increased at first during batch regeneration trials. This was an indication that a Phosfate™ bed will need replacing first. However, during regeneration using rapid scale small columns, the capacity of the steel slag bed decreased with the regeneration cycle. The potential for regeneration will reduce both replacement and disposal costs.

7.2.3 Fine colloids of P in the effluent

It was observed that initially the majority of the effluent was in the form of colloids from the Phosfate™ bed, however stabilised after 71 bed volumes and remained below the targeted 2.0 mg TP L⁻¹ concentration.

7.2.4 Release reaction

The reactions involved during P removal have been shown to be precipitation where the media releases Ca²⁺ and OH⁻ ions. The calcium ions released precipitate phosphate ions present in the feed solution where CaP products such as OCP and ACP are formed first and act as precursors for the formation of the stable HAP crystalline. HAP formation is a slow reaction, taking time. on the other hand, the low strength solution involved the formation of calcium phosphate hydrate (Ca(H₂PO₄)₂.H₂O).

7.3 In what situation can reactive media be used to remove phosphorus?

The use of reactive media will depend on the targeted effluent P concentration as well as the contact time between wastewater and media, with efficiency correlating positively with contact time. Both media evaluated showed that they are capable of reducing P from tertiary effluents to lower than 2.0 mg TP L⁻¹ even down below to 1.0 mg TP L⁻¹. Steel slag proved to be the better of the two during the initial stages as particulate P was observed escaping with effluent from a Phosfate™ bed after 13 bed

volumes, although stabilised to required consent after 61 bed volumes, thereafter. The use of reactive media will be influenced by the availability of land which will be determined by the loading rate on the bed. Treatment of effluents with P concentration $<1.0 \text{ mg TP L}^{-1}$ was successful as 48.0% efficiency was achieved, however feed concentrations of less than 0.3 TP mg L^{-1} resulted in the retained P being flushed from the bed.

7.4 What influence does media selection have on the process?

The results for the two media showed that both are capable of removing P from tertiary effluents, as both had higher efficiencies and can be used at full scale. However, there was a difference in the efficiency pattern observed as bed volume of wastewater treated increased. Firstly, steel slag efficiency was higher at the beginning though fluctuating at times, however decreased as the run progressed. By the time the experiment ended, it was clear that the bed was becoming exhausted. Another observation was of high pH at the beginning which eventually stabilised to around 9.0 after a few bed volumes. These observations make the material a strong candidate for removal of P from tertiary effluents. The robustness of the media indicated by its mechanical strength puts it in a better position for ease of handling during regeneration, suggesting it can be used a number of times before replacement. However, there is a potential risk associated to the leachability of Al from the bed which could restrict its use at full scale. Finally, the media bed was observed to release the retained P back into the bed when feed concentrations were $< 0.3 \text{ mg TP L}^{-1}$, hence eliminating it as a candidate for P removal from effluents with lower concentrations.

In the case of PhosphateTM, the media was very efficient in the first 13 bed volumes with P levels lower than the consent. However, performance decreased thereafter and it was observed that P was escaping as colloidal phosphorus. This was the case until 61 bed volumes and thereafter the bed was very efficient. The media will be a strong candidate for use as a filtration bed; for example, in series with steel slag to further polish effluents lower than 0.3 mg TP L^{-1} . The biggest risk factor will be the elevated pH which will need to be lowered. The strength of the media is low, making it difficult for

handling during regeneration, hence better placed for further treatment after steel slag as P loading will not be high, hence less frequent replacement.

During this study, it was found that both media can be regenerated for reuse, though the capacity was diminishing with each cycle. The selection of the regenerant will be crucial for media reusability. This was shown by the work of Pratt et al., (2011) where HCl stripped more P from exhausted slag than using NaOH solution.

7.5 What is the influence of sewage characteristics on P removal?

Sewage characteristics such as alkalinity, calcium concentration and pH were found to be important in relation to P removal with reactive media.

7.5.1 Alkalinity

Alkalinity decreased P removal through CaP precipitation as CO_3^{2-} ions competes with phosphate ions to precipitate CaCO_3 which in turn reduces P removal.

The level of alkalinity in the treated effluent will need to be determined so that precautions to increase P removal can be put in place. The alkalinity also inhibited the dissolution of steel slag into Ca^{2+} and OH^- ions as the feed already had Ca^{2+} ions in CaCO_3 . For instance, this affected the efficiency of the low strength bed as there was low CaP precipitation as well as low OH^- concentration for the formation of HAP.

7.5.2 Aluminum, Calcium, Iron and Magnesium Concentrations

During batch dissolution of steel slag, it was found that the system with high background Ca^{2+} concentration had high P removal. This was the case during batch isotherm experiments for high strength effluents which had higher background Ca^{2+} ions than in low strength effluent. A Ca^{2+} concentration range of 40 to 60 mg L^{-1} has been reported to be an effective range for HAP precipitation (Jang and Kang, 2002). The slow dissolution of the media into Ca^{2+} ions and the presence of high alkalinity will require the feed water to contain a substantial amount of background calcium ions. The same was observed for other ions such as Al, Fe and Mg where the presence of these in the influent improved phosphorus uptake in the bed.

7.5.3 The influence of wastewater pH

In general, it was found that high phosphorus removal correlated with high effluent pH. This is because HAP formation is favoured at elevated pH values. The precursors such as ACP are also favoured at a wide range of basic pH. The pH of incoming feed was near neutral conditions which favoured the dissolution of steel slag into calcium ions as was found during static pH tests. In the case of low strength effluent whose feed pH was already elevated, the removal rate was low and sometimes the effluent pH was found to decrease, suggesting that the capacity limit was reached. The influence of pH agrees with previous studies by Chazarenc et al., (2007) who reported that elevated effluent pH indicates that the retention capacity limit was not reached. Influent pH can also dictate which CaP precursors are formed as they are pH dependent before the formation of the stable HAP. It has been reported that thermodynamic calculations show that calcium carbonate competes with HAP at pH between 9.5 and 10.5, however HAP formation predominates at pH of between 7.5 and 8.5 and above 10.5 (Jenkins et al., 1971). It has been reported that retention of phosphorus on aluminium and iron oxides/hydroxides is favoured at near acidic to neutral conditions. Influent pH was near these conditions in some cases, favouring removal through Al and Fe fractions of the media.

7.6 What are the main implementation challenges?

The results have shown that both steel slag and PhosphateTM have high potential for use as reactive media in passive systems. However, there are a number of challenges associated with each media which can affect full scale implementation trials.

7.6.1 Elevated pH

As mentioned earlier, the EA consent for pH in receiving waters is 5.0 – 9.0. Effluents from both beds were higher than this range though that from steel slag was closer with the average of 9.3 ± 0.3 even though during the first four bed volumes pH was > 11.0 . The average value from PhosphateTM was 11.4 ± 0.3 throughout the study period. It was only effluent values from low strength beds which were lower than 9.0 but greater than 8.0 throughout the study. The high effluent pH observed will need to be lowered before discharging into the environment. Post treatment will be required by acid

neutralisation, dilution, or putting up a media bed consisting of an acidic media such as peat to lower the incoming pH (Wei et al, 2008). Chazarenc et al., (2010) mixed steel slag with limestone and apatite, and reported an effluent pH of below 8.0. Some studies have introduced such media near the exits of the filter beds for such purposes. Such extra facilities will raise the costs of the treatment process. The effluent pH indicates the probable P removal mechanism and this merits attention to the system. It has been reported that CaP precipitation dominates at elevated pH values. Therefore, monitoring pH can give an indication of the filter system as a decrease will indicate that exhaustion of the bed is near.

7.6.2 Regeneration and regenerant strength

Since reactive materials are not easily available and some are expensive, such as in the case of PhosphateTM which was commercially manufactured, regeneration of the exhausted media is appealing. If successful, this will reduce both replacement and disposal costs. P can also be recovered from the spent regenerant and be precipitated either as struvite or calcium phosphate for use as a fertiliser. If P can no longer be stripped from the exhausted steel slag, the material has the potential for use as soil amendment as previously reported by Bird and Drizo, (2009).

Regeneration of the two media will be a challenge if the right chemicals are not used. During the study, low strength NaOH (0.1 M NaOH) was used to regenerate steel slag which proved successful during media screening as during the first and second cycles, the regenerated steel slag capacity improved compared to fresh media. However, during the trials using rapid small scale columns, the capacity declined with each cycle using the same regenerant with same strength. It will be necessary to try high strength NaOH solution or even use an acid regenerant especially for steel slag where the main removal mechanism was found to be CaP precipitation. Though PhosphateTM was not tested for regeneration through rapid small scale column experiments, the batch regeneration trials conducted showed that the media can be regenerated and reused, though capacity declined with each cycle. Previous studies by Sibrell et al., (2009) reported 76% P recovery using 0.1 M NaOH as a regenerant on acid mine drainage sludge.

7.6.3 Leachability

The high level of aluminum detected in the steel slag beds for both high and low strength effluent will impact negatively on full scale implementation using the media. The level was significantly higher than the EA consent. There is a need to reduce this high level concentration before discharging the effluent. This will need to be carried out during initial phases, as it was observed later that there was no more leaching in the later stages. Further studies on leachability including those metals not studied needs to be considered. Leaching can be influenced by the way production was conducted. Though there was leachability of Al and Fe from Phosphate™ bed, the level did not exceed 1.0 mg L^{-1} never the less relevant action should be put in place before using the media.

7.7 References

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CHAPTER 8: CONCLUSIONS AND FUTURE WORK

8 CONCLUSIONS AND FUTURE WORK

8.1 CONCLUSIONS

- After the initial screening of the six media steel slag, phosfate™ and bauxsol revealed larger P retention capacities which were similar. Gravel, limestone and blast furnace slag revealed lower retention capacities. Blast furnace slag, steel slag, gravel and limestone had higher mechanical strengths than Phosfate™ and bauxsol. All the six media have the potential for regeneration and hence reuse before replacement as revealed through batch regeneration trials.
- Alkalinity in the form of NaHCO_3 or CaCO_3 decreases the dissolution of steel slag into Ca^{2+} ions, thereby decreasing the media performance in removing P through CaP precipitation. Besides HAP formation, other CaP precipitates were formed as revealed through Ca/P ratios either lower or higher than the theoretical value of HAP formation, 1.67. Higher ratios also indicated that CaCO_3 precipitation was taking place.
- Both steel slag and Phosfate™ were basic and this was also confirmed by their high pH values. Elevated pH values were also observed from Phosfate™ bed throughout the duration of the pilot trials. Batch experiments revealed that SO_4^{2-} and CO_3^{2-} reduced P retention capacity of steel slag but not that of Phosfate™. During pilot experiments, colloidal phosphorus was observed to be escaping with effluent from Phosfate™ bed, however none from the steel slag bed. High levels of aluminium were observed in the effluent of steel slag during batch and pilot trials, however minimal values were observed from Phosfate™. The performance of steel slag in removing phosphorus correlated positively with increasing EBCT. Steel slag can remove phosphorus from wastewater with low phosphorus concentration, although the efficiency is lower than from high P concentration. At very low P concentration, the retained P was flushed back into the effluent. It was also observed during small scale rapid columns that the retention capacity of steel slag decreased with each regeneration cycle.

Phosphorus was also recovered from the spent regenerant using calcium nitrate hydrate.

8.2 FUTURE WORK

- Colloidal P observed from the PhosphateTM bed should be a key focus for further investigation as the outcome can influence the decision on where to use the media bed in passive systems. The use of a PhosphateTM bed as a filtration bed following another bed to further reduce P to its lowest levels can be influenced by this colloidal P. Another investigation will be the impact of contact time on performance as it was observed that this parameter influences the performance of steel slag. Such investigations should include a component for lowering effluent pH for both materials.
- Though leachability was conducted during this study, only four metals were investigated. A further investigation which incorporates other metals not covered can further reveal the appropriate use of these materials. Such investigation should be continued from the initial phase until media exhaustion.