CRANFIELD UNIVERSITY

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Reactive Media for Phosphorus Removal in Wastewater Treatment

School of Energy, Environment and Agrifood

PhD
Academic Year: 2017 - 2018

Supervisor: Prof. Bruce Jefferson

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ABSTRACT

The implementation of the Water Framework Directive (WFD) will impose new phosphorus (P) consents (<1 mg/L) for small sewage treatment works (STW) in the UK. This poses a challenge for water utilities, as while the conventional solution of chemical dosing and tertiary filtration would be able to meet those consents, it does not align with the low energy technology requirements of small STW. Constructed wetlands with Basic Oxygen Furnace (BOF) steel slag and apatite not only are passive systems with low maintenance requirements and low energy demand, but they can also effectively meet those new consents, therefore, providing a more sustainable alternative to the conventional solution. This technology has traditionally been tested in small-scale short-term column trials, which limits its full-scale extrapolation potential.

This thesis provides field-scale and long-term direct comparison of both media for P removal, and determines key operational parameters for optimum performance, such as hydraulic retention time and media size, as well as identifying operational challenges. The suitability of the commonly employed column experiments to test reactive media is also assessed and recommendations are provided for extrapolation to other STW. Performance comparison to other two trials with BOF steel slag in the UK allows to determine the potential for full-scale application of this technology in the country. Circumstances under which this technology can be economically viable compared to the conventional solution are then assessed.

Keywords:

apatite, constructed wetlands, phosphorus, steel slag

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In loving memory of El Aitona

Con cariño, en memoria del Aitona

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ADP	Ammonium dihydrogen phosphate
BOF	Basic oxygen furnace
COD	Chemical oxygen demand
EAF	Electric arc furnace
EBCT	Empty bed contact time
GC-MS	Gas Chromatography – Mass Spectrometry
HRT	Hydraulic retention time
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
LC-MS/MS	Liquid Chromatography tandem Mass Spectrometry
PE	Population equivalent
PS	Priority Substance
PSC	Phosphorus sorption capacity
SEM	Scanning Electron Microscopy
SS	Steel slag
STW	Sewage treatment works
TP	Total phosphorus
UC	Uniformity coefficient
XRD	X-ray diffraction
XRF	X-ray fluorescence

1 Introduction

1.1 Background

The implementation of the water framework directive (WFD) in the United Kingdom will impose tighter phosphorus (P) consents to sewage treatment works (STW), in an attempt to reduce P levels in fresh water bodies, as it can lead to eutrophication which has detrimental effects for local flora and fauna (Parma, 1980). Previous legislation has attempted to do so in the last 30 years. The Urban Wastewater Treatment Directive through its national implementation, the Urban Waste Water (England & Wales) Regulations 2003 required compliance to a total P (TP) discharge consent of <1 mg/L for large STW (>100,000 population equivalent), and <2 mg/L for medium STW (10,000 < population equivalent <100,000). Recently, the WFD aimed at further reducing these consents for medium and large STW, and imposing new consents for small STW (<10,000 population equivalent), where previously no P consent was commonly applied. The consent applied to each STW under the WFD is defined through consideration of the size of the STW, the quality of the receiving water body and the catchment in which that STW is located. The expected new levels are mostly set between 1 mg/L and 2 mg/L, further reducing to 0.5 mg/L and below in some cases, and they will start to be imposed after 2020.

This poses a new challenge for wastewater treatment at small STW. Conventionally employed chemical dosing with Al or Fe salts followed by tertiary filtration would be able to meet these new P levels. However, small STW are usually unmanned and located in remote areas with difficult access and often have no current chemical dosing capability. Consequently, implementation of chemical P removal can require substantial infrastructure improvements associated with the storage of chemical, collection and tankering of sludge, safety shower (with a potable supply), upgrades to the electricity supply and the inclusion of a tertiary filtration process to protect against metal non-compliance of the chosen coagulant. Consequently, alternative technologies that maintain the (near) passive, low maintenance attributes of small STW are required.

Horizontal subsurface flow constructed wetlands have been traditionally employed as a tertiary treatment at small STW for solids removal, using gravel as the support material as they require very low maintenance as well as consuming hardly any energy. However, traditional wetland set-ups are not effective for P removal and as such, there has been considerable research over the last decade into materials with high affinity for P removal, with the purpose of replacing the gravel within constructed wetland systems (Table 1-1).

These reactive materials have been categorised into natural materials, industrial by-products and man-made materials by previous research (Volha et al., 2011). Comparison between the effectiveness of the media is challenging, due to many differing parameters, such as experiment scale (batch, column or filter), media size (0.1-12.0 mm), inlet P concentration (3.4-40 mgTP/L), wastewater type (synthetic or real), experiment duration (1-550 days) and experiment design, such as operational HRT or dimensions (not included herein). The most important factor of a potential reactive material is the effectiveness in P removal. P sorption capacity (PSC) should be assessed for comparison, and not P removal rate, as reactive media processes are limited by the media volume. However, other factors such as hydraulic conductivity, physical integrity, metal leaching and price should be taken into account to provide a true holistic picture of a media potential.

Table 1-1 Summary of design and operational parameters of the studies with reactive media with the highest reported P sorption capacities.

Material	Size (mm)	Water type*	Scale**	Inlet P (mg/L)	P removal (%)	PSC*** (gP/kg$_{media}$)	Experiment duration (days)	Exhaustion achieved****	Cost (per tonne)	Reference
Natural materials										
Apatite	0.1-0.9	S	C	20	-	13.9	550	N	-	Molle et al. (2005)
Attapulgite	0.2-0.5	S	C	10	94.3	-	150	N	$250-300	Yin et al. (2017)
Opoka	1-2	R	F	7.8	97	0.38	63	-	-	Jozwiakowski et al. (2017)
Wollastonite	-	R	C	3.4	85	-	411	N	$308	Brooks et al. (2000)
Industrial by-products										
BOF steel slag	6-12	S	F	10.8	>99	1.05	360	N	-	Barca et al. (2014)
EAF steel slag	5-16	S	F	10.8	98	0.91	360	N	-	Barca et al. (2014)
Blast Furnace steel slag	0.25-4	S	C	10	90	-	392	N	-	Johansson (1999)
Fly ash	4	S	B	40	-	1.98	1	Y	-	Li et al. (2017)
Man-made materials										
Polonite®	2-5.6	S	C	5	96.7	19	476	-	-	Gustafsson et al. (2008)
Filtralite P®	0.5-4	S	C	10	91.0	-	300	-	-	Adam et al. (2007)
LECA	2-4	R	F	4.4	89	-	720	-	-	Oovel et al. (2007)
Phosfate™	5-12.5	S	C	6		2.3	150	N	-	Letshwenyo (2014)

*S: Synthetic, R: Real; **B: Batch, C: Column, F: Filter ; ***PSC: Phosphorus Sorption Capacity; ****Y: Yes, N: No.

Among those studies published in literature, the ones with the highest PSC have been selected for comparison (Table 1-1). In general, and with the exception of apatite with one of the highest reported PSC of 13.9 gTP/kg$_{media}$, natural materials show the lowest P removal capacity, with for example a PSC of 0.38 mgTP/kg$_{media}$ for opoka. Industrial by-products and man-made materials show higher P retention potential, with highest reported PSCs of 1.05 gTP/kg$_{media}$, 0.91 gTP/kg$_{media}$, 1.98 gTP/kg$_{media}$, 19.0 gTP/kg$_{media}$ and 2.3 gTP/kg$_{media}$ for Basic Oxygen Furnace (BOF) steel slag, Electric Arc Furnace (EAF) steel slag, fly ash, Polonite® and Phosfate™, respectively. However, the reported PSC reflect, in part, the experimental approach taken. For instance, in the case of fly ash, the PSC was determined in a 1 day small volume batch experiment using ideal mixing and high initial P concentration of 40 mg/L. Such tests are poorly representative of likely performance within constructed wetlands treating real sewage. As such care is required when comparing data. Further, other factors need to be considered in the selection of media for long-term testing. In the case of Phosfate™, physical integrity loss was reported in otherwise successful trials, which currently prevents this material from full-scale implementation and hence was not selected for the trials conducted herein.

BOF steel slag has been reported as an effective P removal material in numerous studies. Importantly, it is locally available and it is inexpensive, due to it being a waste material from the steel making industry. These factors are of major importance in the selection of a potential reactive material, they can substantially affect the economic viability of the technology. Examples of local availability include opoka and Polonite® in Poland and apatite in France. Interestingly, the cost of the material has only been published for two of the contemplated materials. Apatite has also been reported for high P removal capacity on numerous ocassions, being the highest reported PSC of 13.9 gTP/kg$_{media}$. Similarly with opoka and its commercial product Polonite®, apatite has been modified and commercially manufactured as a reactive material for P removal, called *Phosclean*. Both BOF steel slag and apatite (in the form of the product *Phosclean*) have been selected as the most effective materials and have been studied in this thesis.

To date, much of the work has been conducted in synthetic wastewater solutions and in batch tests from which it is difficult to make implementation decisions at full-scale. Experiments at a larger scale (such as continuous flow column experiments) and field-scale trials are needed in order to fully establish the suitability of a reactive material for P removal at full-scale. Furthermore, exhaustion of the reactive materials has not been reached in many studies, which emphasizes the need for longer term experiments to effectively ascertain media lifetime.

1.2 Aims and objectives

The overall aim of this research was to develop a better understanding of the mechanisms, the methods and the economic viability involved in using BOF steel slag and apatite media in constructed wetlands for P removal from domestic wastewater as a tertiary treatment.

Objective 1: To assess the impact of design and operating conditions on the suitability of column experiments to evaluate BOF steel slag and apatite as reactive materials for P removal.

Objective 2: To evaluate the performance of BOF steel slag and apatite in full-scale constructed wetlands as a tertiary treatment for domestic wastewater, and to identify operational challenges that would prevent this technology from being implemented over conventional solutions.

Objective 3: To compare the full-scale BOF steel slag constructed wetland with another two case studies from two UK water companies, and to identify main design and/or operational parameters as to explain differences in performance results.

Objective 4: To identify the major items contributing to the overall economic viability of the technology, and compare this to a conventional approach to establish the potential for a business case for its implementation.

A conceptual diagram of the objectives of this thesis is presented (Figure 1-1).

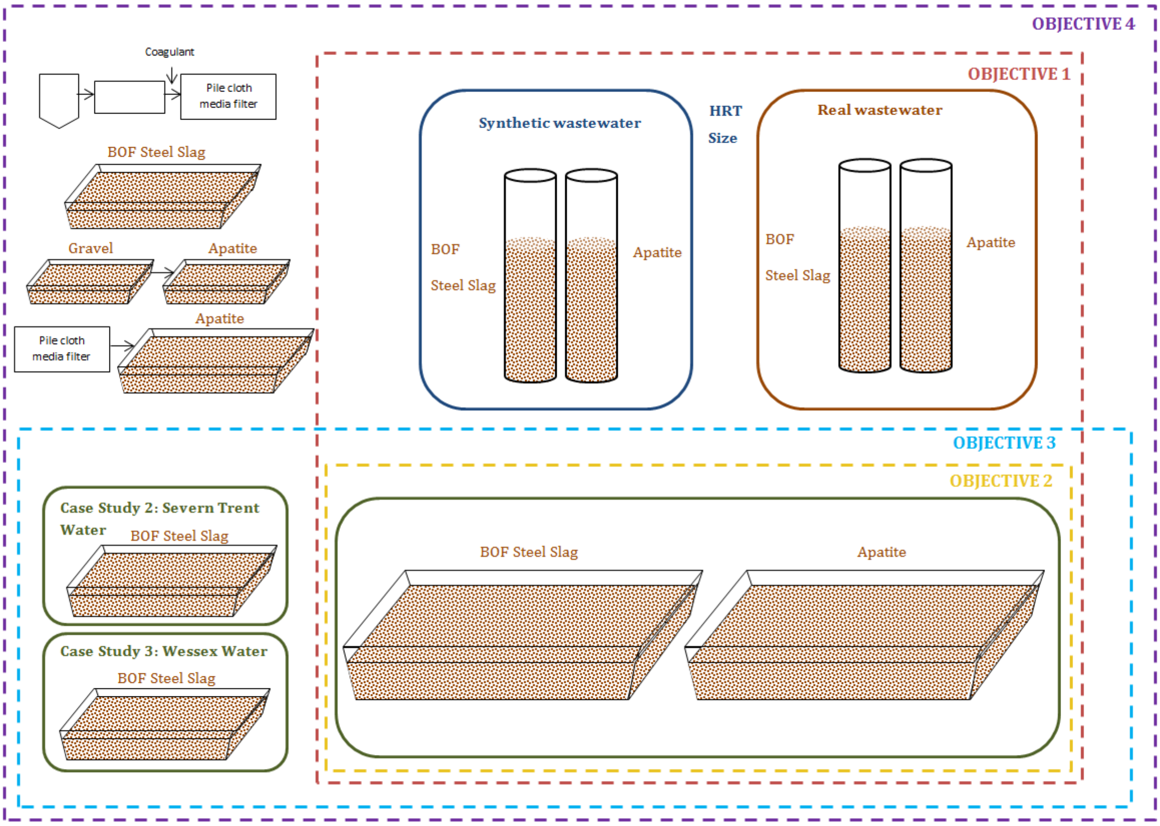

Figure 1-1 Conceptual diagram of thesis objectives and how they are interconnected.

It is hypothesised that column experiments using synthetic wastewater are an appropriate method to assess the PSC of BOF steel slag and apatite, determine the optimum operational parameters to maximise P removal efficiency and identify operational challenges. This was tested by conducting experiments with synthetic and real wastewater in column experiments as well as field-scale trials with the two media. By doing this, the use of reactive media in constructed wetlands could be assessed for economic viability for producing an acceptable effluent water quality as an alternative for conventional solutions currently employed to remove P at small STW.

The work presented in this thesis was performed under the sponsorship of Thames Water Utilities with a focus to developed applied research outcomes associated with the suitability and economic viability of the use of reactive media in constructed wetlands for P removal. Accordingly, the focus of the work was on larger scale, longer term trials with real wastewater. The delivery of the objectives led to a number of areas of novelty that are presented within this thesis:

(1) The first direct comparison of BOF steel slag and apatite based media including a test with BOF steel slag media at an equivalent size to that of apatite to directly compare material impacts over those of media size.
(2) The first reported data on the effectiveness of reactive media constructed wetlands on the removal of metals and priority substances highlighted within the WFD.
(3) The longest running column experiments among those published in literature to ascertain the long-term robustness of the reactive media performance.
(4) The first comparison of real and synthetic wastewater under the same column configuration to assess the effect of wastewater type on reactive media performance.

1.3 Thesis plan

This PhD thesis is structured as a series of chapters formatted as journal papers. All of the chapters were prepared by the main author Naiara Fonseca, and edited by Prof Bruce Jefferson. All the experiments were designed and operated in Thames Water Utilities' facilities (UK) by Naiara Fonseca. However, there were a number of people who contributed to the successful completion of the experiments. Chris Woods provided essential sampling support of the field-scale constructed wetland trial and the column experiments during the last 16 months of this PhD. Ben Morris and Naomi Clay-Michael significantly contributed to column experiment sampling during the last six months of this PhD.

Prior to the start of this thesis, a literature review was performed in order to identify the most promising materials to be used as reactive media in constructed wetlands for P removal from domestic wastewater. BOF steel slag and apatite were selected as the most promising ones, given the high PSC and the high number of studies published researching them.

The selected media were then tested in column experiments treating both synthetic and real wastewater. This included a series of columns containing different sized BOF steel slag to ascertain the impact of media size on performance (Chapter 2, Paper 1 - in preparation: Fonseca, N., Germain-Cripps, E., Dotro, G. and Jefferson, B. Understanding the impact of media size on the effectiveness of basic oxygen furnace steel slag as a reactive media for phosphorus removal, *Environmental Technology*).

Chapter 3 then considered the direct comparison of BOF steel slag and apatite based media including four different formulations of the media using different binding materials. The work also included a direct comparison of a BOF steel slag that was approximately the same media size as the apatite based media to ascertain which performance aspects where related to material properties as opposed to media size. (Chapter 3, Paper 2 – in preparation: Fonseca, N., Germain-Cripps, E., Dotro, G. and Jefferson, B. Comparison of basic oxygen furnace steel slag and an apatite based media for phosphorus removal treating synthetic and real wastewater, *Water Research*).

Selected media based on early results during the column experiments were then used in field-scale constructed wetlands to ascertain the potential of the media as a real solution and identify any specific operational challenges that may occur. The work thus enabled direct comparison of the findings in the column experiments with those in field trials to understand the potential for knowledge transfer across scales of testing. (Chapter 4, Paper 3 – in preparation: Fonseca, N., Germain-Cripps, E., Dotro, G. and Jefferson, B. Comparing the reactive media: Basic Oxygen Furnace steel slag and apatite for phosphorus, metal and priority chemical removal using field-scale trials, *Ecological Engineering*).

Chapter 5 then combined the findings from the current work with two additional field-scale trials conducted by other UK water companies to define the potential of reactive media for use in constructed wetlands and highlights areas of similarities and differences that may require site specific testing prior to implementation. Finally, the work was used to assess the economic viability of reactive media constructed wetlands in comparison to chemical dosing coupled to tertiary filtration. (Chapter 5, Paper 4 – in preparation: Fonseca, N., Germain-Cripps, E., Dotro, G. and Jefferson, B What is the suitability of constructed wetlands with reactive media for wastewater treatment in the UK?, *Environmental Science & Technology*).

Finally Chapter 6 summaries the key conclusions and recommends areas for future research to aid the development of using reactive media in constructed wetlands for P removal from wastewater as a tertiary treatment.

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2 Understanding the impact of media size on the effectiveness of basic oxygen furnace steel slag as a reactive media for phosphorus removal

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Abstract

Basic oxygen furnace (BOF) steel slag has been demonstrated to enable phosphorus (P) reduction effectively. This work evaluates P performance, pH, metal release/uptake and P removal mechanisms through a series of experiments with different BOF steel slag sizes (0.75mm to 10.04mm), hydraulic retention times (HRTs) (2 hours to 48 hours) and wastewater types (synthetic and real domestic). Smaller steel slag sizes were found to reduce P more effectively than larger fractions, and produce higher pH. Two distinct phases of P removal were identified, a first period where the slag was being coated at high pHs due to CaO dissolution, and a second steady-state period where the removal continued at reduced pH and HRTs. Significant differences in P and pH profiles were found between wastewater types, which indicated that the application of results obtained with synthetic wastewater needs to be done cautiously.

Keywords: adsorption, precipitation, retention time

2.1 Introduction

Removing phosphorus (P) from sewage at small sewage treatment works (STW) (<2,000 population equivalent (PE)) whilst retaining the passive attributes of the typical technologies used is very challenging. In particular, avoiding the infrastructure and operations associated with chemical dosing (chemical storage, safety showers, facilities for more regular tanker visits on normally unmanned sites) drives a desire to establish alternative passive solutions. One major option of interest is the use of reactive media in constructed wetlands where a combination of adsorption, precipitation and filtration pathways enables a high level of P removal in low energy and passive technologies such as constructed wetlands. A wide range of natural, industrial by-products and man-made materials have been proposed all containing a different balance of reactive chemicals in media of different sizes (Table 2-1).

Higher removal capacities are normally associated with the industrial by-products and man-made products attributed to their higher content of Ca or CaO, Al, Mg and Fe (Johansson Westholm, 2006; Vohla et al., 2011). Examples include Basic Oxygen Furnace (BOF) steel slag (industrial by-product category) and PhosClean^{TM} (man-made product category) as well as Polonite, Filtralite P$^{®}$, LECA and Phosfate^{TM} (Vohla et al., 2011). Comparison of the different media is typically conducted in combinations of batch, column and field trials with potential variations in the background water (synthetic or real), initial and target P concentration, hydraulic retention time (HRT) and media size. Consequently, effective comparison becomes challenging leading to a wide range of reported removal capacities, efficiencies and operational lifetimes (Cucarella and Renman, 2009). For instance, in the case of water chemistry, the background water constituents (pH, alkalinity, other ions) impacts on the initial dissolution rate, the speciation of the available reactive chemicals (phosphate, carbonate) and the range of potential products formed. At its simplest, the sequence follows: dissolution of calcium oxide, a rise in pH and release of calcium ions, precipitation of phosphate and calcium to form amorphous calcium phosphate and ultimately hydroxyapatite (Equation 1-Equation 4).

$$CaO + H_2O \leftrightarrow Ca^{2+} + 2OH^- \qquad \textbf{Equation 1}$$

$$Ca^{2+} + PO_4^{3-} \leftrightarrow CaPO_4$$ **Equation 2**

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$$ **Equation 3**

$$5Ca^{2+} + 3PO_4^{3-} + OH^{-} \leftrightarrow Ca_5\,(PO_4)_3OH$$ **Equation 4**

However, in real wastewaters the presence of carbonates and other ions in the water result in a much broader range of potential precipitates forming such as calcium carbonate, hematite and magnesioferrite (Desport et al., 2011). The relative abundance of carbonate (typically 100-200 mg/L) over phosphate (typically less than 10 mg/L) in tertiary wastewater coupled with the associated pH rise means that calcium carbonate is likely to be the predominant precipitate. In such cases, phosphate removal occurs through a combination of inclusion into the calcium carbonate matrix, precipitation of calcium phosphate (in a variety of forms), precipitation of other phosphate species linked to iron and manganese and partitioning into organic material (in cases where real wastewater and reeds are used).

The specific performance levels reported are also influenced by the initial P concentration and the contact time utilised with higher levels generating better performance. For instance, in the case of Basic Oxygen Furnace (BOF) steel slag treating a real wastewater in pilot scale columns, the removal efficiency increased from 47 to 83% as the empty bed contact time (EBCT) was increased from 2 to 48 hours (Letshwenyo, 2014). A similar overall trend was observed by Shilton et al. (2005) for Electric Arc Furnace (EAF) steel slag, however the removal levels were lower, only reaching a maximum of 50% at an EBCT of 96 hours. Claveau-Mallet et al. (2013) reported an increase of P sorption capacity (PSC) from 0.737 mg TP/g_{media} to 2.62 mg TP/g_{media} for HRTs of 4.3 and 19.2 hours, respectively. The improved removal with increasing HRT is generally attributed to better contact between the water and the media favouring crystal growth although this is often non P-containing precipitates such as calcite (Claveau-Mallet et al., 2013; Barca et al., 2013). The difference in removal across studies reflects the impact of the other components in the wastewater and the media samples being tested. For instance, the composition of EAF and BOF steel slag differ with the former containing more Al_2O_3 and total Fe compared to the latter, which is richer in CaO (Barca et al., 2014).

In most of the studies, the commercially available form of slag is researched, which has a broad particle size distribution (5-20 mm) compared to the typical size range of 10-12 mm used in horizontal flow constructed wetlands (Dotro et al., 2017). The importance of size is that it impacts the reactive specific surface area, the size of the void spaces through which the components need to diffuse, the capacity to maintain hydraulic throughput as solids accumulate (clogging) and the risk of cementing (Walter, 2012; Dotro et al., 2017). In the only previous study on the impact of media size on steel slags, both BOF (6-12 mm and 20-50 mm) and EAF (5-16 mm and 20-40 mm) slags were compared (Barca et al., 2014). The findings indicated that smaller media sizes led to higher P removals for both types of slags, specifically >99% of P removal and 98% removal for the smaller sizes of BOF and EAF slags, respectively, and 95% and 88% removal for the larger sizes of the same materials. Similar findings are supported with a trial with small calcium rich attapulgite media with sizes of 0.2-0.5, 0.5-1.0 and 1-2 mm (Yin et al., 2017). The smaller media was observed to remove P quicker and raise the pH faster; both aspects were attributed to a greater available surface area for CaO dissolution as the media size decreased. In recent times the use of small size media (0-5 mm) made from apatite has gained interested, looking to translate the use of the media in vertical flow constructed wetlands (Troesch et al., 2016; Fonseca, 2016).

Overall the need for better understanding of the role of media size is apparent. The current paper aims to address this knowledge gap by providing insight from a series of trials in both synthetic and real wastewater for different size fractions of the same media, a BOF steel slag.

Table 2-1 Comparison of operational parameters and PSC of reactive materials reported in literature.

Media*	Media size (mm)	Experiment type**	Water type	Column diameter (mm)	Media height (mm)	Inlet TP (mg/L)	HRT*** (h)	Experiment duration (months)	PSC (mg P/g slag)	References
BF steel slag	0.25-4	C	Synthetic, KH_2PO_4 and K_2HPO_4	300	500	10	47	14	1.25	Johansson (1999)
BF steel slag	0-3	F	Real	8.8 m^3 volume		6.6	70	12	0.15	Asuman Korkusuz et al. (2007)
BF steel slag	0-4	C	Synthetic, KH_2PO_4	100	500	5	7	17	-	Gustafsson et al. (2008)
BOF steel slag	1-2	C	Real	50	500	2.3	~ 60 [a]	-	-	Cha et al. (2006)
BOF steel slag	20	C	Synthetic, KH_2PO_4	-	-	100-300	8	10	8.39	Bowden et al. (2009)
BOF steel slag	7-14	C	Real	160	700	6	2/6/24/48	9	0.32/0.12/0.19/0.24	Walter (2012)
		F	Real	64 m^3 volume		5±1.6	16	24	0.9	
BOF steel slag	20-40	F	Real	6 m^3		8.5	48	24	0.61	Barca et al. (2013)
BOF steel slag	6-12/20-50	F	Synthetic, KH_2PO_4	42 L volume		10.8	24	13	1.05/1.01	Barca et al. (2014)
BOF steel slag	5.0-12.5	C	Real	250	500	6	~ 15 [a]	-	0.34	Letshwenyo (2014)
BOF steel slag	0.1-10.0	C	Synthetic, KH_2PO_4	120	300	15	8	7	3.1	Blanco et al. (2016)
EAF steel slag	-	C	Synthetic	150	1000	10	1.35/5.4/21.6/43.2	7	-	Shilton et al. (2005)
EAF steel slag	2.5-10.0	C	Synthetic, KH_2PO_4	103	150	350-400	8.3	9	1.35	Drizo et al. (2002)
EAF steel slag	10-20	F	Real	1441.5 m^3		8.4	72	132	1.23	Shilton et al. (2006)
EAF steel slag	5-10	C	Real	280	1000	24.3	24	28.5	3.18	Drizo et al. (2008)
EAF steel slag	5-10	C	Synthetic, KH_2PO_4	150	170	107	4.3/19.2	7	0.737/2.62	Claveau-Mallet et al. (2013)
EAF steel slag	20-40	F	Real	6 m^3		8.5	48	24	0.32	Barca et al. (2013)
EAF steel slag	5-16/20-40	F	Synthetic, KH_2PO_4	42 L volume		10.8	24	13	0.91/0.81	Barca et al. (2014)
Apatite	0.1-0.9	C	Synthetic, KH_2PO_4	85	100	20	5.6	20	13.9	Molle et al. (2005)
Apatite	3.0-6.0	C	Synthetic, KH_2PO_4	100	320	30	36	1.5	0.3	Bellier et al. (2006)
Apatite	4.02-9.21	C	Synthetic, -	90	200	1--16	3.3	3	7	Harouiya et al. (2011a)
		F	Real	600 L volume		4.2	48	17	1	
Apatite	1.27-4.02	F	Real	9500 L volume		5.8	69.6	30	0.8	Harouiya et al. (2011b)
		F	Real	600 L volume		5.9	48	16	1.1	
Polonite	2.0-5.6	C	Synthetic, KH_2PO_4	100	500	5	7	17	1.9	Gustafsson et al. (2008)
Attapulgite	0.2-0.5/0.5-1.0/1.0-2.0	C	Synthetic, KH_2PO_4	50	500	10	4/8	5	-	Yin et al. (2017)
Filtralite P®	0.5-4.0	C	Synthetic, KH_2PO_4	140	1500	10	91.2	10	-	Adam et al. (2007)
		C	Real				84	7	-	
LECA	2-4 and 10-20	F	Real	173 m^3 volume		4.4	-	24	-	Oovel et al. (2007)
Phosfate™	5-12.5	C	Real	250	500	6		5	2.3	Letshwenyo (2014)

*BF: Blast Furnace slag, BOF: Basic Oxygen Furnace slag, EAF: Electric Arc Furnace slag; ** C: Column, F: Filter configuration;*** $HRT = \frac{V\cdot\varphi}{Q}$, where V is the volume of the column or filter, φ is the porosity of the material and Q is the inlet flow; [a] Assuming a porosity of 0.49.

2.2 Materials and methods

2.2.1 Wastewater

Real wastewater was obtained from the final effluent of a STW treating approximately 7,500 PE. The treatment process included screens, primary settlement tanks, percolating filters, humus tanks and a pile cloth filtration system. The total P concentration averaged 3.5±0.7 mg/L with a phosphate (PO_4) content of 3.0±0.8 mg/L at a pH of 7.8±0.2 with an alkalinity of 133±17 as $mgCaCO_3$/L. Specific metal concentrations for Ca, Na, Al, Cu, Fe and V were 86.8±7.5 mg/L, 94.6±15.7 mg/L, 52.6 µg/L (12.7 µg/L-632.9 µg/L), 33.8±8.2 µg/L, 299.5±91.9 µg/L and 9.5±3.8 µg/L, respectively. The synthetic recipe consisted of ammonium dihydrogen phosphate (ADP) (Fisher Scientific) dissolved in tap water to mimic the approximate concentration of the real wastewater. Equivalent characteristics of the trials were 3.9±0.8 and 3.7±0.7 mg/L for total P and PO_4 at a pH of 8.2±0.3 and an alkalinity of 187±32 as $mgCaCO_3$/L. More variation was observed with respect to the metal species with significantly higher levels of Cu (112±53 µg/L) and significantly lower levels of sodium (16.2±2.1 µg/L), aluminium (5.2 µg/L (1.4-75.9 µg/L)) and iron (5.0 µg/L (2-140 µg/L)). Levels of calcium (102.2±6.9 mg/L) and vanadium (2.6 µg/L (1.9-39.4 µg/L)) were similar.

2.2.2 BOF steel slag

The BOF steel slag was supplied by Tarmac from the same site (Port Talbot, Wales) in two fractions ('10mm' and '6mm' fractions). The fractions were sieved and mixed to generate different size ranges with an average particle size, based on dry sieving in accordance with BS EN 933-1:2012 (BSI, 2012), of 5.09 mm, 7.60 mm and 10.04 mm. A further two finer fractions were generated by reduction in a ball mill (Fritsch, Laboratory Planetary Mill) to an average size of 0.75 and 1.75 mm (Table 2-2). The bulk density was estimated by measuring the weight of a known volume of material, and the porosity was calculated by measuring the amount of water required to saturate a known volume of media.

In the case of the real wastewater column experiments three media size bands were selected: 2-6 mm, 4-10 mm and 10-20 mm. In addition, the trials on the *stabilisation* phase as a function of HRT were conducted on 4-10 mm media.

Table 2-2. Physical characteristics of BOF steel slag fractions.

Mean particle size (mm)	**Specific surface area (m^2/m^3)**	**Relative gap between media**[*]	**UC**[**] **(d_{60}/d_{10})**	**Bulk density (kg/L)**[***]	**Porosity (%)**[***]
0.75	8.00	0.02	1.2	1.91	45.1
1.75	3.43	0.12	2.0	1.89	46.1
5.09	1.18	1.00	1.4	1.86	47.4
7.60	079	2.23	1.1	1.82	48.3
10.04	0.60	3.89	1.1	1.74	49.8
9.31[****]	0.64	3.34	1.5	1.76	48.3

[*]measured as area between three equal sized circles [see Supplementary Information, Appendix A]; [**]UC= Uniformity coefficient, d_{60}= size opening that allows 60% of the total sample mass to go through, d_{10}= size opening that allows 10% of the total sample mass to go through; [***]Number of replicates (n) =3; [****] 4-10mm steel slag.

2.2.3 Experimental set-up

The experiments were conducted in 1000 mm height Perspex columns containing media to a height of 600 mm (Figure 2-1). The diameter was chosen to ensure the column diameter was at least 20 times the average particle size to negate wall effects and so varied based on the media being tested (Martin et al., 2013). All tests were conducted in parallel from a common feed, which was continuously mixed with a submersible pump (Lowara, model DOC3) at room temperature (20°C). The columns were fed in a downward flow direction at a HRT of 6 hours unless otherwise stated. The HRT was calculated as the EBCT multiplied by the initial porosity.

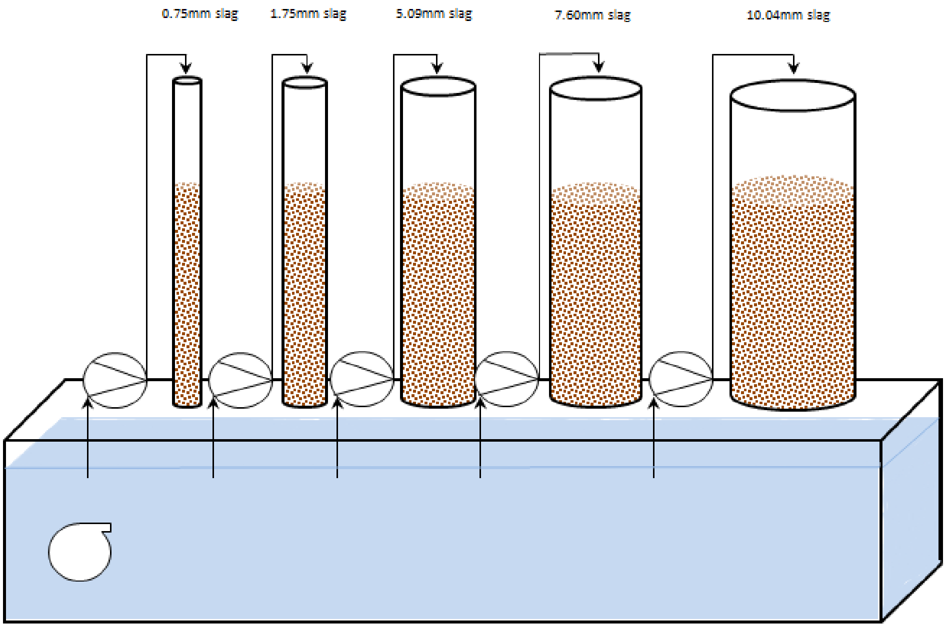


Figure 2-1 Schematic diagram of experiment set-up.

The impact of HRT was investigated with the synthetic wastewater. In the case of the trials with the different media sizes, the HRT was changed after the P removal had stabilised. This was observed at around 500 days. At this point the HRT was changed to 24 hours for 108 days followed by 6 hours for 53 days, then 4 hours for 52 days and finally 2 hours for 283 days. In addition, a separate series of column trials were conducted with new 4-10 mm particles (average particle size of 9.31 mm) at HRTs of 6, 24 and 48 hours for a period of 29-50 days to understand the impact of HRT if set as the operational rate (stabilisation phase). These were conducted in separate columns with similar characteristics as before and with fresh media for each HRT.

2.2.4 Sample analysis

Water samples of 1 L were taken from the inlet tanks and column effluents, approximately three times a week. The samples were analysed by Thames Water laboratories (Reading) following accredited procedures for the following parameters in accordance to standard methods: TP and PO_4 (BS EN ISO 6878:2004, BSI (2004)), alkalinity (BS EN ISO 9963-1:1996, BSI (1996)) and suspended solids (BS EN 872:2005, BSI (2005)). The pH was measured using a pH meter (Hach, probe model pHC201), within 10 minutes after taking the sample, in order to avoid CO_2 dissolution from air.

An array of metals (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Li, Mg, Mn, Mo, P, K, Na, Sr and Zn) were analysed by Thames Water laboratories (Reading) following accredited procedures using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific, model iCAP 6000). In addition, Sb, As, Cd, Co, Pb, Ni, Se, Ag, Sn, Ti, W and V were analysed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Perkin Elmer, model NexION Dual gas). In both cases samples were analysed after acidifying and digesting the sample at 85 °C overnight.

X-ray fluorescence (XRF) was employed to analyse the surface of the 0.75 mm and 1.75 mm column material after 125 days of operation. The samples were taken from the middle of each column and three replicates per sample were analysed.

2.3 Results and Discussion

2.3.1 Effect of BOF steel slag particle size on P removal, pH and metal release

The different BOF steel slag fractions showed two distinct P removal behaviours (Figure 2-2). The two smallest slag fractions (0.75 mm and 1.75 mm) achieved stable effluent TP concentrations below the detection limit of 0.08 mg/L and PO_4-P concentrations below the detection limit of 0.04 mg/L during the whole duration of the experiment. However, the trials with these media were terminated after 125 days due to clogging associated with the precipitated products cementing up the pore spaces (Figure 2-3). In part, it is believed that the process was exasperated by the use of ball milling to reduce the media size, as it generated fresh surfaces that increased the rate of CaO dissolution and hence precipitate generation. X-ray fluorescence (XRF) analysis of the clogged two smallest fractions confirmed that the media was covered in $CaCO_3$ deposits.

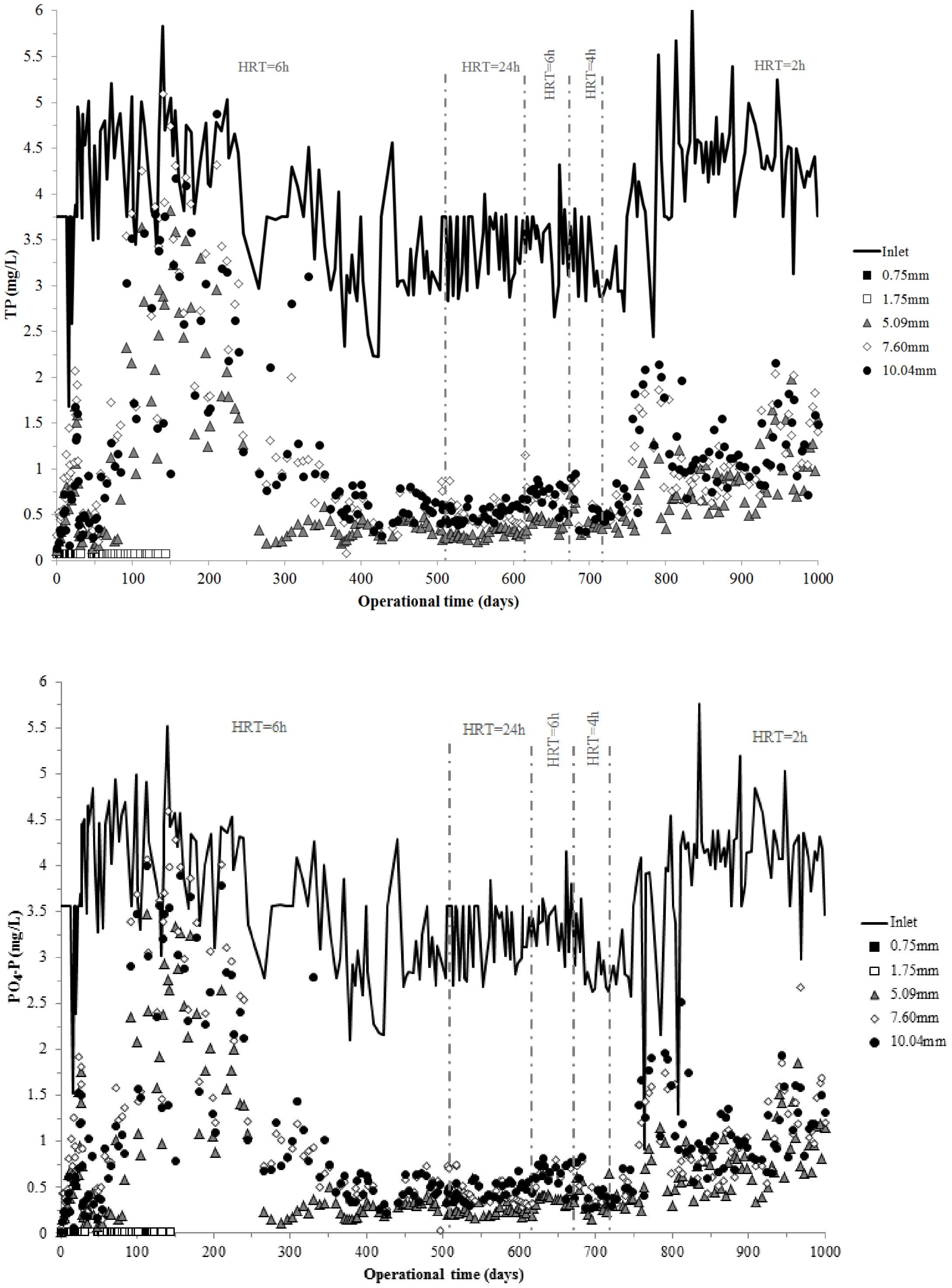


Figure 2-2 Performance of the five different media sizes when treating synthetic wastewater in terms of a) TP and b) Ortho-phosphate.

Figure 2-3 Photograph of cemented steel slag from the column with 1.75 mm sized media.

In contrast, the operation with the three larger media sizes remained active for the duration of trial (1000 days) and exhibited two different phases of operation. In the initial phase, *stabilisation*, the effluent TP concentration initially increased before decreasing to a relatively stable level, the *steady-state* phase (Figure 2-2). The peak concentration and time taken to reach it varied for the different media sizes such that the peak effluent TP concentration for the 5.09 mm media was 3.82 mg/L after 150 days of operation compared to 5.09 mg/L at 140 days for the 7.60 mm fraction and 4.88 mg/L at 210 days for the 10.04 mm fraction. Thereafter the effluent TP decreased until it reached a steady-state value at day 266 for the 5.09 mm slag fraction, and day 360 for the slag fractions 7.60 mm and 10.04 mm. These equated to mass loading levels of 1194.7 mgTP/kg$_{\text{media}}$, 1620.5 mgTP/kg$_{\text{media}}$ and 1732.1 mgTP/kg$_{\text{media}}$ at the onset of the *steady-state* phase.

The observed results are different from the majority of other studies which show low effluent TP concentrations for a period of time followed by gradual increase (Drizo et al., 2002; Bowden et al., 2009; Walter, 2012; Claveau-Mallet et al., 2013; Letshwenyo, 2014). It is posited that differences in the media (some used EAF steel slag) as well as the concentration and composition of the wastewater (some were real municipal and some tap water spiked with different chemicals at different Ca:P ratios) provides a pathway for a series of different precipitation reactions that can include or exclude inclusion of P. One reported study using a media based on apatite showed a similar profile when treating a synthetic wastewater made up from KH_2PO_4 in tap water to an initial P concentration of 20 mg/L, which decreased to below 2 mg/L during the first 150 days, to then increase to a maximum value of 14 mg/L at day 300, and then decreased again to concentration values of below 2 mg/L at the end of the experiment at day 550 (Molle et al., 2005). Further, a reduction in phosphate precipitation has recently been reported in the case of treatment using immobilised algae where similar pH changes occur to the current study (Whitton et al., 2017). In such cases, the exclusion of PO_4 under certain conditions was attributed to changes in the relative kinetics of precipitates that exclude and include P (e.g. calcite and calcium phosphate) (Montastruc et al., 2003).

The *stabilisation* phase ran until the end of the 6 hours HRT experiment at 504 days when the HRT was altered. Over this phase, the average TP concentrations achieved by the three largest slag fractions were 0.96 mg/L (0.11 mg/L-3.82 mg/L), 1.45 mg/L (0.08 mg/L-5.09 mg/L) and 1.29 mg/L (0.14 mg/L-4.88 mg/L) for slag fractions of 5.09 mm, 7.60 mm and 10.04 mm, respectively. It is suggested that during the steady-state phase, P is embedded into the $CaCO_3$ matrix as well as co precipitation of $CaPO_4$ and adsorption of phosphate onto the formed precipitates (Figure 2-4). Once the precipitation reaction is initiated it is reported that it continues even if the pH decreases through an auto catalysed pathway (House, 1999).

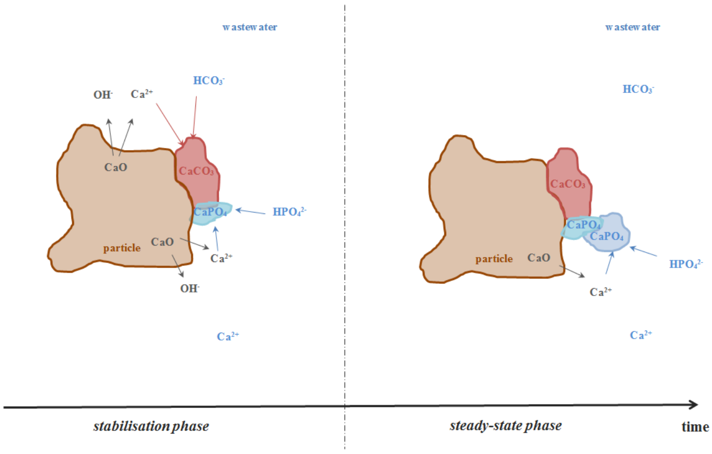


Figure 2-4 Conceptual schematic of hypothesised P removal mechanism.

The equivalent pattern in terms of ortho-phosphate was similar for all media sizes. In the case of the larger sizes the peak PO_4-P concentration was 3.48 mg/L, 4.60 mg/L and 4.0 mg/L for the 5.09 mm, 7.60 mm and 10.04 mm fractions, respectively. The smaller media was observed to reach the steady-state phase sooner and maintain a lower overall level. To illustrate, during the 6 hour HRT steady-state phase the effluent PO_4-P did not exceed 0.5 mg/L in the case of the 5.09 mm media compared to 0.73 mg/L and 0.65 mg/L for the 7.6 and 10.04 mm diameter media respectively. Throughout the course of the experiment the ratio of ortho-phosphate to total P (PO_4-P:TP) decreased slightly from the influent level of 0.93 to 0.84, 0.89 and 0.86 for slag fractions of 5.09 mm, 7.60 mm and 10.04 mm, indicating that the predominate form of P was PO_4-P and that the residual total P was not derived from exiting precipitates. The differences observed with the smallest media size are consistent with other studies across different media types (Barca et al., 2014; Yin et al., 2017) and is attributed to the increased reactive specific surface area generating an increased rate of CaO dissolution. In addition, the space between the media is reduced, enhancing the opportunity to ensure reaction with the available P in the liquid. To illustrate, if the media is viewed as three circles, the area between the media is 3.9 times greater for the 10.04 mm diameter media compared to the 5.09 mm diameter media (Table 2-2).

Operation of the steel slags raised the pH of the synthetic wastewater with the maximum changes observed for the freshly milled media reaching initial pHs of 10.2 and 12.0 for the fractions 0.75 mm and 1.75 mm, respectively (Figure 2-5). The initial rise was lower for the larger media with peak values of 9.5, 9.3 and 9.9 for the 5.09 mm, 7.60 mm and 10.04 mm fractions, respectively. However, the pH decreased below 9 after 6, 10 and 18 days respectively and returned to the inlet level at around day 125. This differs from other reported cases where much higher pH values have been reported and have lasted for prolonged periods. To illustrate, a previous trial with BOF reported a pH increase to 12.3 for 52 weeks during a trial with tap water spiked with KH_2PO_4 (Barca et al., 2014). However, similar results were reported for EAF slags suggesting that the differing material composition, particularly the CaO fraction play an important part in the pH development. The rapid return to the influent levels reflect the relatively high alkalinity of the tap water used in the current study (187±32 as mg$CaCO_3$/L). In fact, the alkalinity increased across the columns reaching a maximum value of 215 as mg$CaCO_3$/L for the 5.09 mm slag fraction (Supplementary Information, Appendix A).

Interestingly, the stabilisation of the pH does not mirror the switch between the two operational phases supporting the idea of auto-catalysed precipitation. This further suggests that the changeover of the phases reflects the conditioning of the surface of the media reducing the ability for further dissolution.

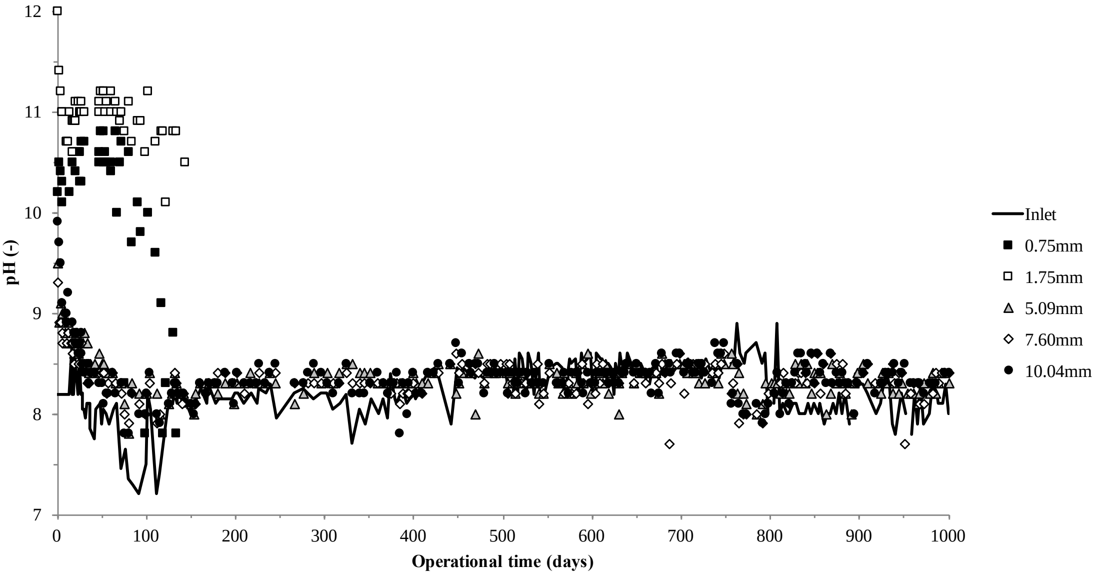


Figure 2-5 pH profile of the treated water during the column experiments treating synthetic wastewater with different media sizes.

No appreciable changes in the metal content of the water were observed with the exception of an increase in iron, manganese, tin and vanadium and a decrease in copper and titanium (Table 2-3). Vanadium is of particular interest as it is not normally considered due to the fact that it is not expected in wastewater. However, the metal is used in the steel making process and is known to be environmentally toxic (Gomes et al., 2017). The two smallest slag fractions leached the most V congruent with the production of fresh surface area and high pH leading to maximum recorded concentrations of 616 µg/L for the 0.75 mm fraction and 585 µg/L for the 1.75 mm fraction, from an inlet concentration of below 1.9 µg/L (Supplementary Information, Appendix A). Equivalent data for the larger fractions showed less initial release at 427, 337 and 351 µg/L for the 5.09 mm, 7.60 mm and 10.04 mm diameter media, respectively. The effluent V concentration then decreased to stable values after 115 days, 99 days and 112 days of operation, respectively (Figure 2-6). The stable values were below the suggested discharge target of 60 μg/L but this was exceeded during the initial stages of operation.

Table 2-3 Change in metal concentration during the trial with synthetic wastewater, average [minimum-maximum].

Metal	Influent (μg/L)	Effluent (μg/L)		
		5.09 mm	7.60 mm	10.04 mm
Copper	123.7 [6.0-780.0]	5.7 [3.0-21.0]	11.2 [3.0-86.0]	11.7 [3.0-87.0]
Titanium	8.5 [1.7-17.1]	2.0 [1.5-8.1]	2.5 [1.5-8.9]	2.6 [1.5-10.0]
Iron	5.0 [2.0-140.0]	19.7 [2.0-478.7]	36.2 [2.0-797.6]	52.1 [2.0-3383.9]
Manganese	1.0 [0.8-34.1]	13.8 [0.8-239.2]	13.3 [0.8-206.1]	16.2 [0.8-959.2]
Vanadium	2.6 [1.9-39.4]	21.1 [1.9-426.8]	12.5 [1.9-337.2]	13.2 [1.9-351.1]
Tin	0.8 [0.8-1.5]	2.9 [0.8-8.0]	3.0 [0.8-8.0]	3.1 [0.8-8.0]

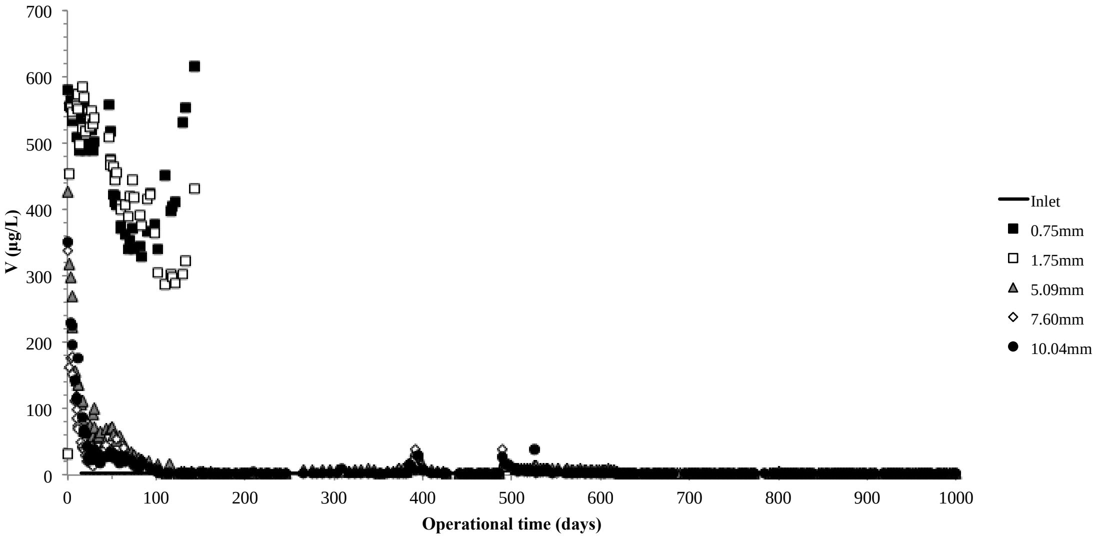
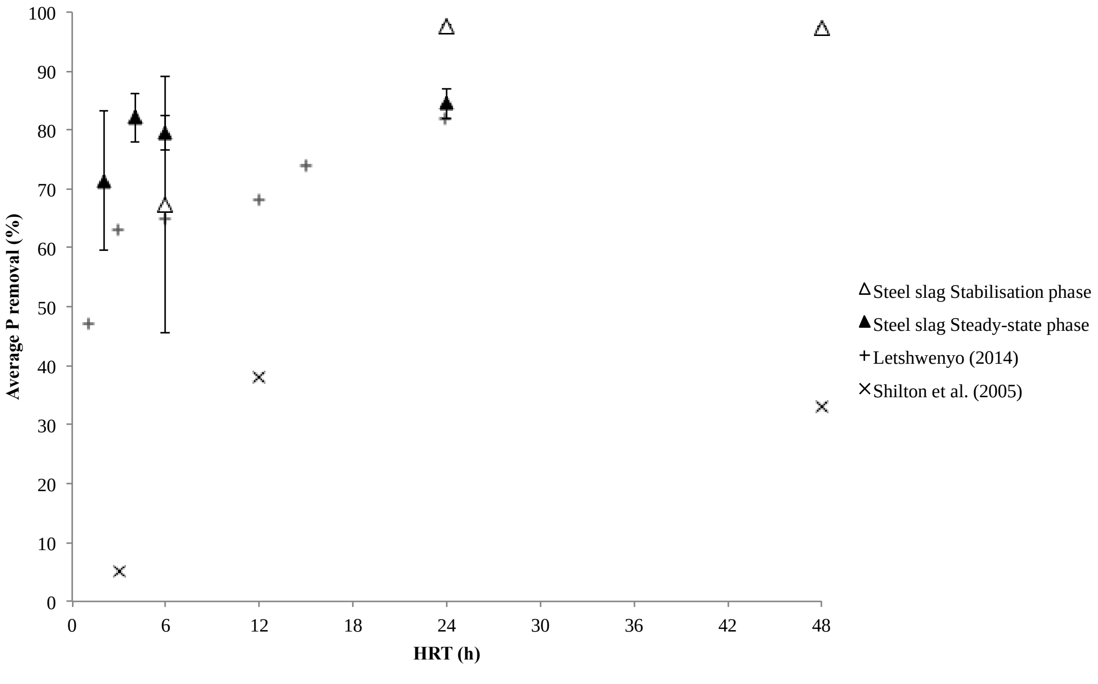


Figure 2-6 Vanadium release from the steel slag.

2.3.2 Impact of HRT

The effect of HRT on steel slag performance differed between the *stabilisation* phase and the *steady-state* phase. During the *stabilisation* phase, the removal increased at elevated HRTs with averages of 67.4±21.8 %, 97.6±0.3 % and 97.3±0.2 % for HRTs of 6, 24 and 48 hours, respectively (Figure 2-7a). The increased removal at higher HRTs is attributed to the prolonged contact with non conditioned media as CaO dissolution is time dependant (Letshwenyo, 2014) and is observed through the difference in pH with values of 8.41 ±0.36, 11.23 ±0.30 and 11.52 ±0.23 for the HRTs of 6, 24 and 48 hours respectively (Figure 2-7b). The trend is consistent with previous trials but the removal levels are significantly greater than previously reported. For instance, Letshwenyo (2014) reported an increase in P removal of 45 to 82% as the EBCT increased from 2 to 48 hours treating a real wastewater with BOF steel slag. Similarly, Shilton et al. (2005) reported an increase from 5% to 48% as the HRT increased from 3 to 72 hours. The differences indicate that selection of appropriate HRT requires pilot testing to reflect the differences observed due to variation in the material and water composition from trial to trial. Effluent V concentrations notably increased with HRT, from an average of 32.0 (1.9 µg/L-755.0 µg/L) to 711.9 µg/L (643.6 µg/L-897.7 µg/L) for HRTs of 6 and 24 hours.



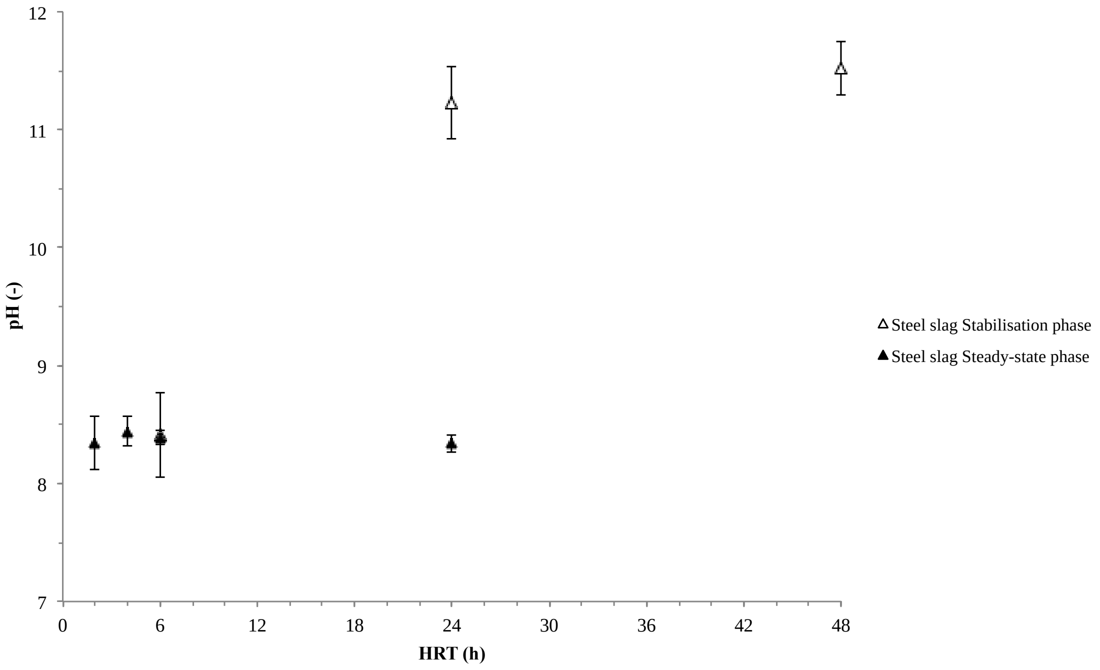


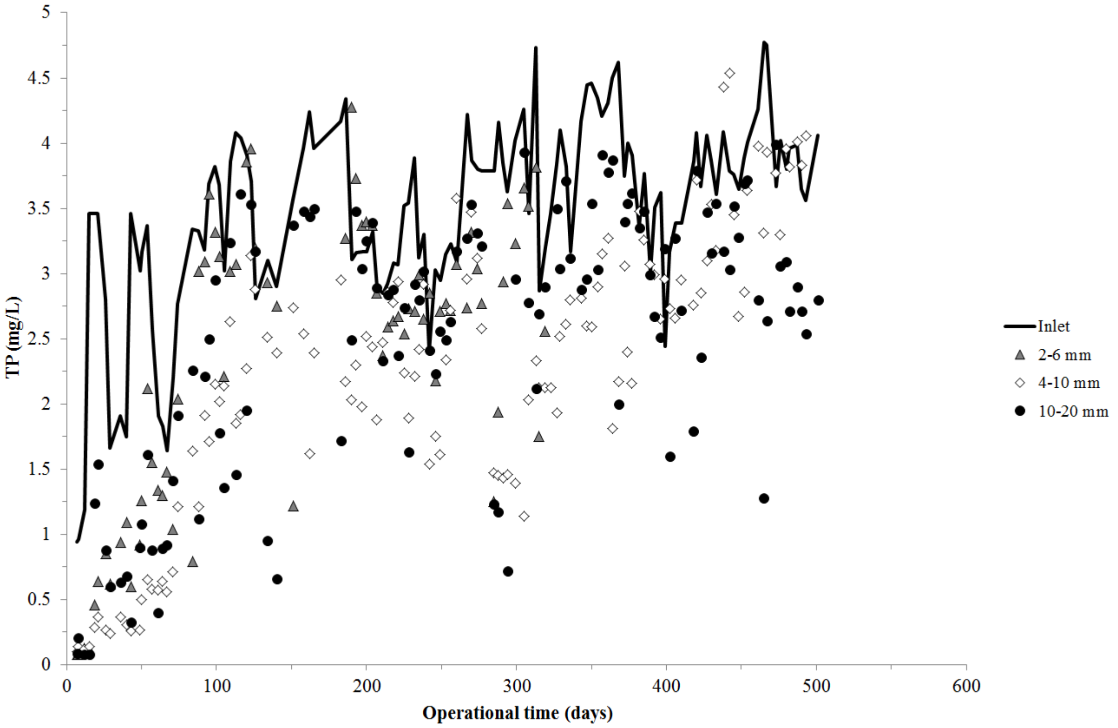
Figure 2-7 Effect of HRT on (a) average P removal and (b) pH rise for BOF steel slag during the stabilisation and steady-state phases.

The effect of HRT on steel slag effluent TP, pH and V during the steady-state phase was considerably less noticeable compared to the *stabilisation* phase (Figure 2-2). To illustrate, average observed P removal was 71.4±11.8 %, 82.1±4.1 %, 79.5±3.0 % and 84.5±2.6 % for HRTs of 2, 4, 6 and 24 hours (Figure 2-7a). These were equivalent to average effluent TP concentrations of 1.2±0.5 mg/L, 0.6±0.2 mg/L, 0.7±0.1 mg/L and 0.5±0.1 mg/L for the same HRTs. The changes in effluent concentration did not coincide with alteration of the pH which remained approximately at the influent level throughout the alteration of HRT during the *steady-state* phase. Accordingly, it is suggested that the change in HRT does not reflect alteration to the dissolution rate or indeed the level of precipitation. Instead it is posited that pre-conditioning of the media through $CaCO_3$ precipitation mean that a switch in predominate removal pathway has occurred to that of precipitate growth and adsorption. In such cases, the effluent P concentration is related to the contact time and the remaining uptake capacity of the coating and hence the cumulative nature of the steady state trial needs to be considered. Overall the trial results indicate that once conditioned short HRT may be possible whilst still retaining good removal and as such only small section of the constructed wetlands may need to include the reactive media.

2.3.3 Comparison of synthetic and real wastewater

Equivalent trials with real tertiary wastewater at a HRT of 6 hours from a municipal sewage works generated a different pattern to that observed with the synthetic wastewater (Figure 2-8). The effluent TP was similar for all three media sizes and increased quickly from zero to that of the influent wastewater. Direct comparison in terms of applied P load (around 282 mgTP/kg$_{\text{media}}$) revealed that for instance, the effluent TP was 3.07 mg/L for the real wastewater compared to 0.32 mg/L for the synthetic wastewater for the 5.09 mm and the 2-6 mm fractions, respectively. Whilst the level of scatter during the initial *stabilisation* phase appeared similar, the effluent TP did not reduce and reach a *steady-state* phase as was observed during the synthetic wastewater trials. The initial pH generated by the steel slag was similar for all three media sizes at around pH 10 which was similar to that observed with the synthetic wastewater. However, the pH reduced more slowly and remained stable at an elevated pH of between 8.1 and 8.7. Whilst these values are similar to those observed during the synthetic wastewater trials, the difference compared to the influent pH is not. Further, no difference was observed in relation to media size unlike previously reported (Barca et al., 2014; Yin et al., 2017) and observed during the synthetic trials. Overall this suggests that the use of smaller media sizes may not be warranted in real systems and that the general results from the synthetic trials may be overly optimistic, especially in terms of the translation of appropriate HRT. This is supported by previous real wastewater column trials with BOF steel slag, albeit with higher initial P concentrations and different wastewater characteristics. A HRT of 6 hours was reported to yield an effluent TP of between 2 and 3 mg/L and a pH of c8.5 to 8.9 (i.e. similar to the current case) (Walter, 2012). In the trials, sustained removal below a TP of 1 mg/L required a HRT of 48 hours yielding a pH of between 9 and 10. Further, in a separate trial of real municipal wastewaters, an EBCT of at least 30 hours was required to ensure a removal efficiency above 70%, approximately the level required to go below 1 mg/L in the current trial (Letshwenyo, 2014). Another study using EAF steel slag reported HRTs higher than 4.8 hours were needed to decrease effluent P concentrations below 1 mg/L (Claveau-Mallet et al., 2013). Interestingly, in both studies by Walter (2012) and Letshwenyo (2014), no specific *stabilisation* phase was observed although the media came from the same stock as in the current trial. Instead, the effluent TP started at its lowest level, remained stable for a while and then gradually increased. This infers that the interaction between the media and the wastewater is critical and is currently not able to be predicted, necessitating the use of pilot trials to establish appropriate design and operating conditions.

Key differences between wastewaters relate to variations in influent P concentration, alkalinity and the background constituents that influence which precipitates form. Another key variable is the organic and solid contents of the wastewater which provide an alternative coating onto the media inhibiting CaO dissolution and therefore, hinder the developments of the P removal pathways.



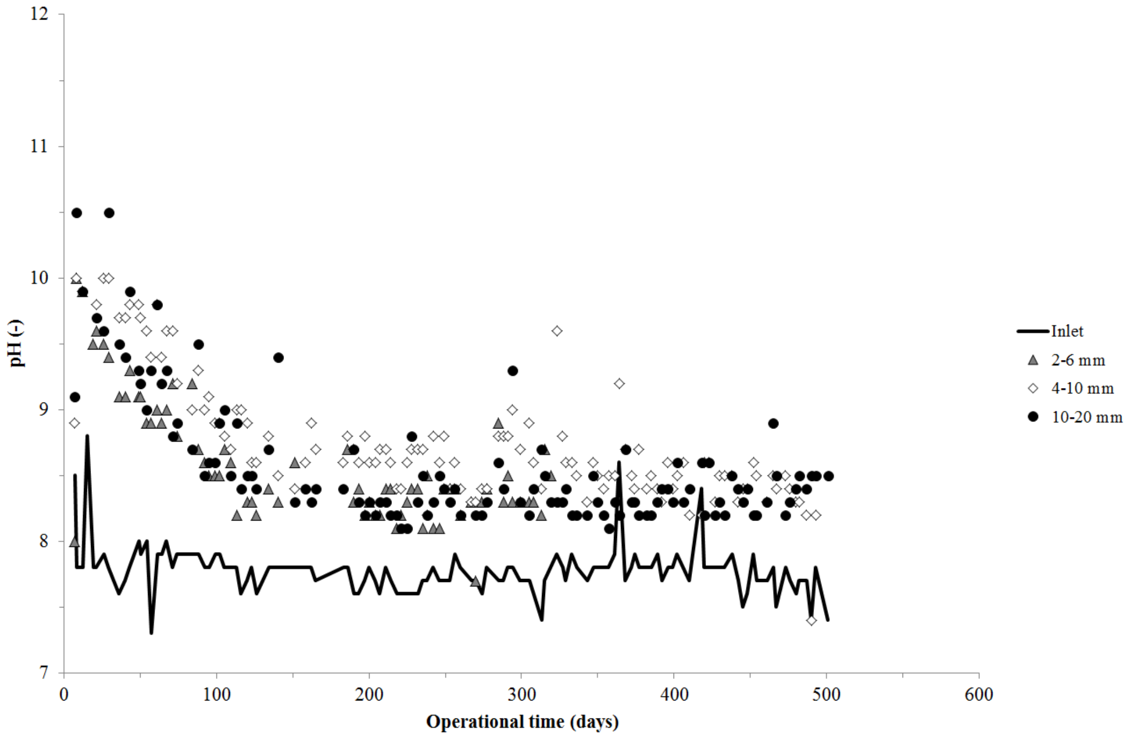


Figure 2-8 Performance of different sized media of BOF steel slag treating a real tertiary municipal wastewater in terms of (a) effluent TP and (b) pH at a HRT of 6 hours.

2.4 Conclusions

- The use of BOF steel slag enables effective reduction of P utilising a range of media sizes and HRTs.
- The trials revealed two distinct phases of operation: a *stabilisation* phase where precipitates coat the media (driven by CaO dissolution rising the pH) followed by a *steady-state* phase where the removal continues at reduced pH and HRT.
- Smaller media sizes produced better effluent P but raised the pH more reflecting a proposed mechanism providing more sites for CaO dissolution and maximised reaction through reduced gap spaces between the media particles.
- Comparison to other trials revealed significant differences in profiles in both P and pH indicating that difference in the components found within both the media and the wastewater necessitate site specific testing.
- Comparison of data from synthetic to real wastewater revealed significant differences in relation to the profile of effluent P and the pH as a function of

media size indicating that translation of synthetic data needs to be considered carefully.

2.5 Acknowledgments

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2.6 References

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3 Comparison of basic oxygen furnace steel slag and an apatite based media for phosphorus removal treating synthetic and real wastewater

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Abstract

Basic oxygen furnace (BOF) steel slag and apatite have been acknowledged as the most promising reactive materials to be used within constructed wetlands for P removal from domestic wastewater. This work compared the performance of both materials, including four different apatite based materials under varying hydraulic retention times (HRT) and wastewater characteristics (synthetic and real wastewater). The effect of HRT on each media was different and was dependant on the phase at which it was varied (*stabilisation* vs *steady-state* phase). Higher HRTs produced higher P removal and higher pH values on the *stabilisation* phase for both materials, although apatite showed higher P removal than steel slag even for short HRTs. Higher HRTs did not significantly affect pH but apatite showed higher P removal than steel slag for shorter HRTs, due to the differences in the conditioning material for apatite (calcium phosphate) and steel slag (calcium carbonate) produced in the *stabilisation* phase. Overall, lower P concentrations appear possible with apatite based media, even at relatively short HRTs. However, preconditioned steel slag at slightly elevated HRT may be able to meet likely effluent TP discharge targets of sub 1 mg/L. Results for different apatite based materials indicated that composition of the binding agents had a significant impact on the overall effectiveness of the media. Trials with synthetic wastewater overestimated the P sorption capacity (PSC) for both materials, so extrapolation to operational lifetimes should be performed cautiously.

Keywords: apatite, phosphorus, steel slag

3.1 Introduction

The replacement of traditional media used in constructed wetlands (soil, sand, gravel) with reactive media is gaining interest as a means of passive phosphorus (P) removal in small sewage treatment works (STW) (Vohla et al., 2011). The process of P removal with such media is thought to occur through a combination of chemical precipitation and adsorption mechanisms and hence are strongly related to the complex interactions between the constituents of the selected media and the wastewater being treated (Joko, 1984; Seckler et al., 1996; Molle et al., 2005). The media provide seed sites, lowering the energy barrier by negating the need for homogeneous nucleation favouring precipitative growth (Jang and Kang, 2002) which is favoured as the pH, calcium concentration and HRT increase (Bellier et al., 2006). The main competing species is thought to be calcium carbonate which co-precipitates and is strongly influenced by the relative alkalinity of the water (Jang and Kang, 2002). The described pathways have been demonstrated in numerous column experiments, but in batch experiments, adsorption is commonly seen to predominate, due to the differences in the profile of the different components (Molle et al., 2005).

Whilst a wide array of materials have been tested to date, those rich in Ca, Fe, Al or Mg have been reported to deliver a higher P sorption capacity (PSC) based on the proposed pathways described above (Drizo et al., 1999; Brix et al., 2001; Cucarella and Renman, 2009; Vohla et al., 2011; Walter, 2012). Additional criteria including hydraulic conductivity, media size, leaching of metals, physical integrity, cost and the potential to reuse the media afterwards require consideration for use in constructed wetlands. Two options gaining significant consideration in the UK and elsewhere are steel slag (industrial by-product) and media based on apatite (man-made material) (Bellier et al., 2006; Harouiya et al., 2011a; Fonseca, 2015; Vale, 2017).

Steel slag is a by-product from the steel making industry when the molten iron formed in a blast furnace is mixed with scrap metal and lime in either a basic oxygen furnace (BOF) or electric arc furnace (EAF). The main difference between them is that BOF slag has a higher content in CaO, whereas EAF slag is richer in Al_2O_3 and total Fe (Barca et al., 2014). Batch, column and field trials have confirmed the effectiveness of the material for P removal treating both synthetic and real wastewater across a range of inlet P concentrations (2.3-300 mg/L) and HRTs (6-132 hours) with reported PSCs of between 0.15 and 8.30 gTP/kg_{media} achieving sub 1 mg/L effluent total P (TP) concentrations (Chapter 2). The use of the media is commonly associated with a rise in the pH of the final water up to pH 12 due to the dissolution of CaO generating fresh OH^- ions. Accordingly, pH reduction is required prior to discharge with a number of approaches being considered including the use of peat filters (Liira et al., 2009; Vohla et al., 2011; Barca et al., 2014) and direct acid dosing (Germain-Cripps, 2016, pers. comms, 15th March). Other concerns include the leaching of metals which include recent evidence of release of vanadium (Chapter 2; Sippula et al., 2017) and the variation in reported performance between trials. This reflect two aspects; firstly, differences in the constituents of both the media and the wastewater lead to different precipitation pathways (Molle et al., 2005) and secondly, the trials are not conducted under identical conditions with differences in the initial P concentration, HRT and wastewater type making direct comparison challenging (Cucarella and Renman, 2009).

Apatite ($Ca_5(PO_4)_3(F, OH, Cl)$) is a natural calcium-phosphate mineral, and it constitutes the major component of phosphorite, also known as phosphate rock, along with calcite and quartz. The media is manufactured in four steps: 1) raw phosphate rock crushing, 2) crushed rock and hydraulic additive mixing, 3) granulation and 4) drying. The final product, *Phosclean*, referred to as apatite, is a near spherical media with a diameter in the size range around 2.5 to 8.5 mm with an average size of 5 mm. The media has been successfully used in vertical flow constructed wetlands for P removal, where smaller media are normally used (Troesch et al., 2016). A more restricted set of trials have been reported for this media than steel slag and have included both synthetic and real wastewater with an influent P range of 1-30 mg/L over a HRT range of 3.3 to 69.6 hours (Molle et al., 2005; Bellier et al., 2006; Harouiya et al., 2011a,b). The resultant PSC ranged between 0.3 and 13.9 gTP/kg_{media}, offering a higher range than with steel slag. The performance of the materials is strongly linked to the relative proportion of apatite to calcite in the mineral (Bellier et al., 2006; Harouiya et al., 2011b) as P retention on calcite is sensitive to the relative carbonate equilibrium within the water matrix (Molle et al., 2005). Apatite derived from phosphate rock has been known for its metal content, such as Sr, Zn, Cd and U (Dybowska et al., 2009) and therefore offers a potential for metal leaching. In addition, the media is manufactured from a mined resource and hence exerts a very different sustainability profile to that of steel slag as well as costing around ten times the price per tonne.

The difference in media size, wastewater characteristics, scale of trial and HRT mean that selection of appropriate media remains challenging. For instance, to the author's knowledge no direct comparison of steel slag and apatite based media has been reported to date. Accordingly, the current paper provides the first direct comparison of the two media in both synthetic and real wastewaters to establish the relative effectiveness of the two media. This includes comparing the two media at approximately the same size to ascertain the relative contribution of material type and particle size to the observed differences in performance.

3.2 Materials and Methods

3.2.1 Wastewater

One set of columns was set up in a local STW and was fed with final effluent. The treatment process was comprised of primary settlement tanks, trickling filters, humus tanks and pile cloth media filters. The other set of columns was fed with synthetic wastewater, made up of ammonium dihydrogen phosphate (ADP) (Fisher Scientific) dissolved in tap water to mimic the strength of the real wastewater (Table 3-1).

Table 3-1 Wastewater characteristics, with n=246, 243 and 117 for the BOF slag synthetic, apatite synthetic and real wastewater columns, respectively (average [minimum-maximum]).

Parameter	BOF steel slag Synthetic wastewater	Apatite Synthetic wastewater	Real wastewater
TP (mg/L)	3.86 [1.69-6.02]	3.44 [1.80-6.24]	3.46 [0.94-4.77]
PO_4 (mg/L)	3.62 [0.92-5.76]	3.21 [0.63-6.02]	2.99 [0.70-4.42]
pH (-)	8.2 [7.2-8.9]	8.2 [6.9-8.9]	7.8 [7.3-8.8]
Ca (mg/L)	102.2 [83.4-125.8]	94.6 [60.6-118.0]	86.8 [55.4-110.0]
Na (mg/L)	16.2 [10.7-22.8]	16.2 [12.0-21.9]	94.6 [2.6-120.6]

Alkalinity (mg CaCO$_3$/L)	186.7 [56.0-241.0]	189.1 [110.0-238.0]	132.8 [95.0-187.0]
Al (µg/L)	5.2 [1.4-75.9]	10.1 [1.4-123.3]	52.6 [12.7-632.9]
Cu (µg/L)	123.7 [6.0-780.0]	106.3 [4.0-387.5]	33.8 [6.0-56.0]
Fe (µg/L)	5.0 [2.0-140.0]	2.6 [2.0-27.6]	299.5 [100.6-706.6]
V (µg/L)	2.6 [1.9-39.4]	1.9 [1.9-2.4]	9.5 [3.7-21.3]

3.2.2 BOF steel slag and apatite

The BOF steel slag was supplied by Tarmac (Port Talbot, UK). Four different size bands were used throughout the trials. In the case of the synthetic trials, media was dry sieved in accordance to BS EN 933-1:2012 (BSI, 2012) to produce two fractions: one to represent the standard media used in constructed wetlands with an average media size of 10.04 mm and the other to mirror the size of the apatite media and so had an average size of 5.09 mm (Chapter 2). In the case of the real wastewater trials two coarser size range fractions were used: 4-10 mm and 10-20 mm to reflect equivalent field-scale trials (Chapter 4).

The apatite material was supplied by Nuwen (Saint Malo, France). Four different media were tested as supplied by the manufacturer based on changes to the hydraulic additive employed (Ca or Fe) termed APA1, APA2, APA3 and APA4. Specific details of the differences in the additive formulation are not available but all contain an apatite rich base material (87-88% apatite).

3.2.3 Experimental set-up

The experiments were conducted in Perspex columns operated in down flow mode at a HRT of 6 hours unless otherwise stated (Table 3-2). The columns were 1000 mm high containing 600 mm of media with a diameter at least 20 times the media diameter to avoid wall effects (Martin et al., 2013). The column trials were all run off a common feed of either synthetic or real wastewater but the start date of each experiment was different with the exception of the two steel slag columns for both synthetic (kept at room temperature – 20°C) and real wastewater. To normalise the data, the performance is plotted in relation to the TP load per kg of media.

Table 3-2 Summary of different experimental conditions, HRT (hours) and [duration of trial (days)] (SS: steel slag).

Media	Synthetic wastewater	Real Wastewater
5.04 mm SS	6-24-6-4-2 hours [1000]	-
10.04 mm SS	6-24-6-4-2 hours [1000]	-
4-10 mm SS	-	6 hours [493]
10-20 mm SS	-	6 hours [493]
APA1	6-24-6-4-2 hours [917]	6 hours [493]
APA 2	6 hours [248]	6 hours [249]
APA 3	6 hours [130]	-
APA 4	-	6 hours [192]

In addition to the investigation of the impact of HRT on stabilised media (Table 3-2) a series of trials were conducted on fresh BOF steel slag and APA1 to investigate the impact of different HRTs on fresh media. For both media, three separate trials of HRT were tested: 6, 24 and 48 hours, and were performed with synthetic wastewater.

3.2.4 Sample analysis

The samples were analysed by Thames Water laboratories (Reading) following accredited procedures for the following parameters in accordance to standard methods: TP and PO_4 (BS EN ISO 6878:2004, BSI (2004)), alkalinity (BS EN ISO 9963-1:1996, BSI (1996)) and suspended solids (BS EN 872:2005, BSI (2005)). The pH was measured using a pH meter (Hach, probe model pHC201), within 10 minutes after taking the sample, in order to avoid CO_2 dissolution from air.

An array of metals (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Li, Mg, Mn, Mo, P, K, Na, Sr and Zn) were analysed by Thames Water laboratories (Reading) following accredited procedures using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific, model iCAP 6000). In addition, Sb, As, Cd, Co, Pb, Ni, Se, Ag, Sn, Ti, W and V were analysed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Perkin Elmer, model NexION Dual gas). In both cases samples were analysed after acidifying and digesting the sample at 85 °C overnight.

3.3 Results and Discussion

3.3.1 Impact of hydraulic retention time with synthetic wastewater

A similar shaped profile was observed with respect to the effluent TP as a function of operating time for all three media (Figure 3-1a). In the initial part of the run, the effluent TP increased until a peak value (*stabilisation* phase) before declining down to a stable value which continued during the *steady-state* phase. To illustrate, APA1 increased to a maximum TP concentration of 0.58 mg/L on day 231 before declining to a stable effluent TP concentration around the detection limit of 0.08 mg/L on day 430. The equivalent peaks for the 5.09 mm and 10.04 mm steel slag fractions occurred at days 150 and 210 at TP concentrations of 3.82 mg/L and 4.88 mg/L, respectively. In addition to the peaks being higher, the effluent TP during the 6 hours HRT *steady-state* phase was also higher for the two steel slags at average concentrations of 0.96 mg/L and 1.29 mg/L for the 5.09 mm and 10.04 mm fractions, respectively. The observed profile is different to many of the other trials reported, where a low stable period is followed by a gradual incline (Drizo et al., 2002; Bowden et al., 2009; Walter, 2012; Claveau-Mallet et al., 2013; Letshwenyo, 2014). However, similar profiles have been reported for specific trials using both apatite (Molle et al., 2005) and steel slag (Barca et al., 2013). For instance, a column trial operated at a HRT of 5.6 hours using 0.9 mm diameter apatite treating distilled water (P = 20 mg/L), reported that the effluent P concentration remained stable below 2 mg/L for 150 days before increasing to a peak value of 14 mg/L after 300 days. Thereafter, the effluent TP started to decline to below 2 mg/L after c420 days. The increase in effluent P was attributed to a lack of Ca dissolution limiting precipitation kinetics which was resolved by switching from distilled water to tap water and then filtered sewage (Molle et al., 2005). Surface analysis by Scanning Electron

Microscopy (SEM) after 305 days of operation supported the suggestion, as the media had accumulated deposits but was far from saturation. In the current cases, Ca is non-limiting and as such it is suggested that the specific combination of material dissolution, the concentration and composition of the wastewater and the prevailing pH favour the formation of non-P-containing precipitates, most likely calcite. Whilst the specific conditions under which this occurs are difficult to define, the fact that it has occurred across multiple water and media types, but not all of them, indicates that the specific performance of all reactive media is governed by a complex set of reactions that currently require site testing to understand and predict.

In all three cases, the pH of the synthetic wastewater initially increased and then dropped to that of the influent (Figure 3-1b). The peak pH observed was 9.5, 9.9 and 10 for 5.09 mm steel slag, 10.04 mm steel slag and APA1 respectively. The pH returned to approximately that of the influent after approximately 125 days for two the steel slags and 26 days for APA1. Much lower changes in pH occurred in the other reported trials with apatite material reflecting the impact of the binding agents contained with the commercial apatite media (Molle et al., 2005; Bellier et al., 2006). The difference in peak TP and the time taken to stabilise the pH during the *stabilisation* phase for the different media can be attributed to differences in the rate of dissolution based on the available CaO. Further, the effectiveness of the apatite media can be attributed more to the material character than its size as the 5.09 mm steel slag more closely mirrored that of the 10.04 mm steel slag than APA1.

Alteration of the HRT after the onset of the *steady-state* phase, did not impact on the effluent TP in the case of APA1 with a maximum reported concentration of 0.18 mg/L which occurred infrequently. This included during the period when the HRT was reduced to 2 hours demonstrating the effectiveness of the media even when used in compact configurations. In contrast, a difference in the effectiveness of TP removal was observed for the different sized steel slag during the *steady-state* phase with effluent TP concentrations remaining below 0.4 and 0.9 mg/L for the 5.09 mm and 10.04 mm diameter steel slags, respectively, until the end of the 24 hour HRT phase. Beyond that the effluent TP began to rise reaching levels above 1.2 and 2 mg/L respectively until day 940 when the effluent raised again to above 2 mg/L for both media (Figure 3-1a).

Overall, the *steady-state* phase is consistent with a switch towards a removal pathway more governed by adsorption and growth. In such cases, the size of the media becomes more important, although the apatite media stills demonstrates a higher affinity for P than steel slag in general.

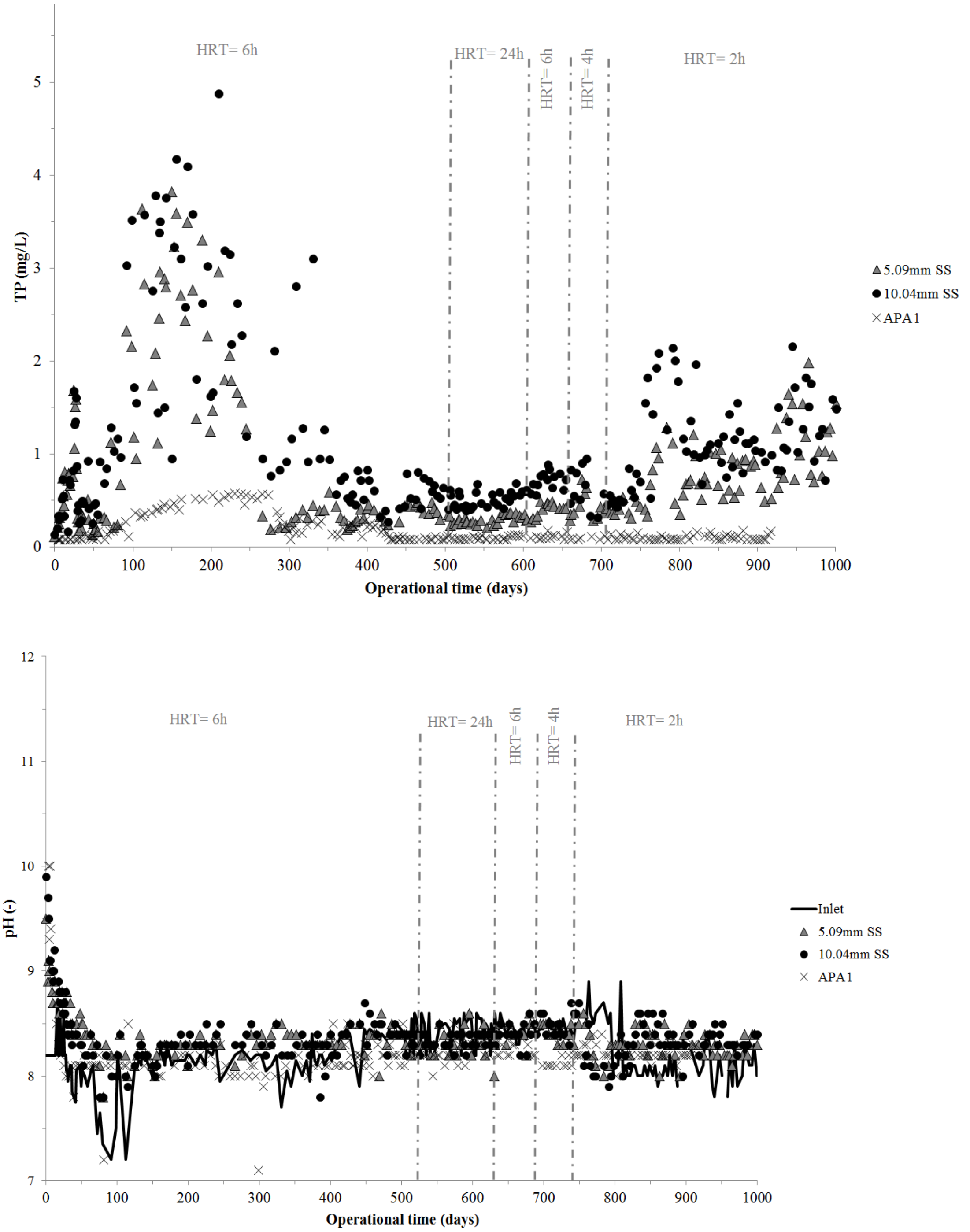

Figure 3-1 Comparison of 5.09 mm steel slag, 10.04 mm steel slag and APA1 columns treating synthetic wastewater with varying HRTs in terms of (a) TP and (b) pH.

The impact of the HRT on both the *stabilisation* phase and the *steady-state* phase was different for the two media types. P removal during the *stabilisation* phase increased from 67.4±21.8 % at 6 hours HRT to 97.6±0.3 % and 97.3±0.2 % at HRTs of 24 and 48 hours for the steel slag (Figure 3-2a). In comparison, much less change was observed for APA1 which increased from 91.9±5.1 % at 6 hours HRT to 95.3±2.9 % and 97.5±0.6 % for the 24 and 48 hours HRT, respectively. Noticeably, the performance of the two medias were similar at elevated HRTs but with the performance remaining high for the apatite even for shorter HRTs. The improvement in the performance of steel slag with increasing HRT has been reported elsewhere and is attributed to enhanced contact and associated dissolution raising both the Ca concentration and the pH (Shilton et al., 2005; Letshwenyo, 2014). In the current trials, the average effluent pH value supported this as it increased from 8.4±0.4 to 11.2±0.3 and 11.5±0.2 for 6, 24 and 48 hours HRTs for the steel slag, respectively (Figure 3-2b). The equivalent pH rise was less significant for the APA1 at 8.2±0.4, 10.1±0.5 and 10.3±0.4 for HRTs of 6, 24 and 48 hours. Previous trials on the impact of HRT on the *stabilisation* phase with apatite reported residual P concentrations of 3.84±1.17 mg/L, 0.55±0.30 mg/L and 0.16±0.08 mg/L for HRTs of 11, 25 and 38.4 hours, respectively, when treating domestic wastewater with an influent P concentration of 5.8±0.9 mg/L (Harouiya et al., 2011b). The extended HRTs required to reach low P concentrations reflects differences in the base apatite. In the reported study the material had an apatite content of 41% compared to 81% in the current case. The difference is predominately made up of calcite, which is known to have a much lower affinity for P.

Alteration of the HRT with preconditioned media during the *steady-state* phase revealed differences in the removal efficiency between the medias at all HRTs but with the difference between the media most apparent at shorter HRTs (Figure 3-2a). To illustrate, for HRTs of 2, 4, 6 and 24 hours, the removal efficiency for steel slag was 71.4±11.8 %, 82.1±4.1 %, 79.5±3.0 % and 84.5±2.6 % compared to 97.1±0.9 %, 95.7±0.9 %, 96.0±0.9 % and 95.4±1.7 % for APA1. No significant difference in effluent pH was observed between the two media during the *steady-state* trials with both around 8.2-8.4. Accordingly, the differences appear to relate to the contrast in the respective conditioning material. In the case of APA1, this is expected to be predominately calcium phosphate whereas in the case of steel slag a much greater proportion of calcium carbonate is expected. This material is known to have a lower affinity for P and is more sensitive to bicarbonate (Jang and Kang, 2002). The overall impact is that lower sustainable P concentrations appear possible with apatite based media, even at relatively short HRTs. However, preconditioned steel slag at slightly elevated HRT may be able to meet likely effluent TP discharge targets of sub 1 mg/L. To illustrate, the average effluent TP observed for the steel slag was 1.2±0.5 mg/L, 0.6±0.2 mg/L, 0.7±0.1 mg/L and 0.5±0.1 mg/L compared to 0.10±0.02 mg/L, 0.12±0.02 mg/L, 0.09±0.01 mg/L and 0.10±0.04 mg/L for APA1 at HRTs of 2, 4, 6 and 24 hours, respectively.

Across the duration of the synthetic trials the overall PSC was 5.3 gTP/kg_{media}, 5.1 gTP/kg_{media} and 6.9 gTP/kg_{media} for the 5.09 mm steel slag, 10.04 mm steel slag and APA1, respectively. This compares to PSCs for apatite of 13.9 g TP/kg_{media} when treating a feed of 20 mg/L at a HRT of 5.6 hours (Molle et al., 2005). The lower levels reported here reflect the larger particle size used, the lower strength and the fact that the media is still removing P to a very low level. Extrapolation of the current data based on the reported PSC suggest that the current application could continue for around another 4 years. However, reported PSC vary considerably across trials (0.3-13.9 $gTP/kg_{apatite}$; 0.15-8.3 $gTP/kg_{steel\ slag}$) so care is required when projecting operational lifetime. However, this can in part be extended as previous work has shown that the capacity of P uptake can be recovered (Claveau-Mallet et al., 2013; Letshwenyo, 2014) such that use of preconditioned steel slag at the correct particle size can also potentially provide an effective media for P removal in constructed wetlands.

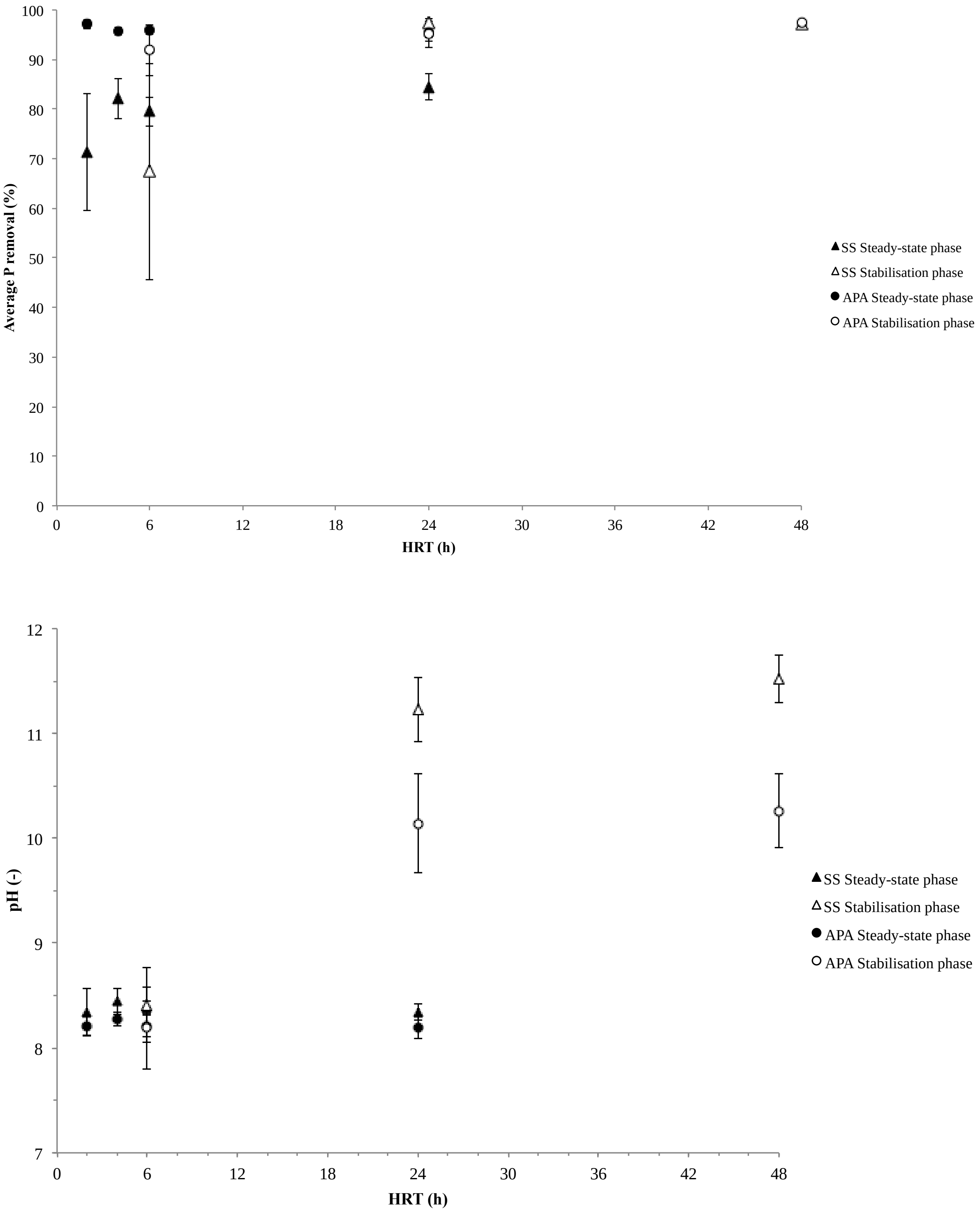

Figure 3-2 Impact of HRT on the *stabilisation* and *steady-state* phase for both steel slag and apatite on a) P removal and b) pH.

3.3.2 Comparison of BOF steel slag and different apatite media treating synthetic wastewater

The use of the apatite based media demonstrated an initial elevation in pH and the period of conditioning similar in nature to that observed with steel slag media. This is congruent with one of the binding agents being lime or one of its derivatives. However, pre-conditioned apatite media also demonstrated high effectiveness for P removal suggesting that alternative binding agents that do not raise the pH could be utilised. Accordingly, three different trial media (APA1, APA2, APA3) were tested in synthetic wastewater across a loading rate of up to 2,000 mgTP/kg$_{media}$ (Figure 3-3a,b). APA2 and APA3 exhibited different profiles to APA1 in terms of both TP removal and effluent pH.

In the case of APA2, the effluent TP remained below the detection limit throughout the trial which lasted up to a load of 1,020 mgTP/kg$_{media}$ apart from a period where the effluent fluctuated slightly reaching a maximum value of 0.17 mg/L (Figure 3-3a). In addition, the pH remained at around the level of the influent throughout the trial. Whilst the performance was exceptionally good, the media unfortunately did not retain a robust structure. At the end of the run, 248 days, the material was examined and found to have disintegrated back to its base powder, resulting in a noticeable rise in water level in the column. Similar findings have been reported for other man-made media such as Bauxsol (a by-product of aluminium mining) and Phosfate^{TM} (made from acid mine drainage waste) where failure strength of 0.05 kN and 0.02 kN have been reported compared to steel slag with a failure strength of 1.48 kN (Letshwenyo, 2014). In the case of Bauxsol, a previous field-scale trial revealed that the media had disintegrated within the wetland and that the flow was by-passing the media section (Walter, 2012). In a different trial, successful alteration of Phosfate^{TM} media enabled long-term operation of the media in column trials but coincided with a sharp rise in pH associated with the inclusion of lime into the binding material (Letshwenyo, 2014).

In the case of APA3, the material retained its physical integrity throughout the trial producing an effluent TP similar to that of APA2 with the majority of the data below the level of detection apart from a few points, which reached a maximum TP of 0.22 mg/L. However, the pH was raised significantly, reaching a maximum value of 11.9

before reducing to 9.9 at the termination of the run, equivalent to a loading rate of 761 mgTP/kg$_{media}$ (c125 days). This was significantly different from the other apatite based media and the steel slag suggesting the media contained a high content of lime based binding agents within it. Interestingly, it did not exhibit the same *stabilisation* profile as observed with APA1 or either of the steel slag media. Overall, the results indicate that composition of the binding agents has a significant impact on the overall effectiveness of the media in addition to the previously reported impacts based on the relative apatite:calcite ratios different source materials contain.

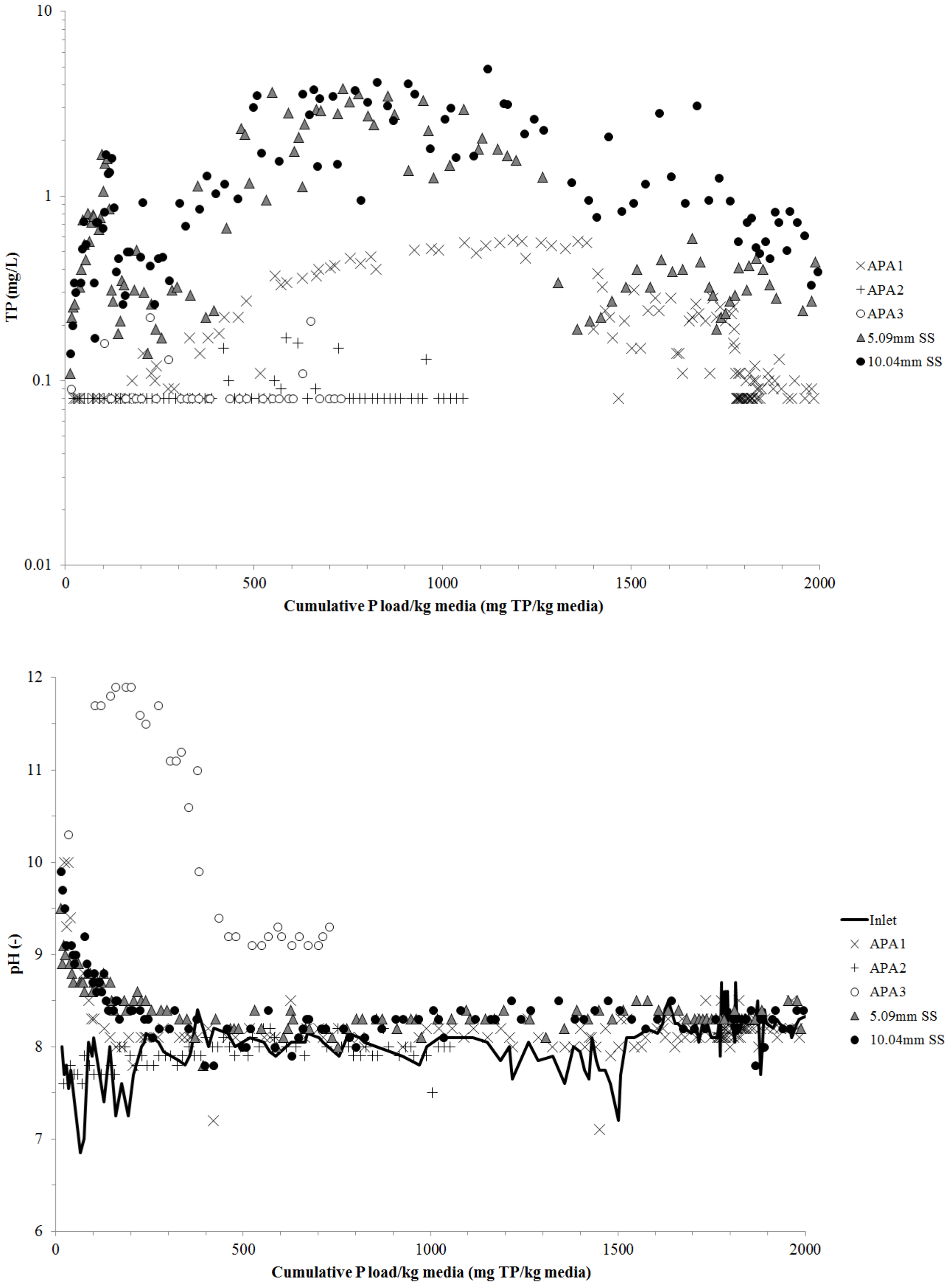

Figure 3-3 Comparison of APA1, APA2 and APA3 at a HRT of 6 hours, treating synthetic wastewater in terms of (a) TP concentration and (b) pH.

3.3.3 Comparison of BOF steel slag and different apatite media treating real wastewater: phosphorus removal and pH

The profiles of both the steel slag and apatite media were significantly different with real wastewater compared to the trials with synthetic wastewater (Figure 3-4a,b). In the case of the steel slag, both size fractions exhibited similar profiles with an effluent TP that increased from the start of the run reaching the approximate level of the influent after a load of c200 mgTP/kg$_{media}$ at which point the effluent TP was approximately 3 mg/L and then fluctuated around this level until the termination of the run. APA1 followed a similar profile with the exception that a lag phase was observed up to a load of 129 mgTP/kg$_{media}$ during which time the effluent TP remained below the limit of detection. Thereafter the effluent TP rose steadily reaching a final stable level once a load of c291 mgTP/kg$_{media}$ was applied. In contrast, APA2 behaved more similarly to the synthetic trial with the effluent TP below the detection limit until a load of 116 mgTP/kg$_{media}$. Thereafter it fluctuated but remained below an effluent TP of 0.38 mg/L until the end of the trial, corresponding to a load of 813 mgTP/kg$_{media}$. However, as observed before, the media disintegrated during the trial and hence was not suitable for real applications. A forth apatite based media was trialled during this phase of the work, APA4, which performed well. The effluent TP was initially measured at 0.68 mg/L but dropped quickly to the detection limit by a load of 14.9 mgTP/kg$_{media}$ and has remained stable at that level up to the maximum load tested to date of 770 mgTP/kg$_{media}$.

With the exception of APA2, all media raised the pH which then remained elevated to that of the influent throughout the duration of all the runs. The most elevated pH was developed by APA1 at an initial pH of 12 (Figure 3-4b). The pH then declined, reaching a level of below 9 once a load of 233 mgTP/kg$_{media}$ had been treated. Thereafter the pH continued to decline reaching its final stable value of c8.3 once a load of c442 mgTP/kg$_{media}$ of feed had been treated. The two steel slag media exhibited similar profiles declining from a starting pH of 10 and 10.5 for the 4-10 mm and 10-20 mm fractions, respectively, to stable levels once c300 mgTP/kg$_{media}$ of feed had been treated. In contrast, APA4 started at a pH of around 9 and then declined to a stable level of c8.1 once a load of 259 mgTP/kg$_{media}$ had been treated.

Overall, the trials in real wastewater demonstrated poorer P removal and more impact in terms of the elevated pH than those observed across the synthetic trials. To illustrate, the effluent TP was 0.35 mg/L and 2.02 mg/L, and 0.14 mg/L and 3.01 mg/L for 10.04 mm steel slag and APA1 when treating synthetic and real wastewaters respectively at a load rate of 254 mgTP/kg$_{\text{steel slag}}$ and 355 mgTP/kg$_{\text{apatite}}$. Comparison of the waters showed that the real wastewater exhibited a lower alkalinity (c130 instead of c187 mg/L as $CaCO_3$) and copper concentration (34 μg/L compared to between 106 and 124 μg/L) as well as elevated levels of sodium (95 μg/L as opposed to 16 μg/L), aluminium (53 μg/L instead of 5.0-10.0 μg/L) and iron (300 μg/L as opposed to 2.6-5.0 μg/L). In addition, the real wastewater contains suspended solids (5.4 mg/L(1.9-51.0 mg/L)), sulphates (65.6 mg/L(40.9-88.9 mg/L)) and elevated organic concentrations (COD around 55 mg/L). The differences suggest a number of factors could be important:

(1) The presence or organics and solids provide an alternative coating inhibiting media dissolution and coat the media inhibiting precipitative growth (Molle et al., 2011; Troesch et al., 2016).
(2) The organic can provide ligand exchange sites to bind the phosphate no longer making it available to precipitate. (Mng'ong'o, 2016).
(3) The much higher levels of iron, aluminium and sulphate in combination with the existing carbonate provide alternative precipitation pathways that may exclude inclusion of phosphates (LeCorre, 2017).
(4) The lower alkalinity reduces the buffering capacity of the wastewater.

Whilst it is difficult to ascertain the exact significance of each component within these trials it does indicate the care required when translating data from synthetic trials, which are likely to overestimate performance and the achievable PSC. Previous trials with BOF steel slag at 6 hours HRT treating real wastewater have shown similar profiles and in fact stable low TP effluent concentrations were not possible until HRTs exceeding 24 hours were employed (Walter, 2012).

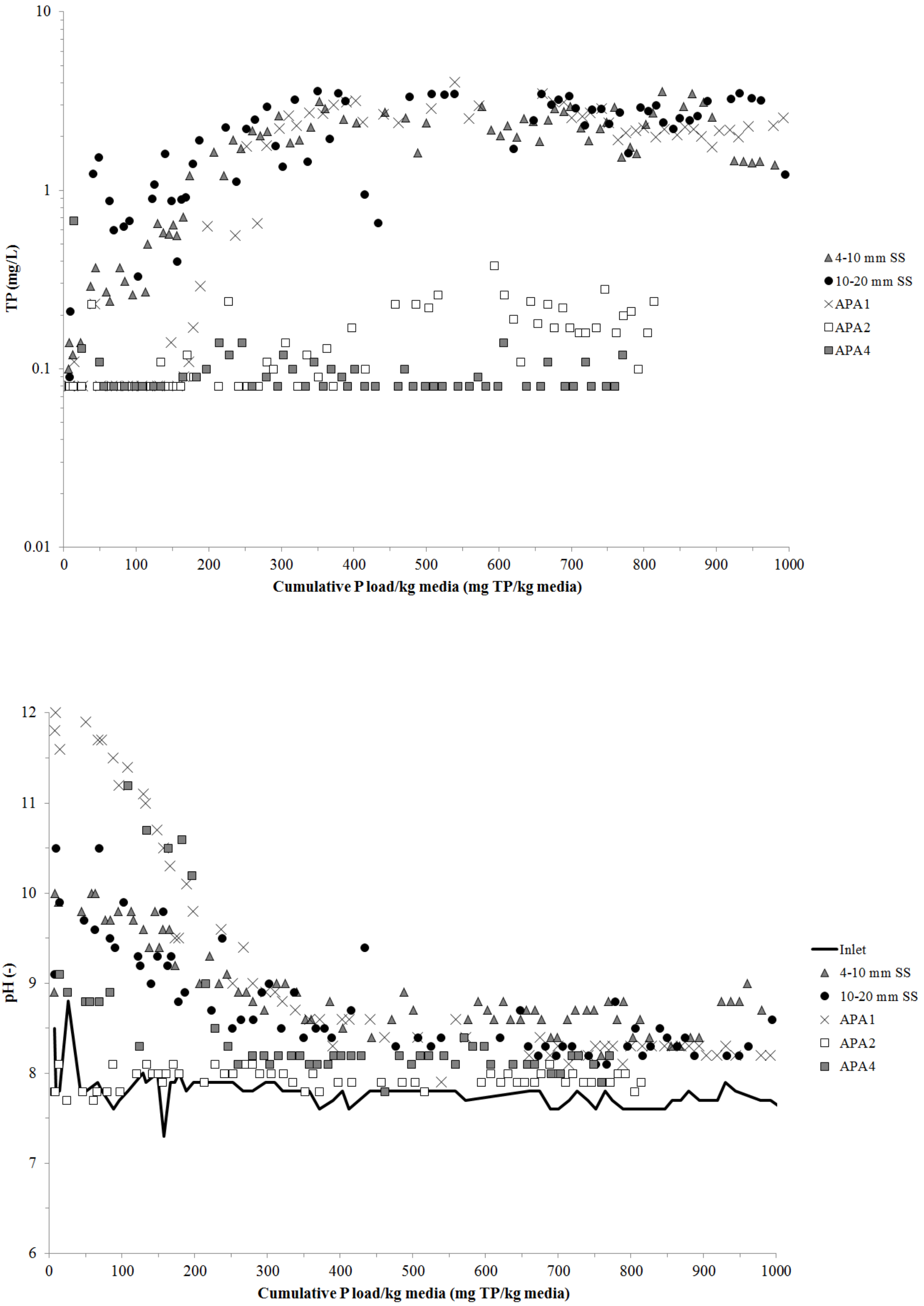

Figure 3-4 Comparison of steel slag and apatite based media treating real wastewater at a HRT of 6 hours in terms of a) TP concentration and b) pH.

3.3.4 Comparison of BOF steel slag and different apatite media treating real wastewater: metals

Across both media types and wastewater sources only 10 of the 29 measured metals showed any change across the trials either through a difference in the average or the observed range (Table 3-1). However, changes in selenium, tin, titanium and zinc were relatively low and occurred mainly due to occasional elevated events and remained below the discharge targets.

The observed changes in the other metals showed difference due to the material and the source water with the exception of barium and manganese where release of both metals was consistently seen. To illustrate, in the case of barium, the average effluent concentration increased from 14.0 μg/L to 17.6 μg/L, 19.7 μg/L, 18.9 μg/L and 25.1 μg/L for SS, APA1, APA2, APA3 during the synthetic trials and from 5.6 μg/L to 17.3 μg/L, 26.1 μg/L, 20.5 μg/L and 92.7 μg/L during the real wastewater trials. More noticeable difference was observed in the case of manganese for SS and APA2 where the average effluent concentration increased from 0.8 μg/L to 13.8 μg/L and 79.4 μg/L in synthetic water compared to an increase from 10.8 μg/L to 121.5 μg/L and 191.9 μg/L in real wastewater for SS and APA2, respectively. The other apatite media showed less significant change congruent with the use of lime as opposed to an iron based binding agent in APA2 (and contained within steel slag), which are known to also contain manganese.

In two cases, copper during the synthetic trials and iron during the real wastewater, the response was similar for both steel slag and apatite media but not the water sources. In the case of copper, the average effluent copper concentration in the synthetic wastewater decreased from an influent level of 106.3 μg/L to 5.7 μg/L, 4.3 μg/L, 5.6 μg/L and 13.3 μg/L for SS, APA1, APA2 and APA3 respectively. This was not mirrored during the wastewater cases were a maximum removal efficiency of 40% was observed based on average values. In part, the difference is attributed to the elevated levels in the influent of synthetic wastewater which have been shown to favour removal pathways such as surface complexation, sorption or ion exchange in the case of apatite media (Dybowska et al., 2009). In contrast, minor differences were observed during the synthetic wastewater trials with respect to iron which increased slightly in the case of SS and APA3, mainly observed through occasional elevated levels. However, a consistent decrease was observed during the real wastewater trials where the average effluent concentration decreased from 299.5 μg/L in the feed to 106.6 μg/L, 120.4 μg/L, 87.4 μg/L and 56.9 μg/L for SS, APA1, APA2 and APA4, respectively. Previous trials with apatite did not show any removal of iron but the initial levels in the wastewater were much lower at 50.0±20.6 μg/L (Molle et al., 2011), similar to the final levels reported here.

Significant specific media related impact was only observed in relation to two metals, vanadium and chromium (Table 3-3; Supplementary Information, Appendix B). In the case of chromium, the impacts were only observed for APA3 and APA4, where the average concentration increased from 0.9 μg/ to 17.8 μg/L during the synthetic trials for the former, and from 0.9 μg/L to 52.5 μg/L during the real wastewater case for the latter. In the case of APA4, the effluent concentration decreased rapidly from an initial value of 1,547 μg/L down to a stable level of around 5 μg/L until day 22 whereafter it decreased down to the influent level on day 42. This compares to a target discharge level of 50 μg/L suggesting that the binding agent in APA4 is generating a source of leaching chromium that needs consideration when using in practice.

In the case of the steel slag media, significant leaching of vanadium was the major issue, which increased from an average concentration of 1.9 μg/L to 21.1 μg/L during the synthetic trials and from 9.5 μg/L to 97.8 μg/L during the real wastewater trials. The effluent concentration for the real wastewater trial decreased from an initial value of 1,023 μg/L before stabilising at a value of around 50 μg/L on day 183, and then further decreased to a stable concentration of 30 μg/L on day 354. In addition, occasional elevated values were observed with APA4 during the real wastewater trials which saw a maximum concentration of 78.3 μg/L. Lower vanadium leached concentrations of 1.31±0.82 μg/L have been reported in other studies (Molle et al., 2011) which indicates variation due to the base source of the material. However, specific issues associated with APA4 reflect additional impacts associated with the choice of binding agent demonstrating that careful screening of potential media is critical. The target level is expected to be 60 μg/L and hence management of vanadium leaching is a requirement for using steel slag. The fact that the vanadium levels decreased once the media entered the *steady-state* phase is consistent with precipitates blocking dissolution sites and hence it may be possible to appropriately pre-treat steel slag to ensure that the effluent concentration does not exceed the target.

Table 3-3 Summary of metal leaching during column trials with synthetic and real wastewater for BOF steel slag and apatite, (all concentrations in µg/L, average [minimum-maximum] (N/A: Not available).

Metal [discharge target]	Synthetic Wastewater					Real Wastewater				
	Feed	SS 5.09	APA1	APA2	APA3	Feed	SS 4-10	APA1	APA2	APA4
Barium	14.0	17.6	19.7	18.9	25.1	5.6	17.3	26.1	20.5	92.7
[130]	[4.8-21.1]	[5.3-69.3]	[3.0-60.0]	[6.3-61.3]	[5.2-107.4]	[0.6-12.0]	[4.5-78.6]	[3.6-249.0]	[3.9-66.1]	[44.5-121.8]
Chromium	0.9	0.9	1.3	0.9	17.8	0.9	0.9	4.1	1.1	52.5
[4.7]	[0.9-1.0]	[0.9-1.6]	[0.9-68.6]	[0.9-2.0]	[0.9-165.0]	[0.9-1.3]	[0.9-2.1]	[0.9-85.0]	[0.9-6.7]	[0.9-1,547.0]
Copper	106.3	5.7	4.3	5.6	13.3	33.8	20.5	25.8	20.1	32.8
[28]	[4.0-387.5]	[3.0-21.0]	[3.0-15.0]	[3.0-21.0]	[3.0-164.0]	[6.0-56.0]	[5.0-51.0]	[4.0-217.0]	[3.0-31.0]	[19.0-104.0]
Iron	2.6	19.7	3.4	3.4	21.0	299.5	106.6	120.4	87.4	56.9
[1000]	[2.0-27.6]	[2.0-478.7]	[2.0-55.8]	[2.0-15.7]	[2.0-269.0]	[100.0-706.0]	[23.5-1,175.8]	[8.0-1,108.0]	[19.0-315.0]	[17.5-550.0]
Manganese	0.8	13.8	13.3	79.4	5.7	10.8	121.5	18.3	291.9	18.8
[123]	[0.8-1.5]	[0.8-239.2]	[0.8-278.0]	[5.5-702.2]	[0.8-101.0]	[0.8-19.8]	[1.0-3,803.0]	[0.8-235.0]	[18.4-862.0]	[1.0-205.9]
Selenium	0.8	0.8	0.8	1.6	0.65	0.7	0.7	0.7	2.4	0.9
[2.1]	[0.6-0.9]	[0.8-0.8]	[0.8-0.9]	[0.8-33.7]	[0.6-2.0]	[0.6-1.9]	[0.6-2.8]	[0.6-2.2]	[0.6-80.8]	[0.6-11.8]
Tin	3.4	2.9	4.0	8.1	19.2	2.37	6.4	5.2	4.1	0.8
[113]	[0.8-8.0]	[0.8-8.0]	[0.8-12.9]	[0.8-59.7]	[0.8-54.3]	[0.8-8.0]	[0.8-227.7]	[0.8-164.0]	[0.8-11.0]	[0.8-1.8]
Titanium	7.9	2.0	1.5	1.5	1.7	5.9	4.5	3.6	1.7	2.0
[N/A]	[1.6-18.0]	[1.5-8.1]	[1.5-1.7]	[1.5-1.5]	[1.7-1.7]	[1.7-13.5]	[1.7-15.0]	[1.5-12.8]	[1.5-3.2]	[1.7-10.9]
Vanadium	1.9	21.1	8.2	1.9	19.6	9.5	97.8	14.2	1.7	28.7
[60]	[1.9-2.4]	[1.9-426.8]	[1.0-38.9]	[1.9-1.9]	[6.7-26.4]	[3.7-21.3]	[23.6-1022.6]	[2.5-32.0]	[1.0-2.3]	[4.8-78.3]
Zinc	4.6	4.2	4.4	6.1	5.0	16.5	6.6	6.6	8.1	4.1
[30]	[0.8-28.0]	[4.0-20.0]	[4.0-27.0]	[4.0-23.0]	[4.0-30.0]	[5.0-32.0]	[4.0-43.0]	[4.0-45.0]	[4.0-54.0]	[4.0-9.0]

3.4 Conclusions

- Trials using synthetic wastewater revealed a consistent profile containing a *stabilisation* and a *steady-state* phase for both materials. Alteration of the binding agents altered this arrangement causing change in P removal, pH, physical integrity and residual metal concentrations meaning that media screening is important to understand the real potential of any potential media
- Higher HRTs produced higher P removals and higher pH values on the *stabilisation* phase for both materials, although apatite showed higher P removal than steel slag even for short HRTs. Higher HRTs did not significantly affect pH during the *steady-state* phase but apatite showed higher P removal than steel slag for shorter HRTs, due to the differences in the conditioning material for apatite (calcium phosphate) and steel slag (calcium carbonate) produced in the *stabilisation* phase.
- Overall apatite was able to reduce the TP concentration to a lower level than steel slag but both were capable of meeting a 1 mg/L standard effluent consent.
- Comparison of the media at an equivalent size revealed that the material properties of apatite are responsible for the improved performance.
- Both media showed poorer P removal and more impact in terms of the elevated pH in real wastewater trials compared to synthetic wastewater trials.

3.5 Acknowledgments

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4 Comparing the reactive media: Basic Oxygen Furnace steel slag and apatite for phosphorus, metal and priority chemical removal using field-scale trials

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Abstract

The application of reactive media in constructed wetlands for the removal of phosphorus (P) enables small sewage treatment works to retain overall attributes associated with low maintenance and chemical usage. Two of the most promising media for the application are Basic Oxygen Furnace (BOF) steel slag and apatite. However, there are only a few field-scale trials to assess their potential and never together. This work presents the first direct comparison of both media in long-term field-scale constructed wetlands under real operating conditions, and it extends the assessment of the media performance to metals and priority substance removal. Two phases of operation were distinguished for both media in relation to the effluent total P profile, a *stabilisation* phase, where non-P-containing precipitate formation was favoured, and a *steady-steady* phase, where P removal was enhanced. Only the effluent of the apatite wetland stabilised below a pH of 9, whereas the effluent pH of steel slag remained above 10, indicating the sustained P removal by CaO dissolution. Clogging of media revealed the need for solid management in the case of smaller media, either by installing a prior pile cloth media filter or by flushing or refurbishing the media more often. Both media showed effective removal of the metals iron, copper, manganese and titanium, and the priority substances nonlyphenol, benzo(a)pyrene, cypermethrin, oestrone and 17B-oestradiol. Specific metal release was observed for each media, chromium and uranium for apatite, and vanadium for steel slag.

Keywords: apatite, constructed wetlands, phosphorus, steel slag

4.1 Introduction

The effectiveness of reactive media in providing a passive treatment approach for phosphorus (P) removal from wastewater has now been demonstrated in numerous studies establishing the potential to achieve an effluent total phosphorus (TP) concentration of below 1 mg/L (Claveau-Mallet et al., 2013; Troesch et al., 2016). The most successful media such as steel slag (industrial by-product) and apatite (man-made media) are rich in calcium oxides, iron and aluminium (Volha et al., 2011). The predominant removal pathway is reported to involve the dissolution of calcium oxide(s) leading to calcium phosphate precipitation (Barca et al., 2013; Claveau-Mallet et al., 2017). However, most of the experiments have been performed in batch or column studies using synthetic water and controlled conditions with only a few examples of field-scale trials conducted under real operating conditions (Table 4-1). Accordingly, there remains need for long-term, field-scale trials treating real wastewater to better explore the impact of aspects like imperfect flow patterns and the potential of complex chemical interactions between the background water chemistry and the reactive media (Drizo et al., 2006; Shilton et al., 2006; Barca et al, 2018). For instance, much of the work exploring mechanisms has been conducted on synthetic water with very low levels of inorganic carbon negating the formation of competing precipitates such as calcium carbonate (Jang and Kang, 2002; Claveau-Mallet et al., 2012). Additionally, alkalinity plays an important role by impacting on the rate of dissolution as well as buffering the pH such that different wastewaters will likely stabilise at different pH values. Real wastewaters also contain other components such as organic compounds, organic colloids, suspended solids and competing ions (Barca et al., 2012). These components potentially coat the media, complex and stabilise the available P and in the case of the other ions either catalyse or inhibit scale formation (Claveau-Mallet et al., 2017). The overall impact is that caution is required when translating data from synthetic trials which tend to overestimate performance and filter life, compared to current field-scale data (Chapter 2, Chapter 3; Shilton et al., 2006; Barca et al., 2012).

Performance evaluation needs to extend beyond P and explore the potential release or removal of other components such as metals and priority substances (PS). For instance, the use of reactive media provides a potential pathway for an increase in some metals through leaching (Yi et al., 2012) including vanadium for Basic Oxygen Furnace steel slag (BOF SS) (Fonseca, 2016) and radioactivity in the case of apatite (Molle et al., 2011) or release through the dissolution of more complex species of calcium oxide such as $Ca_{14}Mg_2(SiO_4)_8$ (bregigite) and $Ca_2Al_2SiO_7$ (gehlenite) (Claveau-Mallet et al., 2017), as well as removal, of other metals species that are incorporated into the precipitate or adsorbed. In addition, the need to understand PS removal is becoming important due to new legislation (Directive 2013/39/EU; Decision 2015/495) and traditional constructed wetlands are increasingly being seen as a potential barrier to some key PS (Gorito et al., 2017). For example, effective treatment has been shown in relation to octylphenol (87%), nonylphenol (90%), diclofenac (98%), 17A-ethinyloestradiol (EE2) (100%) and 17B-estradiol (E1) (100%) (Gorito et al., 2017). Switching to the use of reactive media significantly alters the prevailing pathways that operate within the wetlands and so there is urgent need to understand the potential of such media to remove trace components from real wastewater.

Differences in media and wastewater composition, media size, hydraulic retention time and initial P concentration make comparison across studies difficult such that to better understand the relative effectiveness of different media, direct comparison is critical in field-scale systems treating real wastewater. The current paper embraces this by being the first direct comparison of two of the more promising options: BOF steel slag and apatite in long-term field trials treating real wastewater. In addition, the trials utilise BOF steel slag of different sizes including a match to the size of the apatite media to aid more direct comparison in terms of P removal, pH, metals and PS.

Table 4-1 Overview of field-scale trials and comparison to previous reported cases treating real wastewater.

Material, size (mm)	Scale (p.e.), wetland type*	Dimensions** (L x W x D) (m), Source water	HRT(h) ***	Inlet TP (mg/L)	Run time (days)	Reference
BOF SS 10-20	240, HSSF	6.5x22**x0.6 Domestic WW	24	4.1±1.0	806	Current study
BOF SS 4-10	240, HSSF	6.5x22**x0.6 Domestic WW	24	4.1±1.0	801	Current study
BOF SS	240,	6.5x22**x0.6	24	4.1±1.0	718	Current study

2-6	HSSF	Domestic WW				
Apatite, 2.5-8.5	400, HSSF	6.5x22[**]x0.6 Domestic WW	12	4.1±1.0	850	Current study
BOF SS, 14	240 HSSF	20x4.4[**]x0.75 Domestic WW	16	4.9±1.6	724	Walter (2012)
BOF SS, 8-14	211 HSSF	12x8.4[*]x0.6 Domestic WW	24	7.6±1.7	722	Vale (2017)
BF SS, 0-3	20 VSSF	6.5x4.5[**]x0.3, Domestic WW	70	6.6±1.8	336	Asuman Korkusuz et al. (2007)
EAF SS, 10-20	13,333 HSSF	97.4x29.6[**]x0.5, Domestic WW	72	8.4	48,180	Shilton et al. (2006)
EAF SS, 20-40	10-20 HSSF	5.7x2.1[**]x0.5 Domestic WW	24-48	8.5±1.3	672	Barca et al. (2013)
BOF SS, 20-40	10-20 HSSF	5.7x2.1[**]x0.5 Domestic WW	24-48	8.5±1.3	672	Barca et al. (2013)
Apatite, 4-9	0.8 VSSF	1.5x1[**]x0.4	48	4.2	510	Harouiya et al. (2011a)
Apatite, 1.3-4.0	0.8 VSSF	1.5x1[**]x0.4, Domestic WW	48	5.9	480	Harouiya et al. (2011b)
Apatite, 1.3-4.0	8.2 HSSF	7.2x2.2[**]x0.6, Domestic WW	69.6	5.8±0.9	990	Harouiya et al. (2011b)

[*]HSSF: Horizontal Sub-Surface Flow, VSSF: Vertical Sub-Surface Flow; [**]Width along which the wetland system is fed; [***]HRT estimated as HRT=V·φ /Q, where φ is porosity.

4.2 Materials and methods

4.2.1 Wastewater and field set-up

The constructed wetlands were located at a sewage treatment works (STW) that incorporated trickling filters as the main biological stage and contained a pile cloth media filter as a tertiary treatment. Feed to the constructed wetlands was from a common feed tank and taken from the humus tank effluent (Figure 4-1). The wastewater averaged a total P (TP) concentration of 4.1±1.0 mg/L with a phosphate (PO_4-P) concentration of 3.0±0.7 mg/L, an alkalinity of 144.7±23.1 mg$CaCO_3$/L at a pH of 7.8±0.5 and a suspended solids concentration of 31.1 mg/L (1.9-179.0 mg/L). The effluent of the wetlands was pumped back into the primary settlement tanks.

The constructed wetland system was comprised of four 77.9 m^3 hydraulically separated wetlands operating in parallel containing different media (Table 4-1). The BOF SS were delivered in three size ranges by Tarmac (Port Talbot, UK) and the apatite by Nuwen (Saint Malo, France). The BOF SS 10-20 mm and apatite 2.5-8.5 mm represented the media as supplied for full-scale use whereas the BOF SS 4-10 mm and 2-6 mm were trialled to ascertain the impact of media size on performance and enable a direct comparison with the apatite. Previous work had suggested that the apatite could operate at a shorter HRT than the steel slag and so was run at 12 hours compared to 24 hours for the steel slag. Accordingly, the data is normalised against the P load applied to ensure a comparative assessment. The wetlands were planted with *Typha latifolia* at a density of 4 plants/m^2.

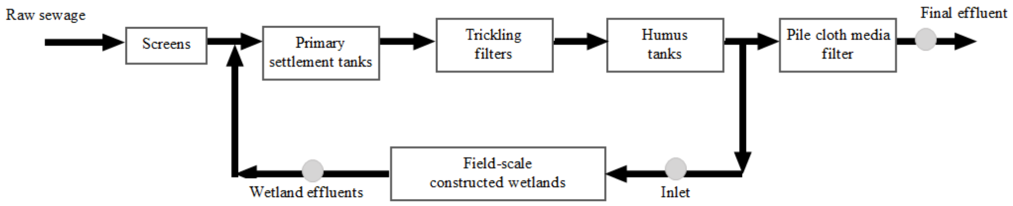

Figure 4-1 Overview of the field trial configuration with location of sampling points.

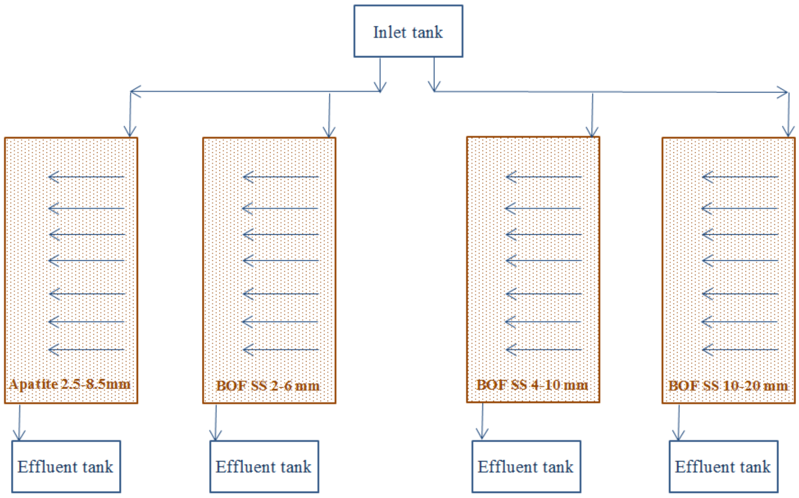

Figure 4-2 Overview of the layout of the four wetlands.

4.2.2 Sample analysis

The common inlet to the constructed wetlands and each wetland effluent were sampled once a week for the whole duration of the trial based on 24h composite samples. The samples were analysed by Thames Water laboratories (Reading) following accredited procedures for the following parameters in accordance to standard methods: TP and PO_4 (BS EN ISO 6878:2004, BSI (2004)), alkalinity (BS EN ISO 9963-1:1996, BSI (1996)), suspended solids (BS EN 872:2005, BSI (2005)), BOD (BS EN 1899-1:1998, BSI (1998)) and NH_4 (BS 6068-2.11:1984, BSI (1984)). The pH was measured using a pH meter (Hach, probe model pHC201), within 10 minutes after taking the sample, in order to avoid CO_2 dissolution from air.

An array of metals (Al, Ba, Be, B, Ca, Cr, Cu, Fe, Li, Mg, Mn, Mo, P, K, Na, Sr and Zn) were analysed by Thames Water laboratories (Reading) following accredited procedures using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific, model iCAP 6000). In addition, Sb, As, Cd, Co, Pb, Ni, Se, Ag, Sn, Ti, W and V were analysed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) (Perkin Elmer, model NexION Dual gas). In both cases samples were analysed after acidifying and digesting the sample at 85 °C overnight. Additional samples were analysed after the pile cloth media filter to compare to the constructed wetlands providing a benchmark based on solids removal.

Three sampling campaigns were undertaken to measure priority substances from the common inlet, 2-6mm BOF steel slag and the apatite effluents. Samples were analysed by RPS (UK) according to in-house developed methods. These included gas chromatography-mass spectrometry (GC-MS) analysis in the case of nonylphenol, benzo(a)pyrene and cypermethrin; and liquid chromatography tandem mass spectrometry (LC-MS/MS) for the rest of the substances. In all cases, these were preceded by different types of extractions, according to the nature of the substance.

Total alpha and total beta radioactivity were measured in wastewater samples from the common inlet and from the effluent of the four wetlands on six occasions in a two year period since the constructed wetlands were commissioned. These were analysed by Thames Water laboratories (Reading) by evaporation of a known volume of samples and analysis of the radioactivity in the dry residue according to the standard methods ISO 9697:2015 (ISO, 2015) and ISO 9696:2017 (ISO, 2017).

4.3 Results and Discussion

4.3.1 P removal

The effluent TP profile produced by the steel slag and apatite media was similar over the same cumulative P loading rate range of up to 1,027 mg/kg$_{media}$ (Figure 4-3a). In all cases the effluent TP followed two phases of operation: an initial *stabilisation* phase where the effluent TP increased before decreasing to a stable value during a *steady-state* phase. The peak P concentration generated by the apatite was 0.58 mg/L and occurred at a P load of 35 mgTP/kg$_{media}$ similar to the 2-6 mm SS with a peak concentration of 0.77 mg/L occurring at a P load of 52 mgTP/kg$_{media}$. Higher peak levels of 1.48 mg/L and 1.14 mg/L were observed for the 10-20 mm and the 4-10 mm SS media respectively but these occurred at a similar P load to the other media (36-54 mgTP/kg$_{media}$). The effluent TP concentration then declined to a stable level at cumulative P loading rates of 153 mgTP/kg$_{media}$, 94 mgTP/kg$_{media}$, 228 mgTP/kg$_{media}$ and 169 mgTP/kg$_{media}$ for the 2-6 mm SS, 4-10 mm SS, 10-20 mm SS and the apatite respectively.

The overall profile replicates that observed during synthetic trials with the same media types albeit run at a shorter HRT of 6 h and an inlet TP concentration of 3.3-3.9 mg/L

(Chapter 3). However, in the case of the synthetic trials, the peak concentration was much higher and occurred after a greater cumulative TP load for the steel slag media (4-5 mg/L, 700-800 mgTP/kg_{media}) and the same peak value but at a larger cumulative load for the apatite (0.58 mg/L, c1110 mgTP/kg_{media}). Further, such profiles do not match those observed in other field trials with BOF steel slag, EAF steel slag and apatite media (Shilton et al., 2006; Harouiya et al., 2011b; Barca et al., 2013; Vale, 2017) where the effluent TP started at a low value and steadily increased. To illustrate, in the case of the previous BOF steel slag trial operated at a HRT of 48 hours, the TP concentration increased to a final level of around 5 mg/L from an influent of 8.5±1.3 mg/L resulting in an overall average effluent of 3.5±1.7 mg/L over the course of a two year trial (Barca et al., 2013). However, similar patterns have been observed, in some but not all studies, for both BOF steel slag and apatite treating synthetic solutions (Molle et al, 2005; Asuman Korkusuz et al., 2007). It is suggested that the initially inclining TP phase represents a period where the combination of the water constituent and the prevailing pH favour the formation on non-P-containing precipitates such as calcium carbonate (Montastruc et al., 2003; Whitton et al., 2017). Further, the reduced performance reported for the previous BOF steel slag trial was attributed to the high alkalinity causing excess precipitation of calcium carbonate (Barca et al., 2013). This is likely to occur with higher retention times and alkalinities which favour precipitation of new calcium carbonate which is known to have a relative poor affinity to P, reducing removal (Jang and Kang, 2002; Claveau-Mallet et al., 2017). The new precipitate will partially coat the media, slowing down the dissolution rate and repositioning conditions to those that favour P removal. The relative short HRT of the synthetic trial delays this transfer of effects by reducing the local saturation index generated and hence extends the stabilisation phase.

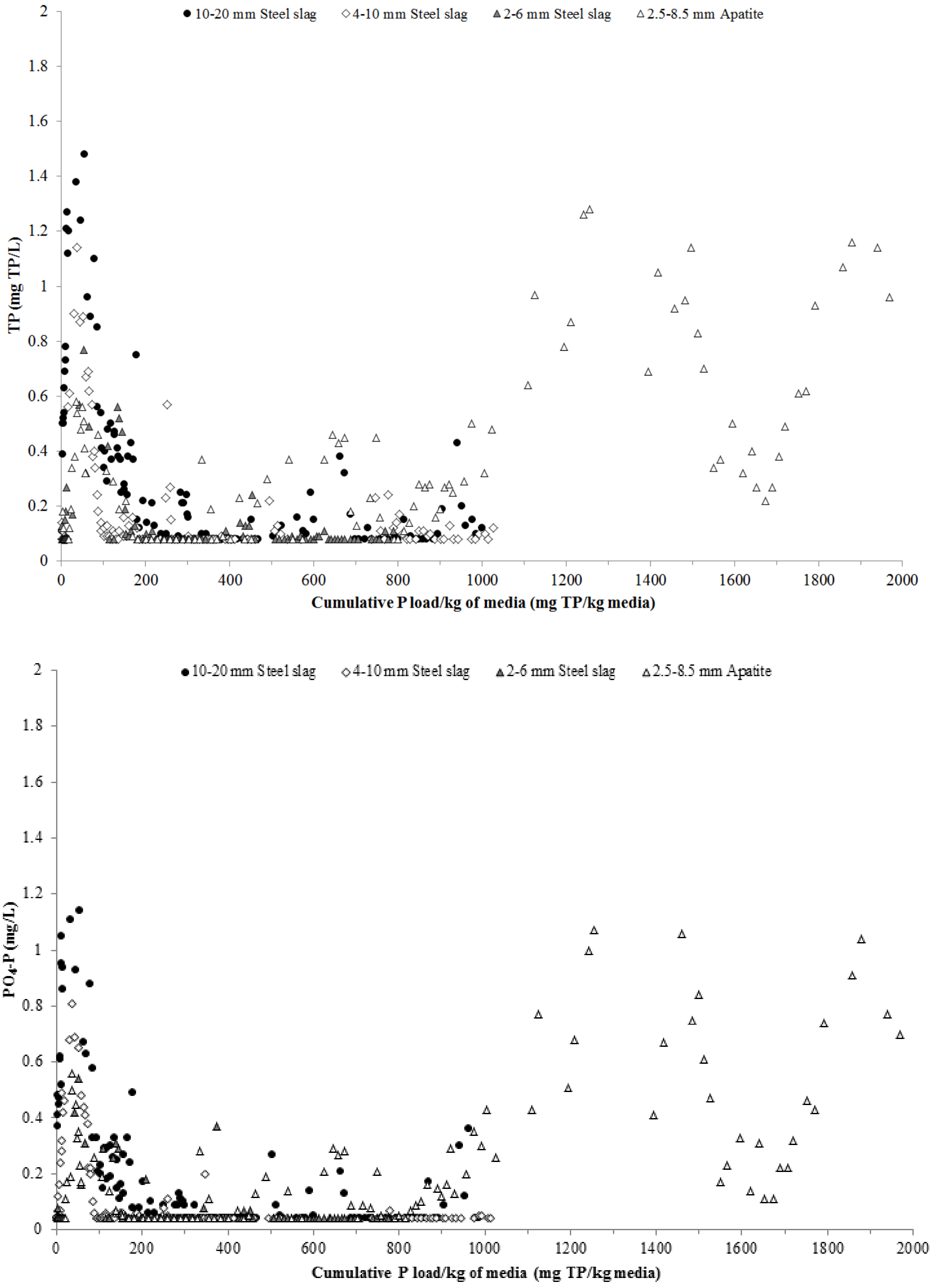

Figure 4-3 Effluent (a) TP and (b) PO_4-P concentration for the three steel slag and the apatite constructed wetlands as a function of cumulative P load.

In the *steady-state* phase (approximately 200-1027 mgTP/kg$_{media}$ cumulative P load), the effluent TP remained below 0.5 mg/L for all media. However, greater variability in the effluent TP was observed for the apatite and the 10-20 mm SS with average effluent TP concentrations over this period of 0.37±0.33 mg/L and 0.13±0.07 mg/L respectively. A similar profile but with less scatter is seen in terms of ortho-phosphate where the average effluent PO_4-P was 0.25 (0.04-1.07) mg/L and 0.07±0.03 mg/L, respectively. This indicates that there was a loss of colloidal precipitates from those two wetlands, as a fraction of the TP was not soluble (PO_4-P) but particulate instead (Figure 4-3b; Supplementary Information, Appendix C). The constructed wetland with the apatite media continued operating up to a load of 1,969 mgTP/kg$_{media}$ over which time the effluent P concentration fluctuated in a cyclical manner initially rising to a peak of 1.26 mg/L at a load of 1,241 mgTP/kg$_{media}$ before reducing down to a minimum of 0.22 mg/L at a load of 1,673 mgTP/kg$_{media}$ and rising again to 1.16 mg/L at a load of 1,879 mgTP/kg$_{media}$ (Figure 4-3a). The same cyclic profile has been reported for BOF and EAF steel slag and linked to seasonal impacts with higher effluent TP reported in winter and lower effluent TP reported in summer months (Shilton et al., 2006; Barca et al., 2012). For instance, in the case of the EAF slag, the effluent TP was below 2 mg/L in the summer and below 4 mg/L in the winter (Shilton et al., 2006). The current data aligns to this with the two peaks occurring on the 26th January and the 4th October as opposed to the minimum which occurred on the 19th July. In part, this relates to the impact of temperature as illustrated through batch tests which showed that the reaction rates of HAP formation were ten times faster at 35°C compared to 10°C under controlled laboratory conditions using synthetic solutions (Jang and Kang, 2002). However, solids management issues also appear important as the inlet section of the apatite wetland was observed to be clogging. This would cover the apatite surface restricting further uptake and, more important, generate a short circuit in the wetland, reducing the effective HRT. Additional solids management issues were observed prior to 1,000 mgTP/kg$_{media}$, related to the need to flush the distribution systems at P loading rates of 673.9 mgTP/kg$_{media}$ and 941.1 mgTP/kg$_{media}$ with corresponding effluent TP concentrations of 0.38 mg/L and 0.43 mg/L for the 10-20 mm steel slag wetland. Interestingly, no clogging was evident with the steel slag wetland with a similar size to that of the apatite media. Although the loading applied to the steel slag wetland was considerably lower than that applied to the apatite wetland (36.3 g BOD/m^2·d and 62.7 g BOD/m^2·d, respectively, and equivalent to solids loadings of 84.3 g solids/m^2·d and 141.4 g solids/m^2·d), both were significantly lower than the maximum recommended value of 250 g BOD/m^2·d to avoid clogging in traditional HF wetlands with larger media (Dotro et al., 2017). The enhanced clogging may reflect the more spherical nature of the apatite media but irrespective of reason, the result suggest that the solids loading rate onto the wetlands needs management when using small media sizes such as pre-treatment with a pile cloth media filter or regular wetland flushing/refurbishment.

More stable performance was observed for the 4-10 mm SS and the 2-6 mm SS with average effluent TP concentrations of 0.11±0.07 mg/L and 0.09±0.02 mg/L over the same load range. In fact, the operational capacity of the media is not exceeded even after 718 days of operation. The results contradict the previous trial with synthetic media (Chapter 3) where, once the operation enters the *steady-state* phase, the effluent TP concentration remained below 0.18 mg/L up to the maximum load treated of 6,147 mgTP/kg$_{media}$ for the apatite media. Whereas the effluent TP from the equivalently sized SS media was 0.29±0.04 mg/L between loading rates of 1,360 and 3,290 mgTP/kg$_{media}$ before it fluctuated more. The HRT of the trial was much shorter at 6 hours where previously trials had shown at least 24 hours was required for stable performance (Walter, 2012).

4.3.2 pH

The effluent pH initially was very elevated at 12.7, 12.7, 12.3 and 12.7 for the 2-6 mm SS, 4-10 mm SS, 10-20 mm SS and the apatite respectively (Figure 4-4). In the case of the apatite the pH then decreased to a level below pH 9 at a load of 974.7 mgTP/kg$_{media}$ before stabilising at around 8.3. This coincides with the start of the cyclic effluent TP profiles and probably indicates a switch in mechanism towards more adsorption and growth. In contrast, the effluent pH from the steel slag wetlands decreased more rapidly than for the apatite wetland but stabilised at much higher final pH values of 10.6, 11.2 and 11.3 for the 10-20 mm, 4-10 mm and 2-6 mm media respectively. This indicates that dissolution of calcium oxides was most likely continuing supported by the sustained very low effluent TP concentrations achieved. This equates to around 800 days of operation and differs significantly from previous field trials with BOF steel slag where the pH decreased to below a value of 9 in c35 days and c60 days (Table 4-2). The importance of this is that it is normally expected to discharge wastewater below pH 9 and hence pH correction would be required in the case of the current constructed wetlands. Correction can be achieved by acid dosing but this negates some of the proposed benefits of the systems (passive, chemical free) and as such current research is investigating alternative methods of passive pH adjustment such as the use of peat filters (Barca et al., 2014).

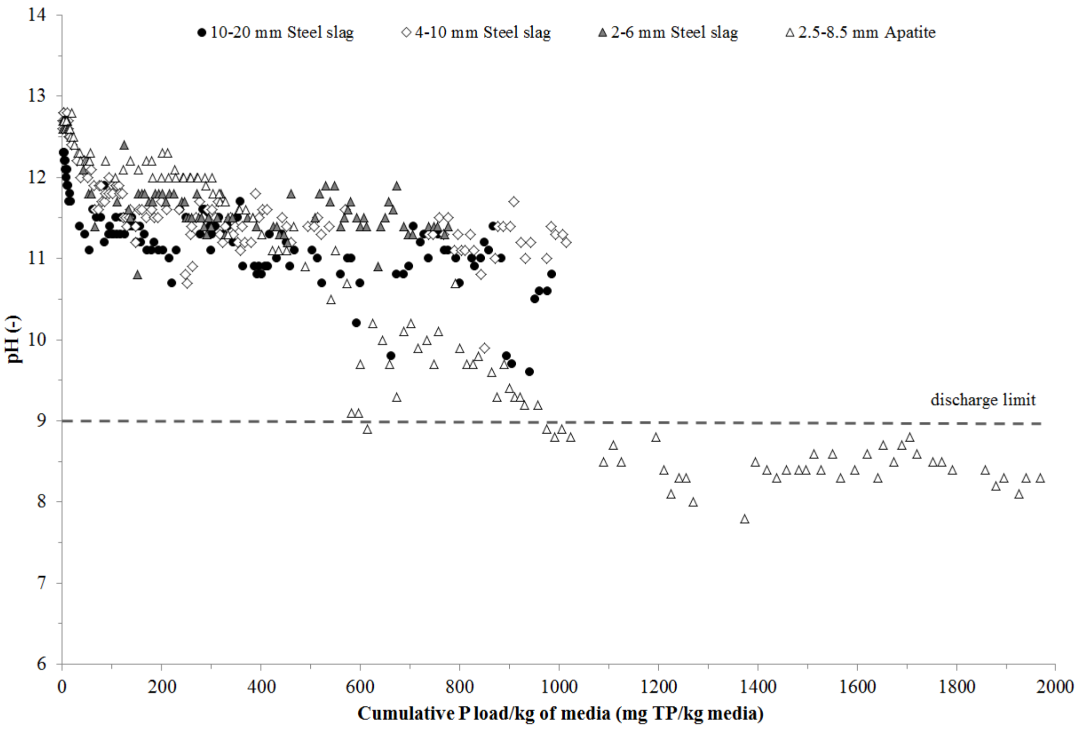

Figure 4-4 pH profiles for the four media constructed wetlands during the field-scale trials.

Comparison of the current data with previous trials reveals a broad range of effluent TP, pH and time to reach pH 9 and Phosphorus Sorption Capacity (PSC) levels (Table 4-2). The difference relates to differences in the alkalinity, HRT and base material properties of the trialled media. For instance, in the previous apatite trials the PO_4-P effluent concentration reduced initially to around 0.6 mg/L the first three months of operation thereafter steadily increasing to 3 mg/L towards the end of the trial at 30 months of operation (Harouiya et al., 2011b). The initial PO_4-P concentration was 5.9 mg/L and the filters operated at a HRT of 48 hours. However, the media contained a much lower apatite fraction at 41.8% w/w compared to 88% w/w in the current case. The other material is either quartz or calcite and both are known to have a substantially lower affinity for P. Similarly, the previous long-term field trial with EAF steel slag showed a low initial residual P concentration rising to the influent TP level of 8 mg/L (Shilton et al., 2006). In this case the difference is attributed, in part, to the much lower Ca content of the slag at 11.4% w/w compared to 29-26% w/w in the current case.

The effluent pH did not show any correlation with the BOD, NH_4-N and suspended solids removal observed for any of the wetlands. Overall, the effectiveness of the media appears to be related to the HRT operated at and the constituents of the background water, especially the alkalinity. Higher removal levels are observed with combination of long HRTs and low alkalinities (Table 4-2) with the case of lower removal attributed to either a short HRT or a high alkalinity. The importance of HRT is less evident in the case of apatite media where values as low as 6 hours have yielded removal levels above 90%. In comparison, equivalent removal with steel slag appears to require a HRT of at least 24 hours. Consequently, it is suggested that design of such systems needs to match an operating HRT to the background water constituents.

Table 4-2 Comparison of field-scale performance of BOF steel slag and apatite treating domestic wastewater (SS: steel slag; HRT=V·φ/Q, where φ is porosity; N/A: not available; NR: not reached).

Material, size (mm)	HRT (h)	Alkalinity (mg $CaCO_3$/L)	Inlet TP (mg/L)	Outlet TP (mg/L)	Peak pH	Time to pH <9 (days)	PSC (gP/kg_{media})	Reference
BOF SS, 10-20	24	144.7±23.1	4.1±1.0	0.37±0.34	12.7	NR	0.94	Current study
BOF SS, 4-10	24	144.7±23.1	4.1±1.0	0.17 (0.08-3.57)	12.8	NR	1.00	Current study
BOF SS, 2-6	24	144.7±23.1	4.1±1.0	0.13±0.13	12.8	NR	0.76	Current study

Apatite, 2.5-8.5	12	144.7±23.1	4.1±1.0	0.25±0.25	12.8	459	1.81	Current study
BOF SS, 14	16	132.8 ±46.5	4.9±1.6	1.6±0.8	10.6	192	0.72	Walter (2012)
BOF SS, 8-14	24	N/A	7.6±1.7	2.9 ±1.9	12.0	283	1.35	Vale (2017)
BF SS, 0-3	70	N/A	6.6±1.8	3.2±1.8	8.6	-	0.07	Asuman Korkusuz et al. (2007)
EAF SS, 10-20	72	N/A	8.4	6.0	N/A	N/A	1.23	Shilton et al. (2006)
EAF SS, 20-40	24-48	282±39	8.5±1.3	4.7±1.7	<9	-	0.32	Barca et al. (2013)
BOF SS, 20-40	24-48	282±39	8.5±1.3	3.5±1.7	c10.8	c35	0.61	Barca et al. (2013)
Apatite, 4-9	48	N/A	4.2	N/A	N/A	N/A	0.44	Harouiya et al. (2011a)
Apatite, 1.3-4.0	48	N/A	5.9	1.1	N/A	N/A	1.1	Harouiya et al. (2011b)
Apatite, 1.3-4.0	69.6	N/A	5.8±0.9	1.6	N/A	N/A	0.8	Harouiya et al. (2011b)

4.3.3 Metals

Only eight of the 29 measured metals showed any change in the effluent of the constructed wetlands during the trial (Table 4-3). Both steel slag and apatite showed a similar behaviour for five of the metals. Specifically, the four wetlands showed release of barium, and removal of copper, iron, manganese and titanium. In the case of barium, the release was higher with decreasing slag fraction, with average values of 150.6 µg/L, 765.5 µg/L and 929.1 µg/L for 10-20 mm, 4-10 mm and 2-6 mm slag fractions, and 568.9 µg/L for apatite, from an inlet concentration of 20.5 µg/L. This compares to a reduced final effluent (and post pile cloth media filter effluent, Figure 4-1) level of 7.6 µg/L, indicating that both media release barium compared to the mainstream treatment.

In the case of steel slag, the higher release by smaller fractions can be linked to their higher surface area.

Copper, manganese and titanium were removed by both materials to similar levels, with average removals of 74.1%, 89.4% and 80.8%, respectively, compared to lower removals achieved by the pile cloth media filter, 58.4%, 52.6% and 29.6%, respectively. The removal of iron, however, was highest for the 4-10mm steel slag, followed by the 2-6 mm steel slag, 10-20 mm steel slag and apatite. To illustrate, from an average inlet concentration of 1,521.4 μg/L, the effluent concentrations were 44.0 μg/L, 50.2 μg/L, 77.6 μg/L and 82.6 μg/L, respectively. This compares to a final effluent level of 354.2 μg/L, suggesting that the constructed wetlands, regardless of the material, can improve iron removal compared to the pile cloth media filter, probably linked to increased adsorption onto the media surface and improved solids removal.

Tin was the only metal that while no change was observed for the wetlands, the pile cloth media filter showed considerably higher removal, 86.4%, reducing the inlet concentration from an average of 5.9 μg/L to an average level of 0.8 μg/L.

Table 4-3 Summary of metal leaching during field-scale constructed wetland trials with three fractions of BOF steel slag, and apatite (all concentrations in μg/L, N/A: not available).

Metal [discharge target]	Feed	10-20 mm Steel slag	4-10 mm Steel slag	2-6 mm Steel slag	2.5-8.5 Apatite
Barium [130]	20.5 [3.7-206.0]	150.6 [7.8-635.0]	765.5 [11.6-2,689.0]	929.1 [23.9-3,461.0]	568.9 [7.9-1,843.0]
Chromium [4.7]	1.2 [0.9-8.6]	1.1 [0.9-2.6]	1.0 [0.9-2.2]	0.9 [0.9-2.7]	23.4 [0.9-103.9]
Copper [28]	89.9 [18.0-845.0]	20.0 [4.0-37.0]	23.8 [3.0-41.0]	23.0 [4.0-61.0]	26.5 [3.0-62.0]

Iron [1000]	1,521.4 [14.1-13,837]	77.6 [3.3-391.0]	44.0 [7.7-630.0]	50.2 [5.6-474.0]	82.6 [8.2-1,139.0]
Manganese [123]	29.3 [3.2-310.0]	4.1 [0.8-24.2]	3.7 [0.8-47.7]	2.5 [0.8-10.1]	2.3 [0.8-21.1]
Tin [113]	5.9 [0.8-15.0]	5.0 [0.8-15.0]	4.4 [0.8-15.0]	7.4 [0.8-15.0]	5.7 [0.8-15.0]
Titanium [N/A]	12.5 [1.7-86.4]	2.7 [1.5-7.8]	2.5 [1.5-15.0]	2.2 [1.5-12.6]	2.2 [1.5-22.8]
Vanadium [60]	8.0 [1.9-34.0]	386.9 [1.9-877.0]	380.4 [1.9-975.0]	327.7 [1.9-1,003.0]	13.2 [1.9-46.2]
Zn [30]	48.0 [7.0-433.0]	6.2 [4.0-49.0]	6.8 [4.0-35.0]	6.3 [4.0-134.0]	6.7 [4.0-47.0]

Two metals showed specific media related behaviour, chromium for apatite and vanadium for steel slag. In the case of chromium, while steel slag effluent and final effluent levels were similar to inlet concentrations (around 1.2 μg/L), apatite increased chromium to a level of 23.4 μg/L. Column trials with synthetic wastewater at HRT of 6 hours did not show any significant Cr release for this material (Chapter 3), it is posited that the higher retention time employed in the field-scale trial could increase effluent concentrations through longer contact time.

On the contrary, while apatite effluent and final effluent showed similar V concentrations to the inlet (around 8.0 μg/L), the three steel slag constructed wetlands increased those levels to average values of 386.9 μg/L, 380.4 μg/L and 327.7 μg/L for 10-20 mm, 4-10mm and 2-6 mm fractions, respectively. The effluent vanadium concentration increased during the initial stage of the run and then remained elevated throughout the trial (Figure 4-5). Maximum recorded concentrations of 877.3, 974.7 and

1,003.5 µg/L were observed at P loadings of 842.1 mgTP/kg$_{media}$, 871.5 mgTP/kg$_{media}$ and 769.4 mgTP/kg$_{media}$ for the 10-20 mm, 4-10 mm and 2-6 mm steel slag fractions, respectively. The average values after a P loading of 200 mgTP/kg$_{media}$ (taken as representative of the stable period) were 551.5±148.8 µg/L, 778.2±105.8 µg/L and 765.0±141.5 µg/L, respectively. Overall, this indicates that dissolution was continuing through the trial congruent with the elevated pH and the very low residual P achieved. This compared to a suggested limit of 60 µg/L indicates that management of the leaching of this metal is critical for its full-scale application. In contrast, V release from the apatite wetland was negligible generating an average effluent concentration of 13.2 µg/L (1.9-46.2) consistent with the mineral containing trace levels of the metal (Khiari et al., 2004; Molle et al, 2011) as well as an increase through the effluent from the steel slag wetlands being recirculated to the head of the works.

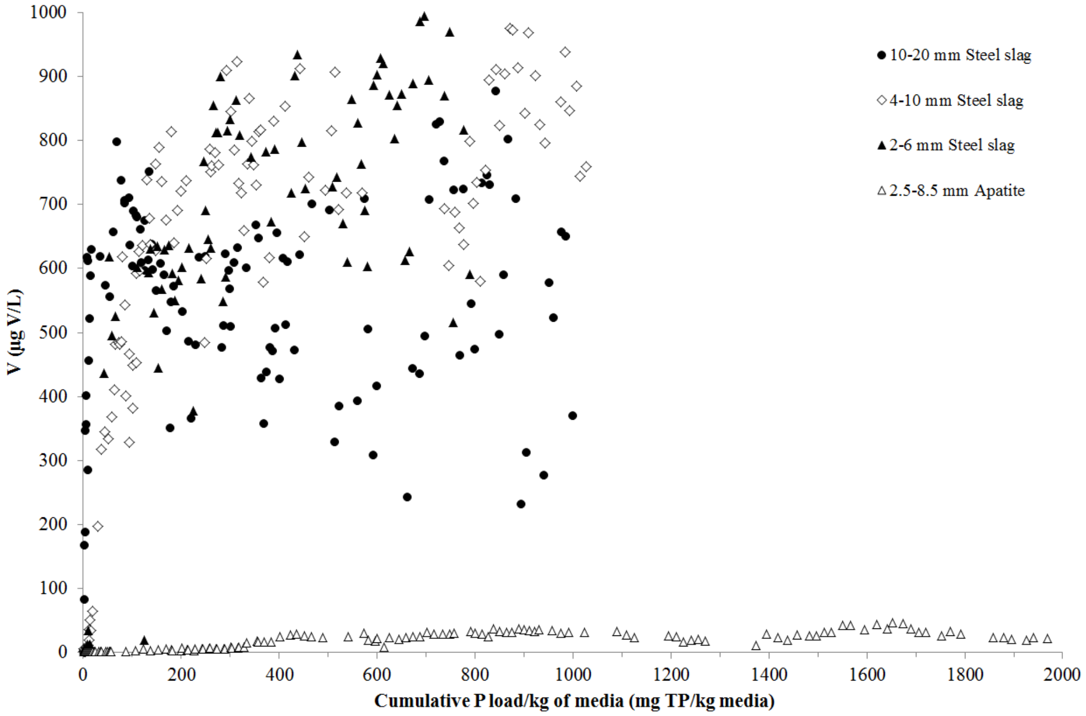

Figure 4-5 Effluent V concentrations from the three steel slag and the apatite constructed wetlands during the field-scale trial.

BOF steel slag and apatite showed different alpha and beta radioactivity levels throughout the duration of the trial (Figure 4-6a,b). Alpha radioactivity for the common inlet and effluent of the three steel slag wetlands was similar and constant at a level of around 0.04 Bq/L. Effluent from the apatite wetland showed higher alpha radioactivity concentrations, with a level of 0.47 Bq/L at the start of the trial, to then decrease to 0.08 Bq/L after one year and increase again to 0.25 Bq/L after another year. Nonetheless, the apatite levels were always below the drinking water standard of 0.5 Bq/L. The beta radioactivity profile was similar to the alpha profile for apatite, but showed more disperse levels for the inlet and three steel slag effluents. To illustrate, inlet concentrations increased throughout the trial, from an initial level of 0.05 Bq/L to a level of 0.67 Bq/L at the end of the trial. The three steel slag effluents showed similar levels, but also varied throughout the trial, showing a decrease from initial values of 0.56 Bq/L, 0.53 Bq/L and 0.40 Bq/L to values of 0.44 Bq/L, 0.43 Bq/L and 0.43 Bq/L after one year, and a further slight increase to levels of 0.48 Bq/L, 0.55 Bq/L and 0.53 Bq/L towards the end of the trial, for decreasing slag fractions, respectively. The beta radioactivity for apatite was similar to the alpha radioactivity and higher than that for all the steel slag fractions throughout the trial.

The higher alpha and beta radioactivity levels of the apatite compared to steel slag are attributed to the higher uranium levels of apatite, which are inherent to the material. Uranium is known to emit alpha and beta radioactivity (WHO, 2008). A reported slight increase in uranium concentrations has been reported for a 1.3-4.0 mm apatite filter treating wastewater at a HRT of 69.6 hours, from inlet concentrations of 0.23±0.04 μg/L to 1.22±0.75 μg/L (Molle et al., 2011). Direct comparison to the radioactivity levels in the current work is not possible, as alpha and beta radioactivity is not solely related to uranium, but other elements, such as thorium, radium, radon or potassium-40. This can explain why positive alpha and beta radioactivity levels were also detected for the steel slag wetland effluents.

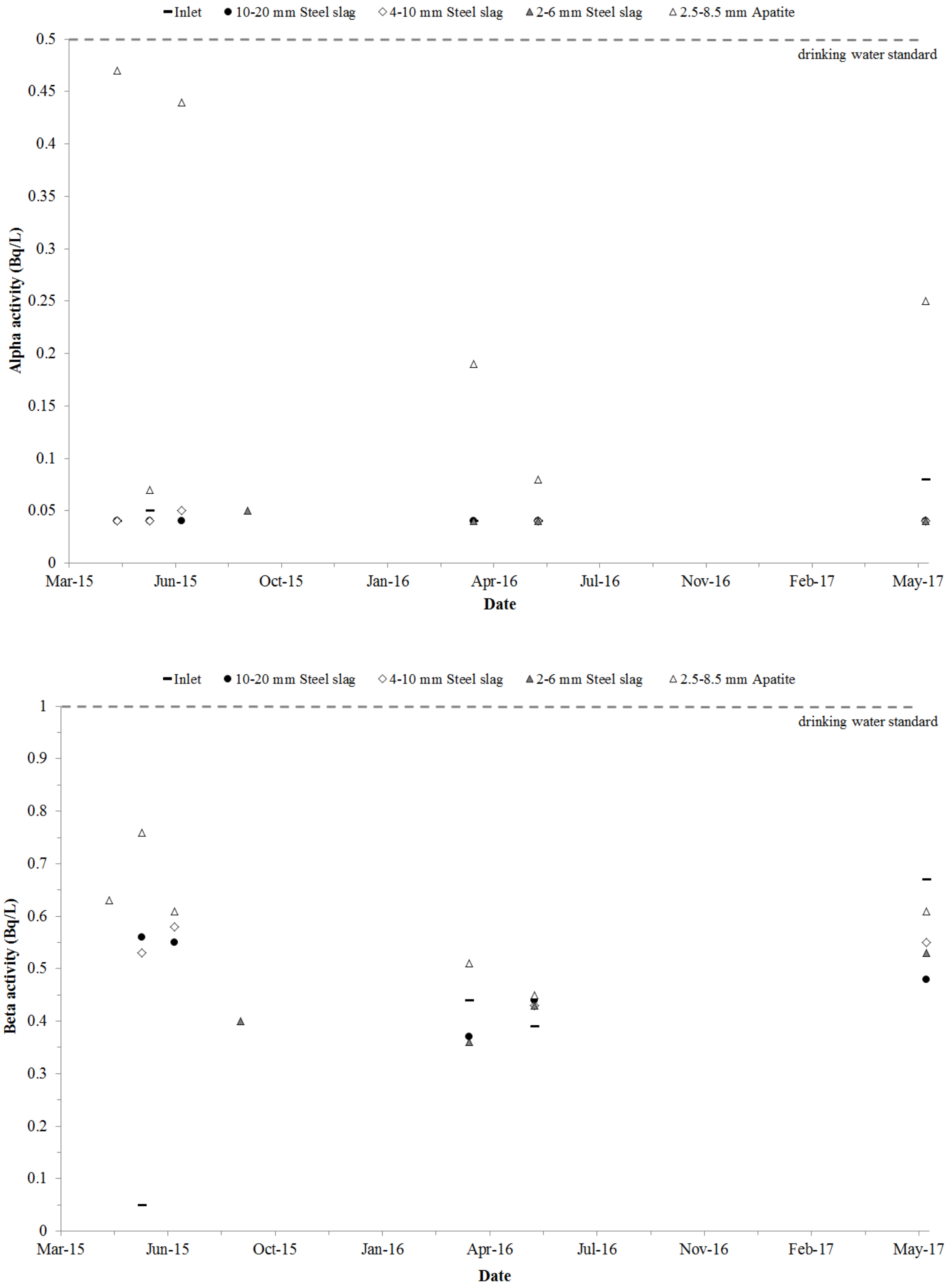

Figure 4-6 a) Alpha and b) beta radioactivity of common inlet and effluent from the three BOF steel slag and the apatite constructed wetlands.

4.3.4 Priority Substances removal

The sampling campaigns for PS showed positive removal for seven out of the ten monitored compounds (Figure 4-7a). Removal levels were similar for both SS and apatite media with respect to nonylphenol (85.3% and 86.7%), benzo(a)pyrene (45.5% and 56.0%), cypermethrin (92.1% and 85.0%), oestrone (94.8% and 84.3%) and 17B-oestradiol (93.2% and 91.1%). However, in the case of hexabromocyclododecane (HBCDD) and 17A-ethinyloestradiol improved removal was observed in the case of the steel slag media with removals of 77% and 72.5% compared to 57.2% and 18.2% in the case of apatite. A slight increase of perfluorooctyl sulphonates (PFOs) was observed for both media possibly reflecting the sampling period being part way through the run offering the potential to release previously retained material. Such behaviour has been previously reported with activated carbon and reflects displacement onto attachment sites with more favourable compounds (Revert, 2014). The reported removal rates are in line with those in literature, with average removal rates of 90% for nonylphenols, 100% for 17B-oestradiol and 100% for 17A-ethinyloestradiol (Gorito et al., 2017). Moreover, if compared to the 17B-oestradiol discharge target of 0.001 μg/L, both steel slag and apatite reduce the exceeding inlet concentration of 0.005±0.001 μg/L to levels of 0.0003±0.000 μg/L and 0.0003±0.002 μg/L, respectively. The fact that the removal rates observed in this study are slightly lower than those for both materials implies that the removal of those compounds is not improved by the addition of the reactive media, and that their removal is more linked to removal mechanisms inherent to the constructed wetland system itself, such as anaerobic redox environments or microbial degradation.

For other compounds of interest, such as pharmaceuticals and steroids, removal was similar or higher for the BOF SS compared to the apatite with the exceptions of triclosan, ibuprofen, propranolol, azithromycin and rantidine where removal was enhanced with the apatite media (Figure 4-7b). The improved removal even though the wetland operated at a shorter HRT implies a material specific affinity for such compounds whereas the elevated removal of compounds with the SS could be a reflection of the longer operational HRT (Chen et al., 2014).

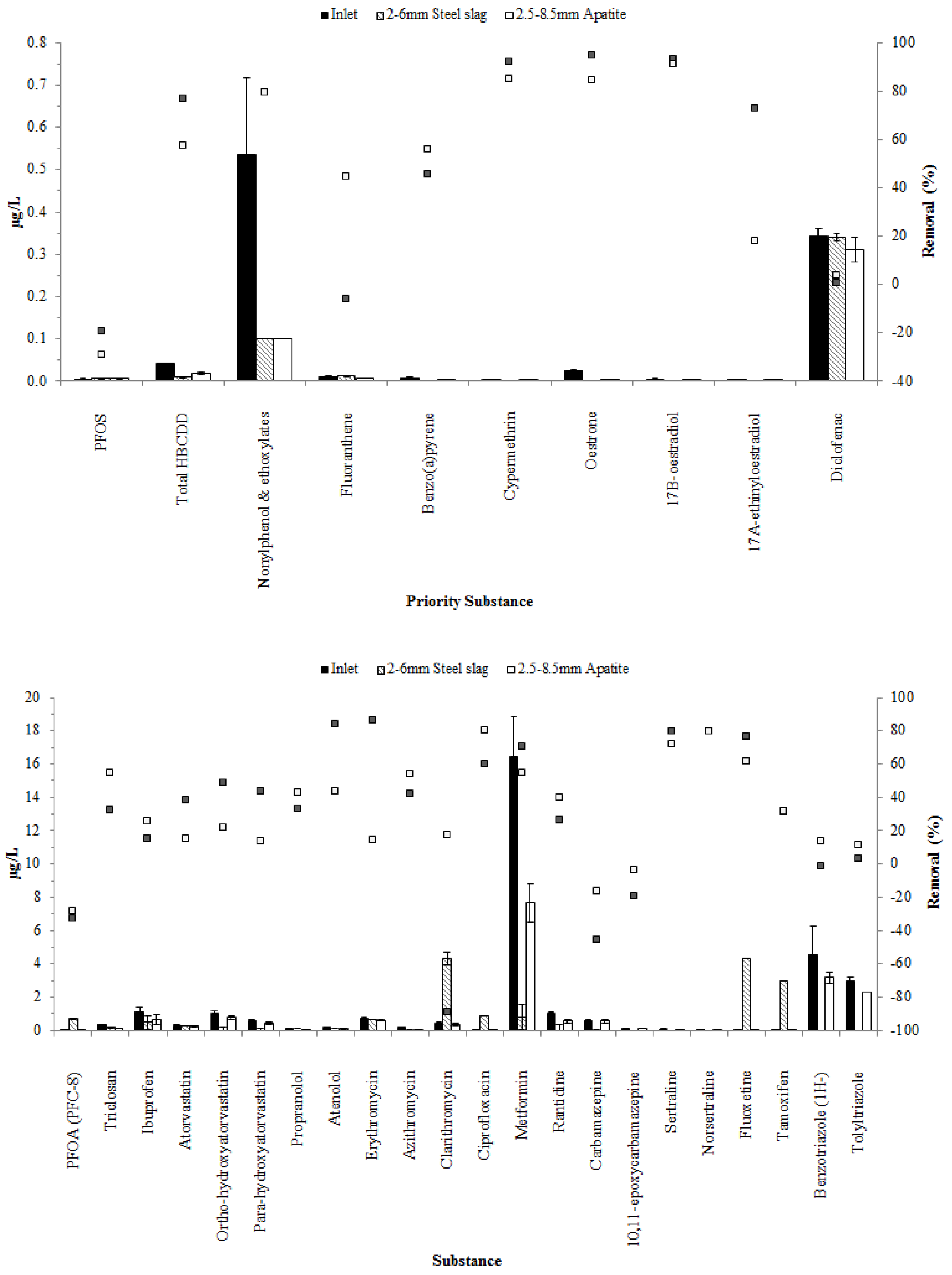

Figure 4-7 Inlet, effluent concentrations and removal rates for the 2-6 mm BOF steel slag and apatite wetlands in terms of a) ten Priority Substances included in Directive 2013/39/EU and Directive Decision 2015/495/EU by the apatite and the 2-6mm BOF steel slag constructed wetlands and b) other substances of interest including pharmaceuticals and steroids.

4.4 Conclusions

- Both media were effective in removing phosphorus (P) to enable compliance with a 1 mg/L total P (TP) targets.
- Two phases of operation were observed for both steel slag and apatite: *stabilisation* phase, where non-P-containing precipitate formation is favoured, and *steady-steady* phase, were P removal is enhanced.
- Only the effluent form the apatite wetland stabilised below 9, whereas the three steel slag effluents remained above 10. For apatite, it reflects a change in P removal mechanism towards adsorption and growth, while for steel slag, it indicates sustained P removal by CaO dissolution.
- Solids management is needed for constructed wetlands with smaller reactive media, either by the installation of a prior pile cloth media filter, or by flushing or refurbishing the media more often.
- Both BOF steel slag and apatite showed release of barium and iron, copper, manganese and titanium removal. Two metals showed specific media related behaviour, chromium and uranium for apatite and vanadium for steel slag.
- High removal was observed with both materials for the priority substances nonlyphenol, benzo(a)pyrene, cypermethrin, oestrone and 17B-oestradiol.

4.5 Acknowledgments

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5 Implications of the work: overall perspective of the suitability of constructed wetlands with reactive media for wastewater treatment in the UK

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Abstract

Basic Oxygen Furnace (BOF) steel slag and apatite are considered two of the most promising materials to be used as reactive materials in constructed wetlands for phosphorus (P) removal at small sewage treatment works. As such, they have been extensively studied although the media source, scale of design and operational parameters have considerably varied, making comparison across trials very challenging. This work presents the first direct comparison of three similar UK based field trials with the same BOF steel slag source and similar wastewater characteristics. Although the three trials achieved effluent P levels below 1 mgTP/L, very different effluent P, pH and V profiles were observed. This was attributed to a complex set of interactions between the components released from the slag and the background chemistry of the water, and the heterogeneity of the slag material, associated with it being a waste product. Economic assessment of constructed wetlands with BOF steel slag and apatite compared to the traditional solution of chemical dosing with tertiary filtration revealed that the constructed wetland options with both media would be economically favourable compared to the conventional solution with minimum media refurbishment frequencies of three and nine years, respectively. However, pH correction and vanadium release would need to be managed in the case of BOF steel slag, and chromium release in the case of apatite based wetlands.

Keywords: apatite, chemical dosing, constructed wetlands, pile cloth media filter, steel slag.

5.1 Introduction

There has been a recent interest within UK water utilities in alternative technologies in order to meet the required new lower total phosphorus (TP) limits for final effluents from sewage treatment works (STW). Current P consents for STW in the UK are driven by the Urban Wastewater Treatment Directive (UWWTD) (Council Directive, 1991). The majority of the STW in the UK can be considered small sites, as they serve populations of less than 2,000 population equivalents (PE) (Upton et al., 1995), for which the UWWTD does not apply. However, the implementation of the Water Framework Directive (WFD) is translated into new P consents being imposed for these small STW, with likely levels of around 1 mgTP/L (Fonseca, 2016). The conventional P removal technology (chemical dosing with Al or Fe salts, followed by tertiary filtration) would be able to meet these new tighter P consents. Nonetheless, this approach may not be the most suitable for small STW, as they are usually unmanned and located in remote areas. This means that electricity and maintenance requirements can be a challenge and that they would greatly benefit from a technology less reliant on energy due to low operational and maintenance requirements, such as constructed wetlands with P reactive media.

There is currently a lack of full-scale applications using reactive media and none that are based on meeting a 1 mgTP/L discharge standard. Accordingly, the work outlined in the preceding chapters have investigated the potential of two of the most promising options: basic oxygen furnace (BOF) steel slag and apatite based media. The key observations from the outlined work in relation to the potential application of these media are:

- The effluent TP profile was characterised by two phases: a *stabilisation* phase where the effluent TP initially increased and subsequently decreased and a *steady-state* phase where the effluent TP remained stable. This was observed during the synthetic column trials and the field-scale real wastewater trials but not during the real wastewater column trials. This was potentially due to the short HRT used during these trials.

- Effective reduction of the effluent TP concentration to below 1 mg/L was possible with apatite media at a relatively short HRTs (6-12 hours) and with steel slag at longer HRTs (24+ hours).
- Low effluent TP concentrations were associated with elevated pH which could be sustained above pH 9 for prolonged time periods consistent with the proposed predominate mechanism of calcium oxide dissolution followed by precipitation growth.
- Reducing the size of the steel slag media improved performance during the field trials and the synthetic column trials but not during the real wastewater column trials.
- The apatite media showed improved performance compared to equally sized BOF steel slag during the column trials. However, the choice of binding material was critical to the effectiveness of the media.
- Both media showed potential for removal of some priority substances (nonlyphenol, benzo(a)pyrene, cypermethrin, oestrone and 17B-oestradiol) and metals (iron, copper and titanium) as well as a potential risk of leaching vanadium, chromium and/or uranium.
- Comparison to other trials revealed significant differences in profiles in both P and pH in both real and synthetic trials as well as with column and field trials. The differences are related to the impact of the background water constituents, mainly associated with alkalinity as well as the operational HRT.

Overall, the observations indicate the importance of media choice (material and size), HRT and alkalinity on the effectiveness of using reactive media for P removal. In addition, previous trials also include variations in inlet P concentration, water chemistry (carbon free synthetic, synthetic and real wastewater), column dimensions and experimental duration generating significant differences in the performance of the system. However, the need for a consensus towards appropriate design and operation is critical in the future uptake of reactive media. Accordingly, the current paper aims at addressing this challenge through:

(1) A comparison between the current field-scale trials and two other similar field trials in the UK using BOF steel slag to treat tertiary wastewater down to below

1 mgTP/L. The wastewater, design and operational HRT of the systems is slightly different but using the same reactive media.

(2) A comparison of current literature data to ascertain the impacts of HRT and alkalinity and to assess the translation of data from synthetic trials to real situations.

(3) An economic assessment of the two reactive media in comparison with a current solution of chemical dosing with tertiary filtration to ascertain the impact of the difference in the operational HRT and media costs.

Overall the paper will outline the potential to use reactive media, identify key remaining challenges and assess the economic plausibility of its use.

5.2 Materials and methods

5.2.1 Case study sites with constructed wetlands with reactive media in the UK

The three sites in the UK where field-scale constructed wetlands with reactive media have been trialled belong to three different water utilities, i.e. Thames Water, Wessex Water and Severn Trent Water. The common characteristic of all sites is that they use BOF steel slag as reactive media in horizontal subsurface flow (HSSF) wetlands.

Site 1 (7,500 PE) treats a domestic wastewater with no industrial inputs and uses trickling filters as the main biological treatment stage and incorporates a pile cloth media filter as a tertiary treatment with no specific P removal component. The trial wetlands had dimensions of 22 m (W), 6.5 m (L) and 0.6 m (H) containing either 10-20 mm BOF steel slag or 2.5-8.5 mm apatite (Chapter 4). The wetlands were fed along the long edge with humus tank effluent, and were operated at 24 hours HRT in the case of steel slag and 12 hours in the case of apatite. The trial was operational for 806 days and 850 days, respectively.

Site 2 (7,900 PE) treats a domestic wastewater with no industrial inputs and uses trickling filters as the main biological treatment stage with no specific P removal component. The wetland had dimensions of 4.4 m (W), 20 m (L) and 0.75 m (H) containing 14 mm BOF steel slag. The wetland was fed along the short edge with humus tank effluent at a HRT of 16 hours (Walter, 2012). The trial was operational for around 730 days.

Site 3 (17,375 PE) treats a domestic wastewater with a 1% trade input and uses an oxidation ditch as the main treatment stage incorporating ferric dosing for P removal and the use of tertiary filtration. The wetland had dimensions of 8.4 m (W), 12.0 m (L) and 0.6 m (H) containing 8-14 mm BOF steel slag. The wetland was fed along the short edge with secondary wastewater supplemented with H_3PO_4 dosing to reach the desired inlet concentration at a HRT of 24 Hours (Vale, 2017). The trial was operational for around 720 days.

5.2.2 Wastewater

The inlet and effluent wastewater to and from the wetlands was frequently analysed across the three sites for TP, ortho-phosphate (PO_4-P), pH, alkalinity, suspended solids, calcium, vanadium and copper according to standard methods (BS EN ISO 6878:2004, BSI (2004); BS EN ISO 9963-1:1996, BSI (1996); BS EN 872:2005, BSI (2005)). Calcium and copper were analysed using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), and vanadium by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Sites 1 and 2 had similar inlet levels of P and alkalinity with Site 1 containing more solids. Site 3 operated at a higher P concentration with much lower solids and periods of low alkalinity (Table 5-1).

Table 5-1 Summary of inlet wastewater characteristics for the three sites, average values [minimum-maximum]. n= 180 (Site 1), n=48 (Site 2), n=118 (Site 3).

Material (Site)	**TP (mg/L)**	**PO_4 (mg/L)**	**pH**	**Alkalinity (mg $CaCO_3$/L)**	**Suspended solids (mg/L)**
10-20mm SS (Site 1) 2.5-8.5mm APA (Site 1)	4.0 [2.2-6.5]	3.0 [1.0-5.8]	7.8 [7.3-8.3]	144.7 [89.0-227.0]	31.1 [1.9-179.0]
14mm SS (Site 2)	4.9 [1.8-7.9]	4.3 [1.2-6.7]	7.4 [7.0-8.3]	132.8 [70.0-213.0]	17.5 [8.0-58.0]

8-14mm SS (Site 3)	7.7 [5.3-12.4]	7.6 [1.1-12.8]	6.8 [6.3-7.4]	139.0 [11.0-199.0]*	7 [3-27]

*measured between February and August.

5.2.3 Economic assessment

5.2.3.1 Scenarios, assumptions and design parameters

The assessment of economic plausibility of using reactive media was based on the scenario of needing to upgrade a 400 population equivalent (PE) STW with no P removal system in place, with a potential new P consent of 1 mgTP/L. Four scenarios were chosen for the economic assessment (Figure 5-1):

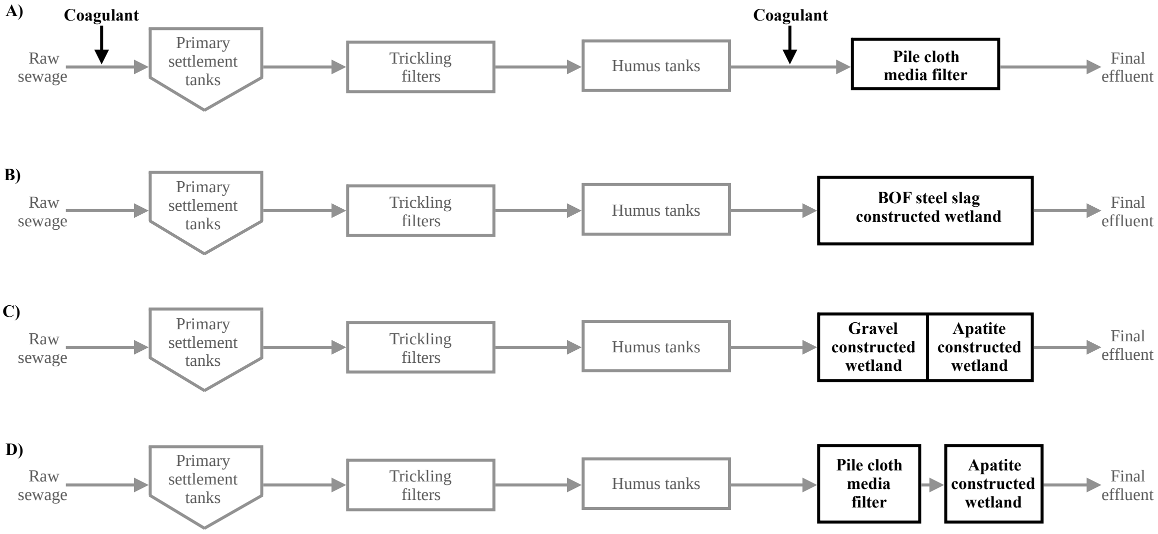

Figure 5-1 Scenarios for economic plausibility assessment, with the upgraded components highlighted.

(A) Chemical dosing with iron salts and pile cloth media filtration. This is the current preferred system for P removal for Thames Water (Jarvis, 2017). The system is based on two point dosing assuming a coagulant dose of 10 mg Fe^{3+}/L for average incoming flow. The pile cloth media filter operates on a duty/standby basis with the cloth requiring replacement every 5 years. The use of coagulant requires the inclusion of chemical storage and a safety shower on site with additional tankering due to increased sludge production. Each dosing point requires a continuous onsite P analyser equipped with a continuous filtration unit for sample preparation.

(B) BOF steel slag constructed wetland based on using 10-20 mm media in horizontal subsurface flow (HSSF) at a HRT of 24 hours. The wetland is estimated to operate for 5 years before the media requires replacement.

(C) A HSSF gravel constructed wetland and vertical subsurface flow (VSSF) apatite constructed wetland operated at the same overall HRT as option (B). The gravel wetland is based on standard 5-10 mm media and is there to reduce solids loading onto the apatite media. The wetland is estimated to operate for 10 years before the media requires replacement.

(D) Pile cloth media filtration followed by constructed wetlands containing apatite media. This is an alternative to (C) to reduce footprint. Options (C) and (D) included solids pre-treatment reflecting operational issues encountered during the field trials (Chapter 4).

The four scenarios are based on design parameters derived from findings of the current thesis, with values from literature or provided by technology suppliers, with omissions and assumptions for each scenario detailed in Table 5-2. All the estimates have been calculated in British Pound Sterling (£). The whole life cost (WLC) estimate was done for 40 years based on an interest rate of 9%, taking into account all the calculated yearly CAPEX and OPEX costs, based on design parameters (Appendix C), and the assumptions and omissions in Table 5-2.

Table 5-2 Summary of assumptions and omissions taken for each scenario.

Scenario	Assumptions and omissions
General	Acceptable tertiary effluent quality: BOD=50 mg/L, SS=60 mg/L and TP=5 mg/L. Influent and effluent pipework not included in CAPEX calculations
Site conditions	Enough gradient on site to function by gravity Enough space on site for CW to be installed

	Groundwater level lower than potential CW base
Chemical dosing and pile cloth media filtration	Ferric sulphate preferred coagulant, with specific gravity of 1.55 kg/L and Fe concentration 11.75% w/w. Cost is commercially sensitive information Two point dosing required at a dose of 10 mg Fe^{3+}/L for an average daily flow of 1.3*PE*D+ Infiltration, where infiltration is 0.4*PE*D and D=150 L/person·day Each dosing point requires a continuous onsite P analyser equipped with a continuous filtration unit for sample preparation Sludge density is 1 kg/L All sludge produced to be tankered off site. Cost is commercially sensitive information Cloth of pile cloth media filter needs to be changed every 5 years
BOF steel slag constructed wetland	HSSF operation for media size of 10-20 mm Cost of media is commercially sensitive information Density of media is 1.65 kg/L Media to be replaced every 5 years Wetland service maintenance contract needed
Apatite constructed wetland	VSSF operation for media size of 2.5-8.5 mm Cost of media is commercially sensitive information. Density of media is 1.37 kg/L Media to be replaced every 10 years Wetland service maintenance contract needed

5.3 Results and Discussion

5.3.1 Effect of design of constructed wetlands with reactive media on performance

The three sites showed different effluent TP concentration profiles when comparing the steel slag constructed wetlands (Figure 5-2a). In the case of Site 1, the TP profile showed an initial increase to a peak concentration of 1.5 mg/L at a P load of 54 mgTP/kg$_{media}$ followed by a decrease to a concentration below the detection limit (<0.08 mg/L) at a P load of 228 mgTP/kg$_{media}$ and remained at this level until the end of the trial which lasted until 1,000 mgTP/kg$_{media}$. In contrast, Site 3 which operates at the same HRT as Site 1, delivered a low stable effluent TP of 0.05 mg/L up to a P load of 447 mgTP/kg$_{media}$ whereafter the effluent concentration increased to a peak of 2.8 mg/L at a load of 1,022 mgTP/kg$_{media}$ (Figure 5-2a). The effluent TP then decreased again to a minimum concentration of 1.2 mg/L at a P load of 1,336 mgTP/kg$_{media}$ before increasing again for the remainder of the trial reaching a peak level of 7.3 mg/L at a P load of 1,729 mgTP/kg$_{media}$ just before the trial finished at a load of 1,784 mgTP/kg$_{media}$. Site 2, which operated at a lower HRT of 16 hours, showed a different profile again. In this case the effluent TP increased rapidly to 2.1 mg/L after a P load of 8.5 mgTP/kg$_{media}$ until a P load of 78 mgTP/kg$_{media}$ at which point it decreased to between 0.2 and 0.4 mg/L up to a P load of 211.9 mgTP/kg$_{media}$. It then increased to a value that fluctuated between 0.7 and 3.3 until the termination of the run at a P load of 1,046 mgTP/kg$_{media}$. In comparison, the apatite based media operated at a HRT of 12 hours and it produced a similar profile to the steel slag over the initial 1,000 mgTP/kg$_{media}$ (Figure 5-2a). However, the initial peak was lower at 0.6 mg/L and occurred sooner at a P load of 35 mgTP/kg$_{media}$. Beyond a P load of c1000 mgTP/kg$_{media}$, the effluent TP started to fluctuate with peaks of 1.3 mg/L and 1.2 mg/L at P loads of 1,256 mgTP/kg$_{media}$ and 1,879 mgTP/kg$_{media}$ respectively.

The effluent pH profiles were also different in terms of the initial effluent pH and the time taken to reduce below a pH of 9 (Figure 5-2b). The initial effluent pH was 12.7, 10.6 and 11.6 for Sites 1, 2 and 3 respectively with regards to the steel slag. The pH then decreased in all sites with the level dropping below pH 9 once a P load of 774 mgTP/kg$_{media}$ and 755 mgTP/kg$_{media}$ had been treated in Sites 2 and 3, respectively. In contrast, Site 1 showed no signs of the effluent pH decreasing below 9, and was in fact maintained above 10.5, apart from a few scattered samples. The equivalent data for the apatite was an initial pH of 12.7 before decreasing to below a value of 9 at a P load of 974 mgTP/kg$_{media}$ reaching a stable range of between 7.8 and 8.8 thereafter.

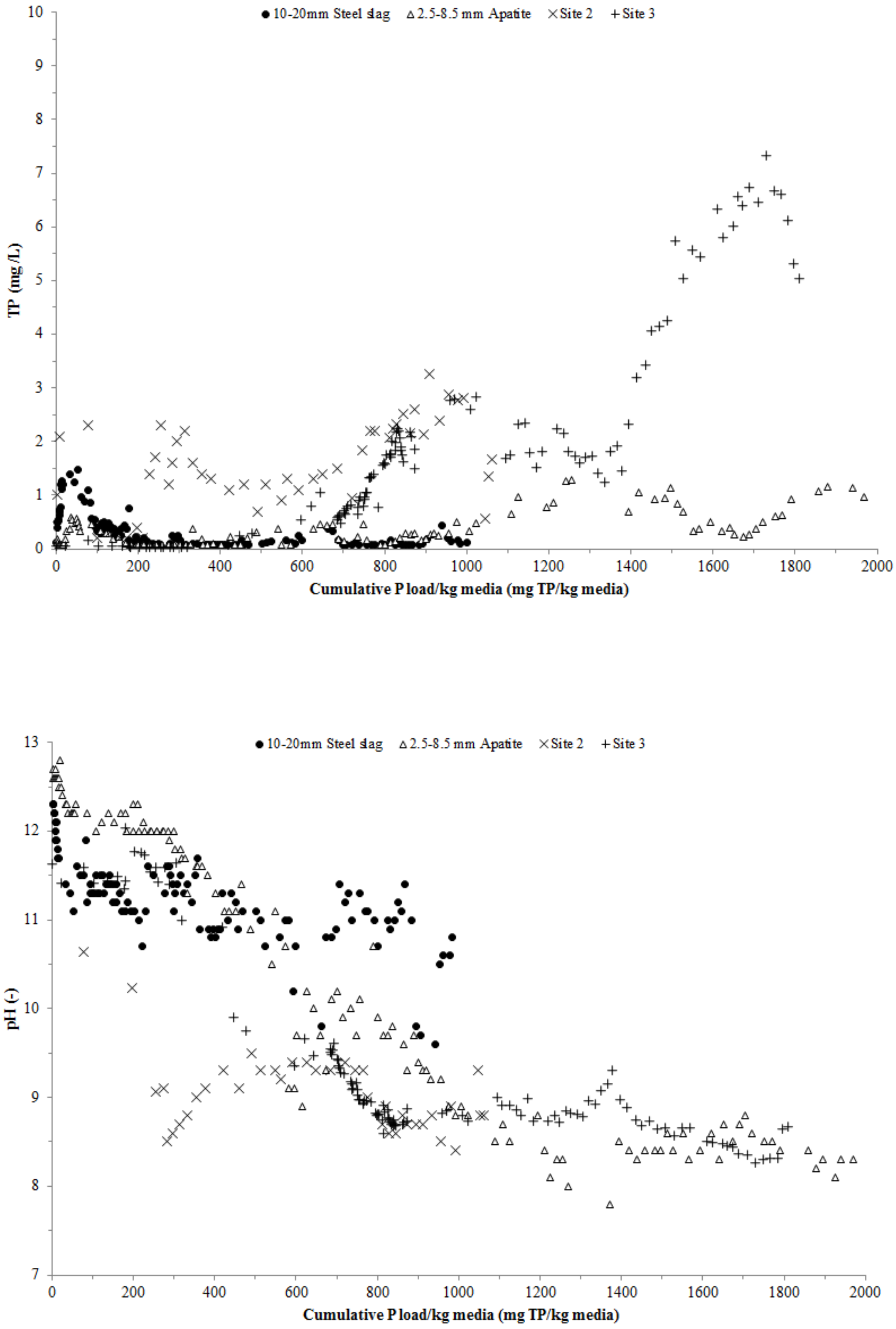

Figure 5-2 Effluent a) TP concentration and b) pH profiles of the three trials with BOF steel slag and apatite in the UK.

The previous research in the thesis highlighted potential issues with respect to vanadium leaching beyond the anticipated discharge target of 60 µg/L (Chapters 2, 3, 4). Vanadium was not measured for Site 2 but in the case of Site 3 a very different profile to Site 1 was observed (Figure 5-3). The effluent V concentration rose rapidly to maximum levels of 797.5 µg/L and 92.2 µg/L at loads of 70 mgTP/kg$_{media}$ and 22.1 mgTP/kg$_{media}$ for steel slag in Sites 1 and 3, respectively. However, in the case of Site 3, the vanadium concentration decreased to below 60 µg/L at a P load of 305 mgTP/kg$_{media}$ before reaching a stable level of c6.4 µg/L at a load of 418 mgTP/kg$_{media}$. In contrast, in Site 1, the vanadium concentration remained high with a large degree of fluctuation between 231-842 µg/L. Effluent V levels for apatite were considerably lower in Site 1, with no major increase from average inlet concentrations of 8.0 µg/L.

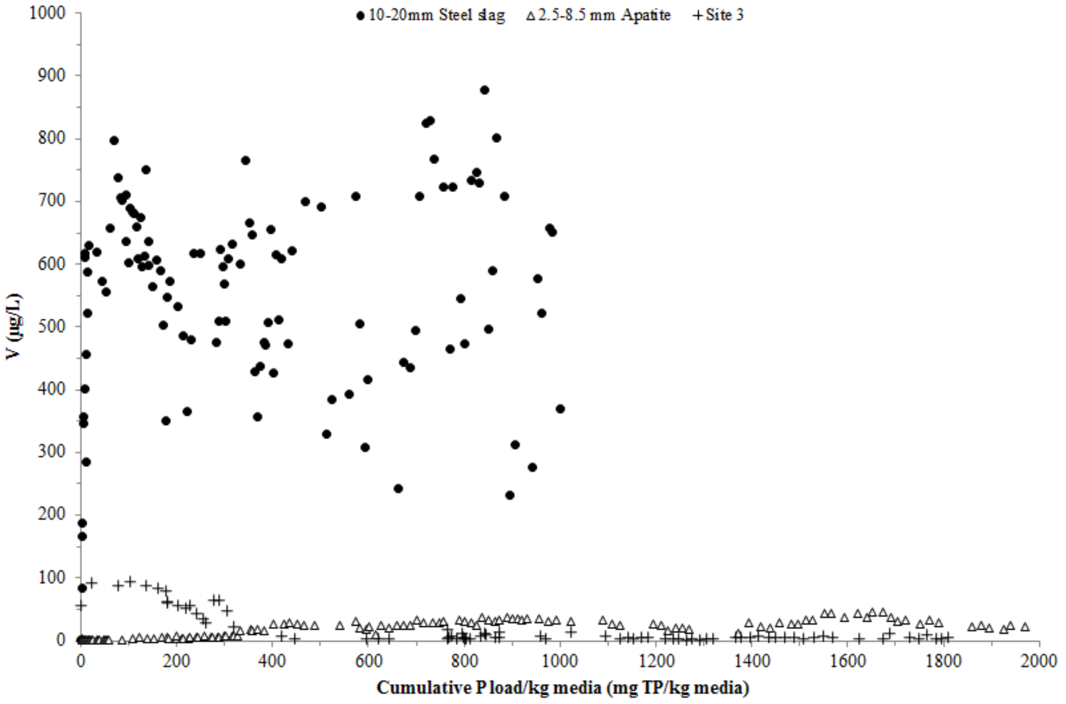

Figure 5-3 Effluent V concentration profile of two field trials with BOF steel slag and apatite in the UK.

Other parameters, such as suspended solids, copper and aluminium also showed considerable differences among the three trials (Table 5-3). In particular, the three parameters had higher effluent levels for BOF steel slag in Site 1 compared to Sites 2 and 3. The average effluent suspended solids concentration for the same sized BOF steel slag for Sites 1 and 3 were 18.8 mg/L and 6.4 mg/L, respectively. This could be linked to the slightly higher incoming solid concentration for Site 1. Similarly, the copper and aluminium effluent concentrations were higher in Site 1 than in Site 3, with average levels of 20.0 μg/L and 3.5 μg/L, and 133.5 μg/L and 19.3 μg/L for copper and aluminium, respectively. The potential discharge targets would be met in Site 3 but not in Site 1. This could be attributed both to slag heterogeneity, which would potentially release more Al, and to higher incoming concentrations, 619 μg/L and 8 μg/L for aluminium and 90 μg/L and 5 μg/L for copper, for Sites 1 and 3, respectively.

Table 5-3 Summary of effluent wastewater characteristics for the three sites against potential discharge targets, average values [minimum-maximum]. n= 180 (Site 1), n=48 (Site 2), n=118 (Site 3), (N/A: Not available).

Material (Site)	Suspended solids (mg/L)	Cu (μg/L)[28]	Al (μg/L) [50]
10-20mm SS (Site 1)	18.8 [1.9-64.0]	20.0 [4.0-37.0]	133.5 [14.1-411.2]
2.5-8.5mm APA (Site 1)	9.1 [1.9-60.5]	26.5 [3.0-62.0]	181.2 [5.5-3164.2]
14mm SS (Site 2)	6.4 [5.0-25-0]	N/A	<300
8-14mm SS (Site 3)	N/A	3.5 [0.9-10.5]	19.3 [2.1-94.2]

5.3.2 Effect of wastewater chemistry and HRT on performance

Comparison of the three sites demonstrates that use of reactive media in constructed wetlands has the ability to delivery effluent TP concentrations below 1 mg/L as seen with Sites 1 and 3. However, all three sites demonstrated very different behaviour in terms of pH, effluent TP profile and vanadium concentration. The sites used the same source of steel slag, had similar average alkalinities with differences in the influent P and suspended solids concentrations (Table 5-1). This indicates that the effectiveness of the media is based around a complex set of interactions between the dissolving components from the slag and the background water matrix beyond the simplified reaction scheme that is commonly reported. Importantly, the slag is a waste material with a corresponding variation in content (Barca et al., 2014) combined with wastewater that will have a variation in other trace species enabling a broad spectrum of precipitation reactions to occur. The impact is that pilot testing is likely to be required prior to implementing reactive media to ascertain the required HRT, longevity of the wetland and potential issues surrounding residual pH and vanadium concentration.

To further investigate the potential criteria for using reactive media, the current field study data has been compared to existing literature information to explore the role of HRT and alkalinity (Table 5-4). Analysis of the data indicates that removal is enhanced for wastewater with lower alkalinities and when the wetlands are operated at longer HRTs. To illustrate, for BOF steel slag operated at a HRT of 48 hours, Walter (2012) reported 85.6% of P removal treating a wastewater with an alkalinity of 132.8 mg$CaCO_3$/L. The removal efficiency decreased to 68% once the HRT was reduced to 24 hours which was insufficient to ensure the effluent TP remained below 1 mg/L TP. However, in a separate trial, even 48 hours was insufficient to meet such a standard when treating a wastewater with an alkalinity of 282 mg$CaCO_3$/L. In comparison when treating low alkalinity wastewater (84 mg$CaCO_3$/L) a HRT of 15 hours has been reported to be sufficient to meet a sub 1 mg/L standard with a removal efficiency of 84.3 % (Letshwenyo, 2014). This is in line with a reported study with synthetic batch experiments, where an increase in alkalinity from 100 mg$CaCO_3$/L to 300 mg $CaCO_3$/L halved the P removal velocity (Jang and Kang, 2002). The lower P removal for higher alkalinity values was attributed to the co-precipitation of $CaCO_3$, which would compete with $CaPO_4$ precipitation. Interestingly, in the current field trials, greater removal efficiencies were observed than previously reported although the alkalinities and the HRTs are in a similar range. In these cases, the improved removal coincides with the prolonged period of elevated pH indicating the dissolution of calcium oxides into the water was continuing. This is further supported by Site 3, where the removal efficiency decreased once the pH was reduced and a net release of calcium ions was observed across the wetland. Consequently, it is important to factor in variations in the potential dissolution profile of the media when considering the correct HRT for a given alkalinity.

Overall the analysis suggests that the likely required HRT for steel slag is around 24 hours and for apatite based media is around 12 hours. Below these levels, the performance of both media deteriorates such that a sub 1 mg/L effluent TP concentration would be unlikely. However, site specific testing appears to be required to ensure appropriate design parameters are used. This is particularly relevant with respect to wetland life and hence refurbishment frequency. To illustrate, in the case of Site 3, the effluent TP profile started to deteriorate after a P load of around 600 mgTP/kg$_{media}$; whereas for Site 1, the effluent TP remained very low and stable even after a P load of 1,000 mgTP/kg$_{media.}$ Reported Phosphorus Sorption Capacity (PSC) from previous field trials have been exceeded in the current work and the constructed wetlands have not reach a working limit and have been running for 850 days. Consequently, it is currently not possible to estimate the likely refurbishment frequency required. In the case of apatite based media commercial design are currently estimating a 10 year refurbishment frequency with the performance fluctuating seasonally with the same frequency of 10 years for steel slag (Germain-Cripps, 2017). Previous estimates of refurbishment frequency for steel slag have suggested around five years which appears more consistent with the current data (Letshwenyo, 2014).

Table 5-4 Comparison of HRT and alkalinity on P removal with reactive media treating real wastewater (N/A: not available).

Scale	Material	Alkalinity ($mgCaCO_3/L$)	HRT (h)	P removal (%)	Reference
Column	BOF SS	132.8	2	47.3	Walter (2012)
Column	BOF SS	132.8	6	62.5	Walter (2012)
Field	BOF SS	132.8	16	61.0	Walter (2012)
Column	BOF SS	132.8	24	68.4	Walter (2012)
Column	BOF SS	132.8	48	86.6	Walter (2012)

Column	BOF SS	94	15	84.3	Letshwenyo (2014)
Column	BOF SS	182	15	45.2	Letshwenyo (2014)
Column	BOF SS	N/A	15	75.3	Letshwenyo (2014)
Field	BOF SS	282	48	58.8	Barca et al. (2013)
Field	EAF SS	282	48	44.7	Barca et al. (2013)
Field	BOF SS	139	24	75.1	Vale (2017)
Field	BOF SS, 2-6 mm	144.7	24	96.3	This study
Field	BOF SS, 4-10 mm	144.7	24	95.4	This study
Field	BOF SS, 10-20 mm	144.7	24	91.8	This study
Field	Apatite	144.7	12	91.6	This study
Column	BOF SS, 2-6 mm	132.8	6	27.1	This study
Column	BOF SS, 4-10 mm	132.8	6	36.1	This study
Column	BOF SS, 10-20 mm	132.8	6	30.4	This study
Column	Apatite	132.8	6	45.0	This study

5.3.3 Comparison of Real versus Synthetic wastewater

Comparison of the relative effectiveness of the two media studied herein was wastewater type specific with the apatite performing better than the steel slag during the column trials with synthetic wastewater, but this observation was not replicated in the field trials where the steel slag performed slightly better (Figure 5-4). To illustrate, steel slag showed a range of effluent TP concentrations between 0.1 mg/L and 3.6 mg/L for columns with synthetic wastewater compared to effluent concentrations of real wastewater constructed wetland of around 0.1 mg/L. In contrast, concentrations in the range of 0.08 mg/L-1.20 mg/L were observed for apatite in the constructed wetland treating real wastewater as opposed to 0.08 mg/L during the synthetic column trials. The overall impact is a large discrepancy in the estimated PSC of the media. To illustrate, the PSC of the apatite decreased from 6.90 gTP/kg_{media} during the synthetic trials to 1.81 gTP/kg_{media} during the field trials. Similarly for steel slag, the PSC reduced from 5.34 gTP/kg_{media} to 0.76 gTP/kg_{media} respectively.

The differences extend to the expected pH profiles, the time required to reduce pH below 9 and the potential levels of released metals, especially vanadium. For instance, for steel slag, effluent concentrations ranged between 1.2-426.0 μg/L with an average of 21.2 μg/L during the synthetic trials compared to 1.9-1,003.5 μg/L with an average of 327.7 μg/L during the field trial. The average alkalinity of the two waters were 145 and 186 $mgCaCO_3/L$ for the field and the synthetic trials, respectively. However, such difference are not expected to equate to the difference in pH profile observed with for instance the steel slag not reducing to below 9 in the field trials but reached a pH of 9 after a P load of 25.2 $mgTP/kg_{media}$ in the synthetic columns. Consequently, it is suggested that the use of data generated by treating synthetic wastewater should be used with caution when applying it to real scale design and operation. The differences reflect the impact of the other constituents on the overall process including dissolved organics, solids, and other ions. The specific impact of each of these remains unclear emphasising the importance of testing with real wastewater.

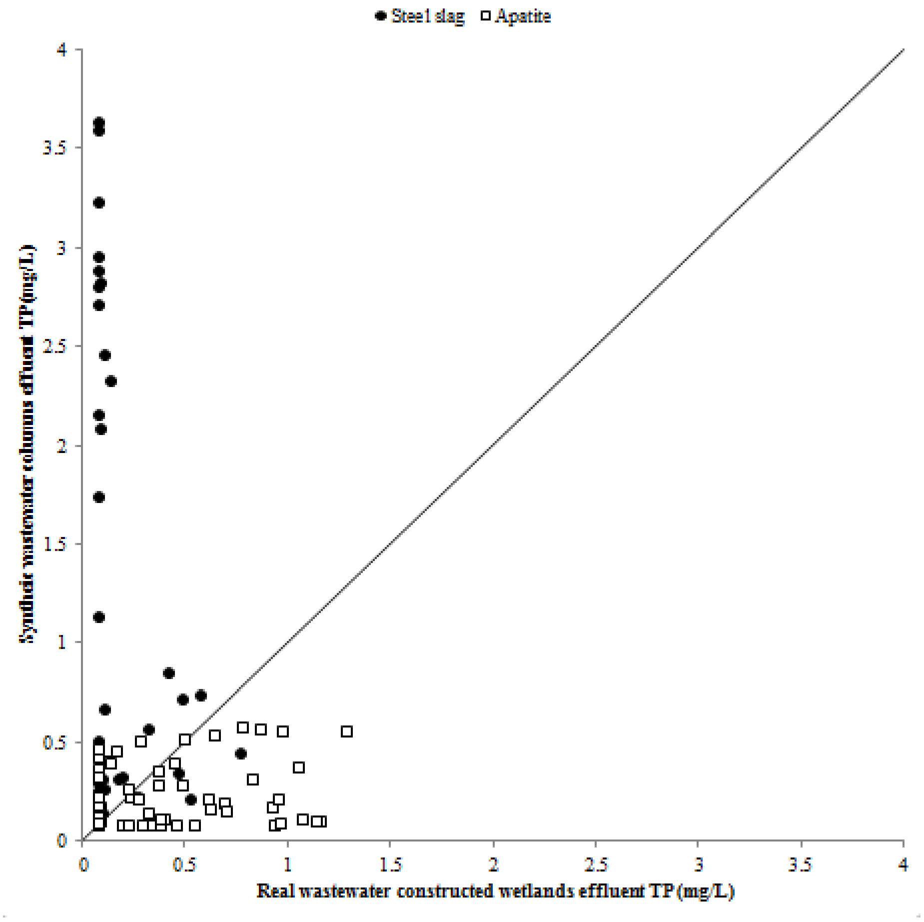

Figure 5-4 Comparison of effluent TP concentrations for BOF steel slag and apatite in column experiments with synthetic wastewater and field-scale trials with real wastewater.

5.3.4 Economic assessment

The Capital expenditure (CAPEX) estimates determined that the conventional option of chemical dosing with tertiary filtration posed the highest CAPEX costs at £508,473, compared to the lowest option associated with BOF steel slag at £78,984 (Figure 5-5). The two options with the apatite constructed wetland showed significantly different CAPEX costs, £270,339 and £500,132 for the gravel wetland and the pile cloth media filtration, respectively. The major contributors to the CAPEX for Scenario A were the dosing systems with the associated chemical storage and safety shower which account for £137,050, and the filtration units which alone accounted for 58% of the total CAPEX. This also translated into the difference between scenarios C and D where a pile cloth media filter or a gravel based wetland was used for suspended solids management. Comparison of the two different media constructed wetlands revealed a significantly different CAPEX, mainly due to the difference in the base media cost, apatite price being ten time higher than the price for steel slag.

The option with the lowest operational expenditure (OPEX) costs was scenario B at £641,774. This compares to £867,612 for scenario C, gravel and apatite wetlands, followed by scenarios A and D at £844,546 and £755,503, respectively. The lower OPEX of Scenario B reflects the low maintenance requirements associated with constructed wetlands apart from a refurbishment of the wetland every 5 years to maintain hydraulic conductivity or P sorption capacity, in the case of constructed wetlands with reactive media (Dotro et al., 2017).

The Whole Life Cost (WLC) estimate determined that the conventional option in Scenario A (chemical dosing and tertiary filtration) gave the highest WLC, followed by Scenario D, Scenario C and Scenario B with WLC of £1.4M, £1.3M, £1.2M and £0.7M, respectively (Figure 5-5). These equate to treatment costs of £0.91/m^3, £0.48/m^3, £0.76/m^3 and £0.84/m^3, respectively. The fact that the non-conventional alternatives presented in the current thesis allowed for lower WLC indicates the potential for full-scale application, which is what commonly prevents innovative technologies for being implemented at full-scale at water utilities, with other factors such as slow implementation strategies and reluctance to such innovative technologies (Coward et al., 2018).

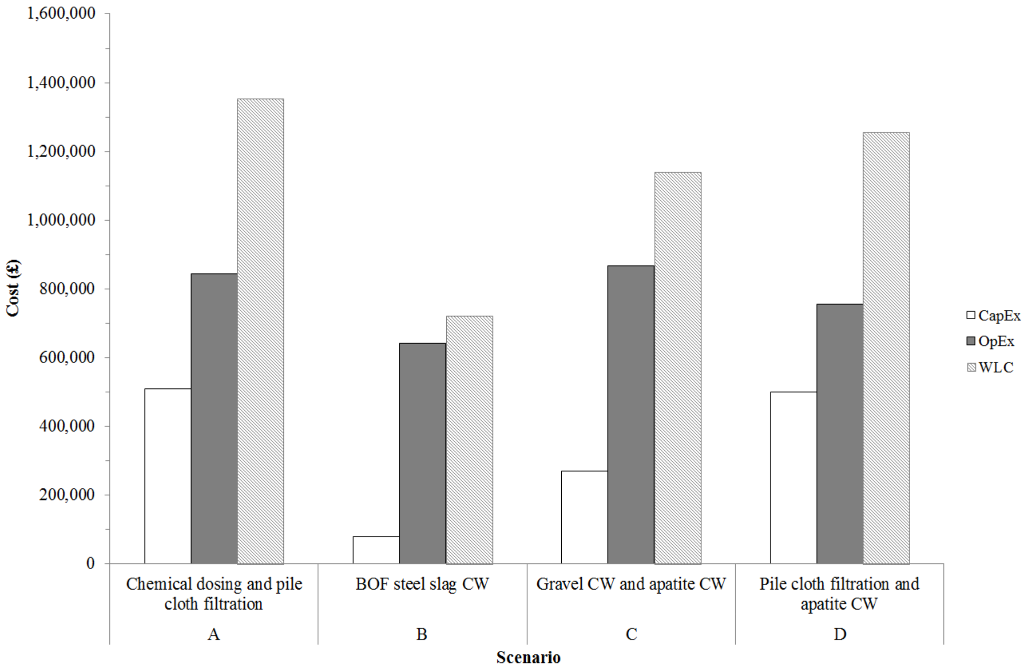

Figure 5-5 Summary of the Capex, Opex and WLC estimated for the four scenarios contemplated.

Scenarios A, C and D are subject to changes in future coagulant and apatite costs, respectively, and so, the WLC analysis may vary according to these and could be decisive in decision making for the lowest WLC option. In the case of coagulant cost (ferric sulphate), it has been found to be linked to the cost of sulphuric acid (Henderson et al., 2009). As such, sulphuric acid cost has decreased in recent years. A decrease of 35% in cost from 2014 to 2017 has been recently reported (Argus, 2016). However, ferric sulphate prices can be noticeably unpredictable and are expected to increase in the future.

The cost of the apatite based media studied in the current thesis is strongly linked to the cost of phosphate rock, as it is its main constituent. The cost of phosphate rock fluctuated considerably in the past, showing periods where it stayed fairly constant (2001-2007) to periods when the price quadrupled (2007-2009) to then decrease to former cost levels (Van Kauwenbergh, 2010). However, phosphate rock is a finite reserve, and has been reported that its production is meant to reach a peak (Cordell et al., 2009). After this, the remaining phosphate rock resources will become depleted and more expensive to extract, which indicates that that future cost of the phosphate rock may increase, and so may the cost for the apatite based material studied herein.

The effect of coagulant and apatite costs on WLC of Scenarios A, C and D indicated that WLC for Scenarios C and D are considerably more affected by the apatite cost than Scenario A by coagulant cost (Figure 5-6). To illustrate, a 10% change in current coagulant cost increased WLC for Scenario A from £1,370,643 to £1,372,161, which represented an increase of 0.11%. For the same change in current apatite based material price, Scenario C increased from £1,138,021 to £1,202,134 and from £1,255,704 to £1,319,817 for Scenario D, representing a 5.3% and 4.9% increase respectively. Any increase of apatite base material beyond 36% of the current price would make the WLC for Scenario C (gravel and apatite constructed wetlands) higher than that for Scenario A (chemical dosing and pile cloth media filtration). Similarly, any increase in apatite base material price beyond 17% of the current price would make Scenario D (pile cloth media filtration and apatite constructed wetland) less favorable than Scenario A.

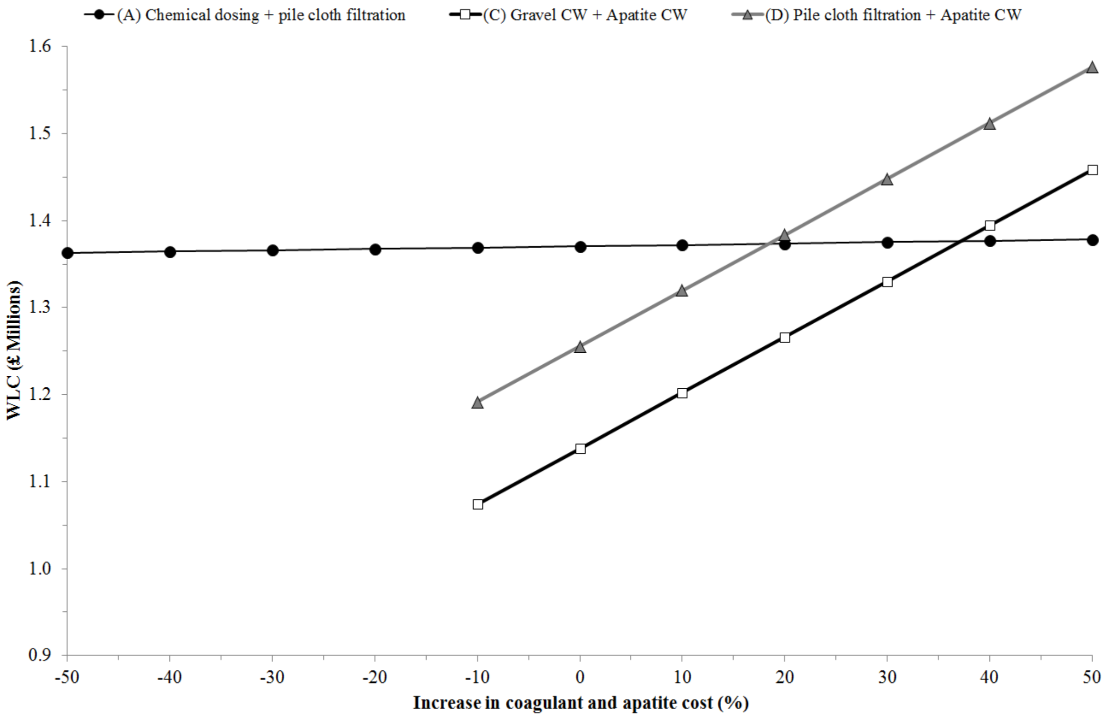

Figure 5-6 Effect of -50% to +50% change in the current price of ferric sulphate and apatite based media on WLC for Scenarios A, C and D.

Scenarios B, C and D are subject to changes in media refurbishment frequency. Wetland refurbishment frequencies of 5 and 10 years have been estimated for BOF steel slag and apatite wetlands, respectively, based on findings in Chapter 4. However, due to specific reactive media and/or wastewater characteristics, the constructed wetlands could be exhausted or become clogged quicker, and therefore the wetland refurbishment frequency may need to be altered.

Scenarios C and D including apatite wetlands, with gravel wetlands or pile cloth media filtration respectively, are considerably more affected by media refurbishment frequency than Scenario B, with BOF steel slag wetlands (Figure 5-7). A reduction in frequency by 2 years (from 5 to 3 years) for BOF steel slag would increase the WLC by 29.6%. For the same frequency reduction for apatite (from 10 to 8 years), the WLC for Scenarios C and D would increase 11.5% and 10.5%, respectively. A reduction of apatite refurbishment frequency to 8 years or less would make the WLC of Scenario D higher than that of Scenario A, £1,403,035 compared to £1,353,019, which would make Scenario D the least favorable option among the four options. In this case, Scenario C with a WLC of £1,285,351 would still remain a more economically viable option compared to Scenario A. BOF steel slag refurbishment frequency would need to be reduced to 2 years or less for the WLC of this option to surpass that of Scenario A.

Therefore, the minimum apatite media refurbishment frequency for Scenarios C and D to remain economically viable options against Scenario A would be 9 years, whereas it would be 3 years for BOF steel slag refurbishment frequency for Scenario B.

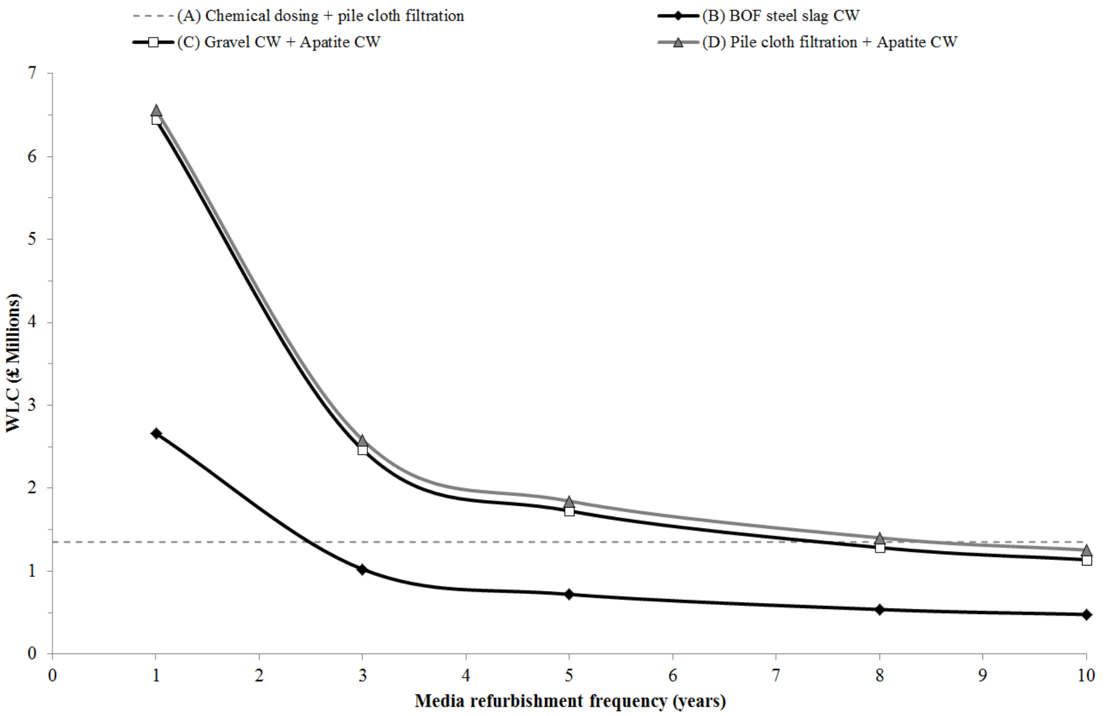

Figure 5-7 Effect of media refurbishment frequency on WLC for Scenarios B, C and D.

There are several aspects that need to be taken into account for potential future application. Both media generated periods of elevated effluent pH, as already discussed in Chapter 4. With those pH values, the effluent cannot be discharged into the environment, and would therefore need pH correction, which would increase the OPEX cost of Scenario B and therefore its WLC. pH correction alternatives would include direct acid dosing (Germain-Cripps, 2017) or peat filters (Liira et al., 2009; Vohla et al., 2011).

Vanadium and chromium were leached above the potential discharge target in the case of BOF steel slag and apatite, respectively (Chapter 4). Options to reduce this would include conditioning the surface of the media with $CaCO_3$ in a controlled environment to limit metal leaching (LeCorre, 2017). This would again increase OPEX costs and would therefore also increase WLC of Scenarios B, C and D.

The apatite based media herein presents a high cost, and no alternative materials can be found in the market. However, a potential option would be to source this material from the fertilizer industry directly, as the source material they use is pure apatite, which has already been linked to high P removal (Chapter 3). The fertilizer industry handles a broad range of apatite material granulometry and a certain fraction could be targeted if discussed with them. Among the two options presented with apatite for the economic assessment, Scenario C and Scenario D, the former presented a slightly lower WLC than the latter. However, it is acknowledged that many small STW do not have the available land to implement Scenario C, with two constructed wetlands. To illustrate, two pile cloth filters would have a footprint of around 28 m^2, compared to a gravel constructed wetland with a footprint of 300 m^2, which would serve the same objective. Therefore, there are certain situations where Scenario C would not be taken into account as an option with the apatite based material, but only Scenario D.

5.4 Conclusions

- BOF slag has been demonstrated to be effective in achieving a sub 1 mg/L total phosphorus discharge level during field-scale trials when the HRT was 24 hours or above, whereas apatite was shown to be effective at one site at the lower HRT of 12 hours.
- The effluent P, pH and V profiles were considerably different among the three UK trials, which is attributed to the complex set of interactions between the dissolving components from the media and the background water chemistry. Accordingly, pilot testing remains required prior to full-scale implementation to properly ascertain operational HRT, the longevity of the wetland and potential operational issues regarding pH and vanadium.
- Both BOF steel slag and apatite present economically viable cases as an alternative to traditional chemical dosing with pile cloth filtration. Media replacement frequency is the key criteria in defining the overall economic suitability with minimum economic replacement frequencies of 3 years for BOF steel slag and 9 years for apatite media.
- The future application of BOF steel slag constructed wetlands would need to consider options to manage pH correction and vanadium leaching, while

chromium leaching needs to be considered in the case of apatite based constructed wetlands.

5.5 Acknowledgments

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6 Conclusions and Future Work

6.1 Conclusions

The findings of this research demonstrate that Basic Oxygen Furnace (BOF) steel slag and apatite based media present a viable alternative for phosphorus (P) removal from domestic wastewater. The specific conclusions linked to the initial objectives are:

Objective 1: To assess the impact of design and operating conditions on the suitability of column experiments to evaluate BOF steel slag and apatite as reactive materials for P removal.

- Apatite was able to reduce the total P (TP) concentration to a lower level than BOF steel slag but both were capable of meeting a 1 mg/L standard effluent consent, and the material properties of apatite are responsible for the improved performance (Chapter 3).
- Reducing the size of the BOF steel slag improved P removal but raised the pH more reflecting the proposed mechanism of generating more CaO dissolution sites and maximising the reaction through the reduced gap spaces between the media particles (Chapter 2).
- Trials using synthetic wastewater revealed a consistent profile containing a *stabilisation* and a *steady-state* phase for both materials (Chapter 3).
- Higher HRTs produced higher P removals and higher pH values on the *stabilisation* phase for both materials, although apatite showed higher P removal than steel slag even for short HRTs (Chapter 3).
- Higher HRTs did not significantly affect pH during the *steady-state* phase but apatite showed higher P removal than steel slag for shorter HRTs (Chapter 3).
- Comparison to other BOF steel slag trials revealed significant differences in profiles in both P and pH indicating that difference in the components found within both the media and the wastewater necessitate site specific testing (Chapter 2).

- Comparison of data from synthetic to real wastewater revealed significant differences in relation to the profile of effluent P and the pH as a function of media size indicating that translation of synthetic data needs to be considered carefully (Chapter 3).

Objective 2: To evaluate the performance of BOF steel slag and apatite in full-scale constructed wetlands as a tertiary treatment for domestic wastewater, and to identify operational challenges that would prevent this technology from being implemented over conventional solutions.

- Both media were effective in removing P to enable compliance with a 1 mg/L TP target (Chapter 4).
- Two phases of operation were observed for both media: *stabilisation* phase, where non-P-containing precipitate formation is favoured, and *steady-steady* phase, were P removal is enhanced (Chapter 4).
- Only the effluent form the apatite wetland stabilised to a pH value below 9, whereas the slag effluents remained above 10. For apatite, it reflects a change in P removal mechanism towards adsorption and growth, while for steel slag, it indicates sustained P removal by CaO dissolution (Chapter 4).
- Solids management is needed for constructed wetlands with smaller reactive media, either by the installation of a prior pile cloth media filter, or by flushing or refurbishing the media more often (Chapter 4).
- Both media showed removal of copper, manganese and titanium but release of barium and iron. Three metals showed specific media related behaviour, chromium and uranium for apatite and vanadium for steel slag (Chapter 4)
- High removal was observed with both materials for the priority substances nonlyphenol, benzo(a)pyrene, cypermethrin, oestrone and 17B-oestradiol (Chapter 4).

Objective 3: To compare the full-scale BOF steel slag constructed wetland with another two case studies from two UK water companies, and to identify main design and/or operational parameters as to explain differences in performance results.

- BOF steel slag was effective in removing P to levels of sub 1 mgTP/L in two of the three UK field trials. Operation at a HRT of 24 hours or greater was associated with the sites that met the sub 1 mg/L target (Chapter 5).
- The effluent P, pH and V profiles were considerably different among the three UK trials, which is attributed to the complex set of interaction between the dissolving components from the media and the background water chemistry (Chapter 5).
- Pilot testing would be required prior to full-scale implementation to ascertain operational HRT, the longevity of the constructed wetland and potential operational issues regarding pH and vanadium (Chapter 5).

Objective 4: To identify the major items contributing to the overall economic viability of the technology, and compare this to a conventional approach to establish the potential for a business case for its implementation.

- Apatite based constructed wetlands need to include a prior solids removal step, either with a gravel constructed wetland or a pile cloth media filter (Chapter 5).
- The major contributor to the WLC of constructed wetlands with both materials is OPEX costs, linked to the cost of media refurbishment (Chapter 5).
- Present day application of both BOF steel slag and apatite constructed wetlands for achieving sub 1mgTP/L concentrations would be considered economically viable options compared to the conventional solution involving chemical dosing and tertiary filtration with a pile cloth media filter (Chapter 5).
- Apatite refurbishment frequency could be reduced to nine years for apatite based constructed wetlands to remain economically viable compared to chemical dosing followed by tertiary filtration, whereas media refurbishment could be further reduced to three years in the case of BOF steel slag (Chapter 5).

- The future application of BOF steel slag constructed wetlands would need to consider options to manage pH correction and vanadium leaching, while chromium leaching should be managed in the case of apatite based constructed wetlands (Chapter 5).

6.2 Future Work

Several areas for research have been identified in the development of this thesis, all of which are listed below:

- Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) techniques could be employed on used BOF steel slag and apatite to confirm the hypothesised P removal mechanisms and precipitated compounds. These and similar techniques have previously been employed to identify types of precipitates on used steel slag (Barca et al., 2014).
- The X-ray diffraction (XRD) technique could be used to determine the exact binders and quantities employed in the different apatite formulations and confirm the exact contribution to observed performance.
- Continue the operation of the field-scale trial with the three BOF steel slag and the apatite based constructed wetlands, in order to exhaust the media and ascertain the P sorption capacity (PSC) of those and therefore confirm the wetland lifetime.
- Bacterial identification of the BOF steel slag and the apatite in the constructed wetland trial would help understand how different bacteria contribute to observed wetland performance, specifically ammonia, BOD and priority substance removal. The best technique to be employed for this purpose is ribosomal RNA sequencing (Metcalf and Eddy, 2004).
- This thesis has highlighted the need to test both BOF steel slag and apatite in pilot trials to stablish appropriate design and operating conditions of wetlands. However, there is no standard method currently in place for carrying out these pilot tests. Standardisation of the pilot testing would be beneficial to test not only these two materials but any other reactive media in any sewage treatment works (STW).

- Investigate ways of regenerating exhausted BOF steel slag and apatite as a means of improving affordability, especially in the case of apatite based material. Previous research has found potential for BOF steel slag regeneration with 0.1M NaOH (Letshwenyo, 2014) or acids such as HCl (Pratt et al., 2011). Other solutions should be researched to maximise regeneration efficiency and prolong the lifetime of the wetland and therefore reduce WLC costs.
- Investigate availability of P precipitates for plant uptake, as a means of reusing the exhausted media as a P containing fertilizer, and therefore increase the sustainability aspect of the technology. Previous research has found potential for blast furnace steel slag to promote barley growth (Hylander et al., 2006). No previous work has reported results for apatite based material, although the potential is thought to be higher, as the same source (phosphate rock) is used for fertilizer and the apatite base material production.
- Ways of reducing the price of the apatite based material should be investigated. At present, a commercial product is employed, as the manufacturer mixes phosphate rock with different binders to pelletize it. Employing non-pelletised apatite directly from the fertilizer company while still maintaining an appropriate particle size to favour wetland hydraulics would considerably reduce OPEX costs and therefore make this technology even more economically favourable.
- Methods of limiting vanadium leaching from BOF steel slag and chromium leaching from apatite should be researched. The potential for reducing V release from steel slag has already been reported by precipitation of $CaCO_3$ under controlled environments (LeCorre, 2017). This would increase OPEX costs for both technologies, but a cost-benefit analysis of the solution would ascertain its suitability.

6.3 References

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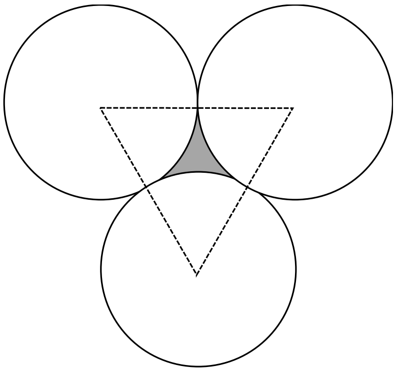
Appendix A Understanding the impact of media size on the effectiveness of basic oxygen furnace steel slag as a reactive media for phosphorus removal

The area between media particles is calculated based on assuming three similar circles of diameter (d):



The area is calculated by subtracting the area of the three segments from the triangle which is positioned at the centre point of each circle. The angle of the triangle has 60°, so the three segments equate to 180° and hence half the area of a circle:

$$A_{segments} = \frac{1}{2}\frac{d^2}{4\pi}$$

$$A_{triangle} = \frac{\sqrt{3}}{4}d^2$$

Therefore, the area of the gap is:

$$A_{triangle} = \frac{\sqrt{3}}{4}d^2 - \left(\frac{1}{2}\frac{\pi d^2}{4}\right)$$

Table A-1 Calculation of relative gap compared to the 5.09 mm diameter media.

Diameter (mm)	Area of gap (mm^2)	Relative gap compared to the 5.09 mm diameter media
0.75	0.0226	0.02
1.75	0.1234	0.12
5.09	1.0441	1.00
7.60	2.3277	2.23
10.04	4.0623	3.89
9.31	3.4931	3.34

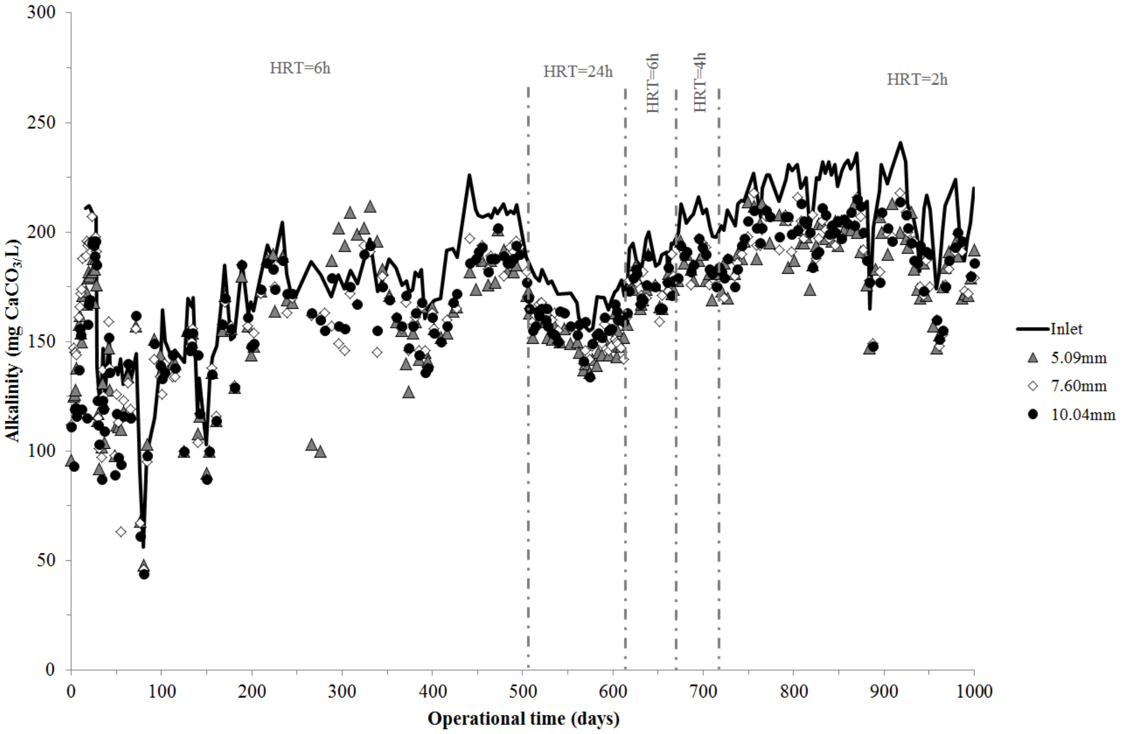


Figure A-1 Effluent alkalinity different fractions of steel slag during synthetic wastewater column trials.

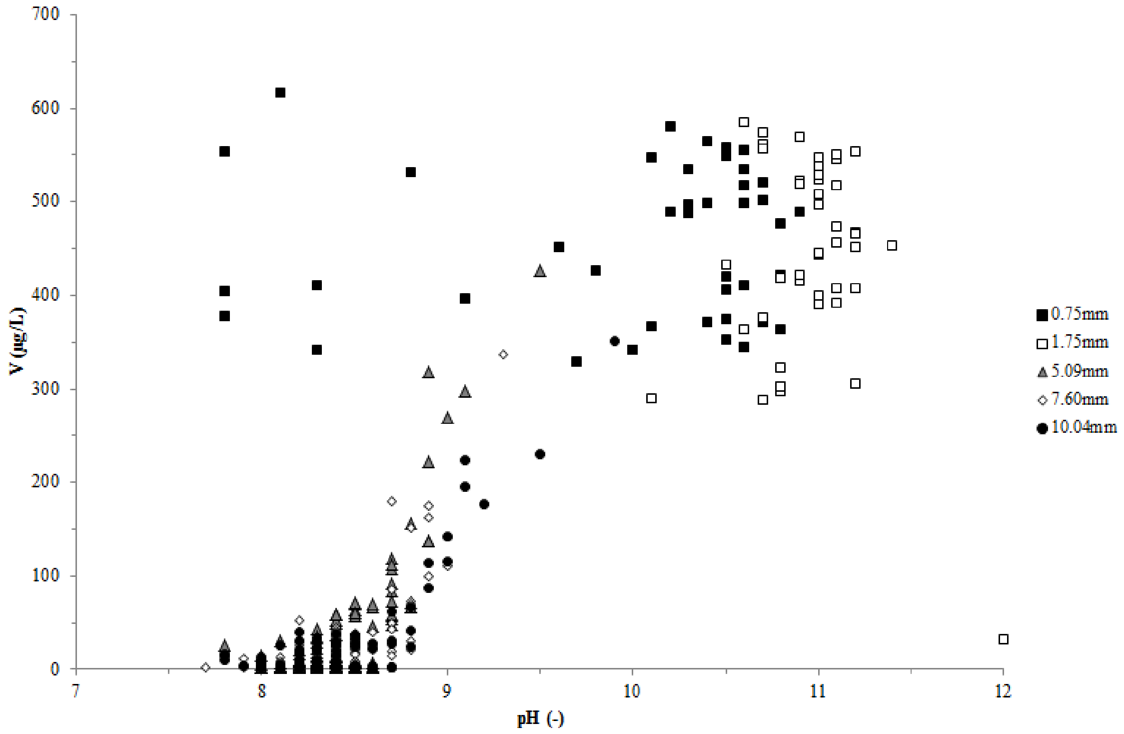


Figure A-2 Effluent V concentration and pH for different fractions of steel slag during synthetic wastewater column trials.

Appendix B Comparison of basic oxygen furnace steel slag and an apatite based media for phosphorus removal treating synthetic and real wastewater

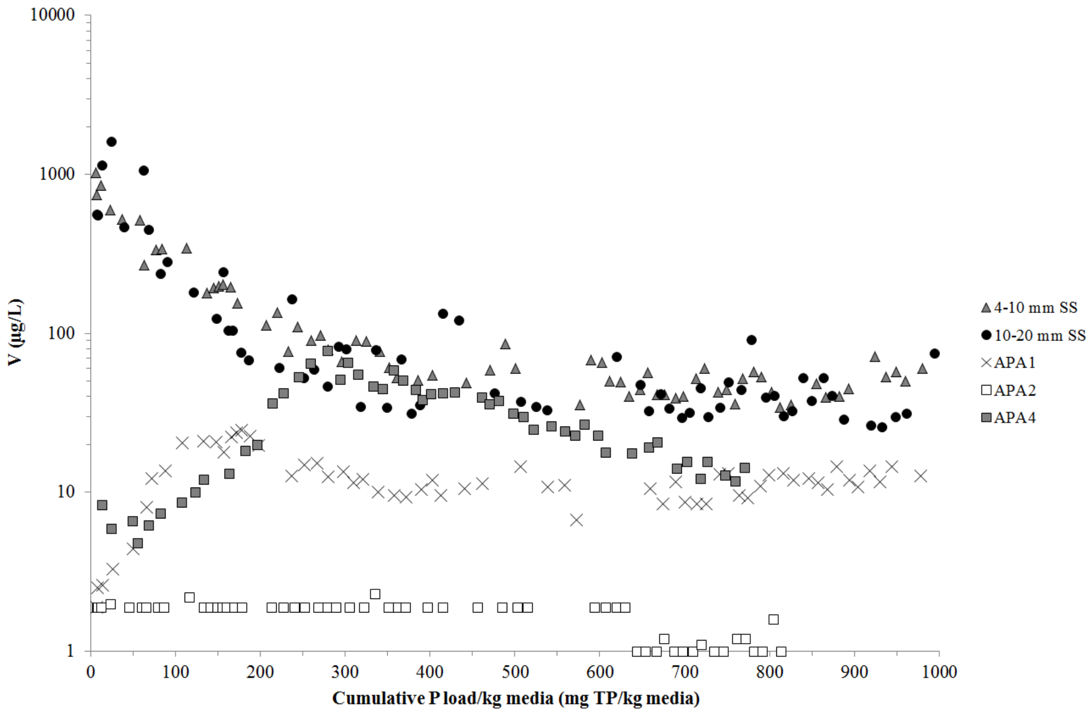


Figure B-1 Effluent vanadium concentration for steel slag and apatite treating real wastewater at a HRT of 6 hours.

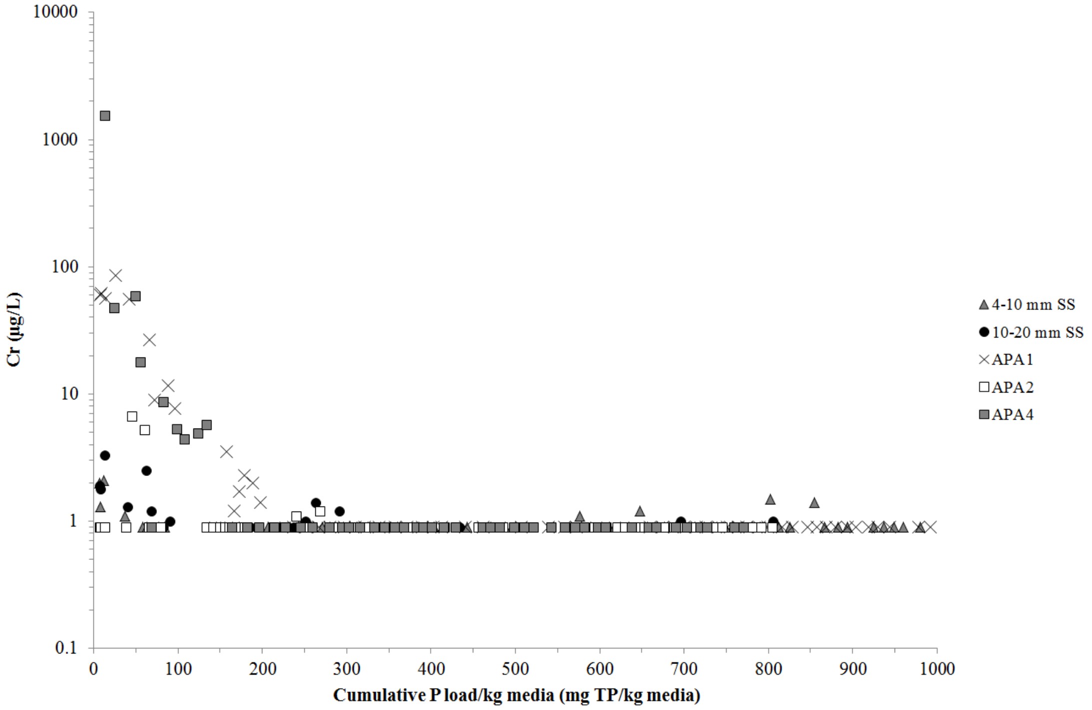


Figure B-2 Effluent chromium concentration for BOF steel slag and apatite treating real wastewater at a HRT of 6 hours.

Appendix C Comparing the reactive media: Basic Oxygen Furnace steel slag and apatite for phosphorus, metal and priority chemical removal using field-scale trials

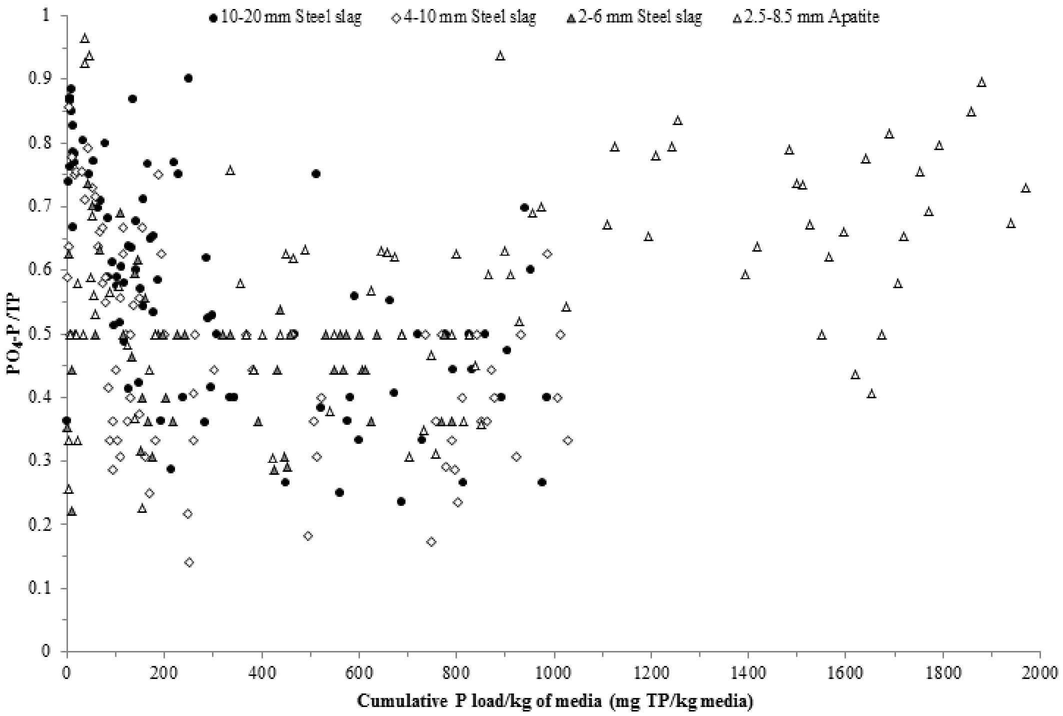


Figure C-1 Effluent PO_4-P/TP ratio for the three steel slag fractions and apatite in the field trial.

Appendix D Implications of the work: overall perspective of the suitability of constructed wetlands with reactive media for wastewater treatment in the UK

Table D-1 Design parameters for Scenario A: chemical dosing and pile cloth media filtration.

Design parameter	**Value (unit)**	**Note**	**Reference**
CAPEX			
Dosing equipment	Commercially confidential information	Based on design load.	Germain-Cripps, 2017
Washwater system	Commercially confidential information	Based on design flow.	Germain-Cripps, 2017
P monitoring unit	Commercially confidential information	Two units needed, commissioning and installation included.	Butterfield, 2014
Filtration unit	Commercially confidential information	Two units needed, commissioning and installation included.	Butterfield, 2014
Pile cloth filter	Commercially confidential information	Two units needed. Based on design loading rate of 30 m/h. Commissioning and installation included.	Germain-Cripps, 2017
Cloth unit	Commercially	To be changed every 5	Germain-Cripps, 2017

	confidential information	years	
Electrical distribution	Commercially confidential information		Germain-Cripps, 2017
OPEX			
Average daily flow	1.3*PE*D+ I	D=150 L/person·day I=Infiltration=0.4*PE*D	Germain-Cripps, 2017
Coagulant dose	Commercially confidential information		Germain-Cripps, 2017
Coagulant Fe content	Commercially confidential information		Ellis, 2017
Coagulant density	Commercially confidential information		Ellis, 2017
Coagulant price	Commercially confidential information		Ellis, 2017
Sludge production	Commercially confidential information		Perrault, 2017
Sludge density	1 kg/L		Perrault, 2017
Sludge tanker off-site	Commercially confidential information		Perrault, 2017

P monitoring unit maintenance	Commercially confidential information	2 service contracts needed.	Butterfield, 2014
Filtration unit maintenance	Commercially confidential information	2 service contracts needed.	Butterfield, 2014
Extra energy used	Commercially confidential information	Based on estimated consumption.	Germain-Cripps, 2017
Extra general site O&M	Commercially confidential information	4 extra hours per week needed.	Germain-Cripps, 2017

Table D-2 Design parameters for Scenario B: BOF steel slag constructed wetland.

Design parameter	**Value and unit**	**Note**	**Reference**
CAPEX			
Wetland construction	Commercially confidential information	Two wetlands, design based on design flow, expected consent, and PSC of 2 gTP/kg_{media}	Germain-Cripps, 2017
BOF steel slag	Commercially confidential information		Thomas, 2015
OPEX			

Wetland maintenance	Commercially confidential information	Based on quote provided by supplier.	Murphy, 2017
Wetland refurbishment	Commercially confidential information	Two wetlands, one refurbishment every 5 years.	Germain-Cripps, 2017
Extra general site O&M	Commercially confidential information	1 extra hour per week needed.	Germain-Cripps, 2017

Table D-3 Design parameters for Scenario C: gravel constructed wetland and apatite constructed wetland.

Design parameter	**Value and unit**	**Note**	**Reference**
CAPEX			
Gravel wetland construction	Commercially confidential information	Two wetlands of 150 m^2 and 0.6 m (H) each. Design based on design flow and solids loading, calculated by supplier.	Germain-Cripps, 2017
Apatite wetland construction	Commercially confidential information	Two wetlands, design based on design flow, expected consent, and PSC of 3 gTP/kg_{media}, calculated by supplier.	Germain-Cripps, 2017
OPEX			
Wetland maintenance	Commercially confidential information	Based on quote provided by supplier.	Murphy 2017
Gravel wetland refurbishment	Commercially confidential information	Two wetlands, one refurbishment to be done every 20 years, estimated by supplier.	Germain-Cripps, 2017
Apatite wetland refurbishment	Commercially confidential information	Two wetlands, one refurbishment every 10 years, estimated by supplier.	Germain-Cripps, 2017

Extra general site O&M	Commercially confidential information	1 extra hour per week needed	Germain-Cripps, 2017

Table D-4 Design parameters for Scenario D: pile cloth media filtration and apatite constructed wetland.

Design parameter	**Value and unit**	**Note**	**Reference**
CAPEX			
Pile cloth filter	Commercially confidential information	Two units needed. Based on design loading rate of 30 m/h. Commissioning and installation included.	Germain-Cripps, 2017
Cloth unit	Commercially confidential information	Two cloths needed, to be changed every 5 years.	Germain-Cripps, 2017
Apatite wetland construction	Commercially confidential information	Two wetlands, design based on design flow, expected consent, and PSC of 3 gTP/kg$_{media}$, calculated by supplier.	Germain-Cripps, 2017
OPEX			
Wetland maintenance	Commercially confidential information	Based on quote provided by supplier (ARM Ltd.)	Murphy, 2017
Apatite wetland refurbishment	Commercially confidential information	Two wetlands, one refurbishment every 10 years for two wetlands, estimated by supplier.	Germain-Cripps, 2017
Extra general	Commercially	1 extra hour per week	Germain-Cripps,

site O&M	confidential information	needed	2017
Extra energy used	Commercially confidential information	Based on estimated consumption.	Germain-Cripps, 2017

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