Removal of phosphorus from water using treated Acid Mine Drainage solids and pellets made thereof

A thesis submitted for the Degree of Doctor of Philosophy

By

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Abstract

This thesis presents work carried out to further the understanding of the use of waste Acid Mine Drainage (AMD) solids to remove phosphorus from wastewaters. AMD can result in serious pollution and so is often treated by the Coal Authority in the UK the resultant solids being a costly disposal issue. Currently the Water Framework Directive (WFD) is putting increased strain on technology used to remove phosphorus at WasteWater Treatment Works (WWTWs). The work presented in this thesis therefore investigates the use of a problematic waste to provide a novel solution to the issue of phosphorus removal at WWTWs.

There has been previous work carried out on the use of both AMD solids and AMD-cement pellets to remove phosphorus from wastewaters. This thesis builds upon this work, firstly the phosphorus removal achieved by unpelletised materials studied in this thesis are compared to those studied by others through the comparison of adsorption isotherms. Mirroring other studies, the principal material studied in this thesis was then pelletised using Portland cement as a binder. Phosphorus removal by these pellets in batch tests was determined and optimised. Phosphorus removal was found to increase with a reduction in pellet size and an increase in test length up to the maximum length studied of three weeks.

This increase in performance was attributed to the introduction of a calcium phosphate precipitation removal mechanism as a result of the use of cement as a binder for the pellets. This was highlighted through the correlation of phosphorus removal with a drop in calcium concentrations and pH values. It was concluded that the end product of this precipitation was hydroxyapatite.

Continuous column tests were performed on the pellets, it was found that the pellets not directly involved in phosphorus removal were still having their reactivity leached out by passing water and so when these pellets became involved in removal, the columns quickly failed.

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1. Introduction

This thesis considers two problems, that of the control of phosphorus in wastewaters and also that of finding a positive use for treated waste Acid Mine Drainage (AMD) solids.

Phosphorus is often the limiting nutrient in freshwater systems (Mainstone and Parr 2002). Anthropogenic inputs of phosphorus can lead to problems such as eutrophication and therefore phosphorus is often controlled at WasteWater Treatment Works (WWTWs). The Water Framework Directive (WFD) (2000/60/EC) is putting further strain on the current technology used for phosphorus removal, particularly on the use of ferric salts, the supply of which is limited and prices are rising (Ofwat 2005). The cost of removing phosphorus is especially high for WWTWs serving smaller populations Wood *et al.* (2007) and so this is the area particularly addressed by the work presented in this thesis.

AMD can occur due to the flooding of abandoned mines and pollution of watercourses by AMD can have serious environmental consequences. AMD is often treated by the Coal Authority and the resultant solids are an expensive disposal problem for them to deal with and so they are actively seeking positive uses for it (Coal Authority).

This thesis presents work which investigates the potential for the practical application of waste AMD solids for the removal of phosphorus from wastewaters. This is achieved through the testing of the raw waste materials and the testing of pellets made from waste AMD solids and cement. The tests performed include both batch and continuous column tests.

1.1 Aims and objectives

1.1.1 Aims

The work presented in this thesis aims to asses the phosphorus adsorptive capacities of waste iron oxyhydroxides, pelletise one of these materials using cement, asses and maximise the phosphorus removal capability of these pellets and determine the dominant phosphorus removal mechanism. Finally to gain an appreciation of the suitability of these pellets for real world use continuous column tests are performed.

1.1.2 Objectives

- Produce adsorption isotherms for phosphorus removal by waste iron oxides and compare these to those for other waste materials and commercial sorbents
- Develop a method of pelletisation for waste AMD sludge using cement
- Asses the phosphorus removal capability of the produced pellets and optimise their removal capability.
- Determine the phosphorus removal mechanism by these pellets
- Determine the performance of these pellets in continuous column tests and therefore asses their suitability for use at WWTWs

1.2 Thesis structure

Chapter 2 describes the background to the problems addressed by this thesis i.e. the driving forces of this study. The problems with anthropogenic sources of phosphorus are discussed as are the increasing strains on current phosphorus removal technology at WWTWs. The production of AMD and the resultant pollution issues are then presented.

Chapter 3 reviews work that has been carried out by others in related fields to this study. The phosphorus removal performances of other waste materials are discussed as are those of iron oxides. Studies that have directly looked at the use of AMD solids to remove phosphorus are then evaluated and finally the potential of the recovery of phosphorus is discussed.

Chapter 4 discusses the theoretical background to the processes touched on in this thesis. Firstly the basics of adsorption are discussed as are the calculation of the theoretical adsorption isotherms. Theories pertaining to the pellet study are then dealt with, this includes cement theory and the basics of chemical precipitation. The classical column theory is then presented as are the theories behind up scaling models. Finally the methods of calculation behind the statistics used in this thesis are shown.

Chapter 5 describes the materials tested in this study and presents the experimental methods used. Firstly the raw materials used are described and data such as their chemical composition and surface area are presented. The methodology of batch adsorption tests carried out on these materials is then shown. The method of pellet production is discussed, the resultant pellets described and the experimental methods for these pellets is shown. The design of the columns used for the continuous column tests is then presented and the experimental procedures for these tests described.

Chapter 6 presents the results for the batch adsorption experiments on the four raw materials studied. Each material is dealt with in turn, the results presented, and the theoretical isotherms are calculated. These isotherms are then compared to those of the other materials studied and select materials from the literature review.

Chapter 7 discusses the results for the tests on the pellets produced from the addition of cement to the sludge from the Horden minewater treatment plant. The improvement in performance with the reduction in pellet size is shown as is the improvement in phosphorus removal with the extension of test lengths up to three weeks. The introduction of a calcium phosphate precipitation removal mechanism due to the use of cement as a binder in the pellets is also investigated. Tests on pellets devoid of the solids from Horden are performed to highlight the dominance of the calcium phosphate precipitation removal mechanism.

Chapter 8 describes the results for the continuous column tests that were carried out using the pellets produced from the Horden solids and cement. The progression of the effluent phosphorus concentration with the volume of water treated is shown and this is linked to the effluent calcium and pH values.

Chapter 9 surmises the key conclusions and recommendations that this thesis has resulted in

2. Background

This chapter discusses the background issues or driving forces for the work presented in this thesis. These derive from two sources, the problem of increasing pressure on current phosphorus removal techniques at WasteWater Treatment Works (WWTWs) and the problem of disposal of Acid Mine Drainage (AMD) sludge. The role of phosphorus in nature is discussed as is how anthropogenic sources can affect the aquatic environment. The control of phosphorus, both in terms of legislation and treatment methods at WWTWs is explained. The formation of AMD is then described along with its environmental impacts and disposal issues.

2.1 Phosphorus

Phosphorus is a non-metallic element, atomic number 15 with an atomic weight of 30.97(Emsley and Hall 1976). It is essential to all aspects of life, present in areas from bones to D.N.A. Phosphorus is a reactive element and never found in its elemental form, in nature it is found in the biosphere, lithosphere and hydrosphere but is only present in the atmosphere in particulate form. As an essential nutrient to life phosphorus is generally omnipresent in the biosphere. In the lithosphere phosphorus is predominantly present in sedimentary rocks, weathering gradually liberates the phosphorus from these rocks, and this process can be aided by plant life. Sedimentary rocks can contain up to 80% apatite and this is where the bulk of mined phosphorous originates, the most common mined mineral being fluorapatite ($Ca_5(PO_4)_3F$) (Emsley and Hall 1976). In the hydrosphere phosphorus only exists in its pentavalent forms such as orthophosphate and polyphosphate (Corell 1996)

Figure 2.1 shows the primary and secondary phosphorus cycles. In the primary cycle, represented in blue, the phosphorus bound in rocks is slowly weathered and washed into the sea. Once in the sea calcium phosphates can precipitate and form part of the sediment where it again forms part of the lithosphere. The secondary cycle, represented in red, adds the cycling of phosphorus around both land and aquatic life cycles, where organic matter can also form sediments and renter the lithosphere.

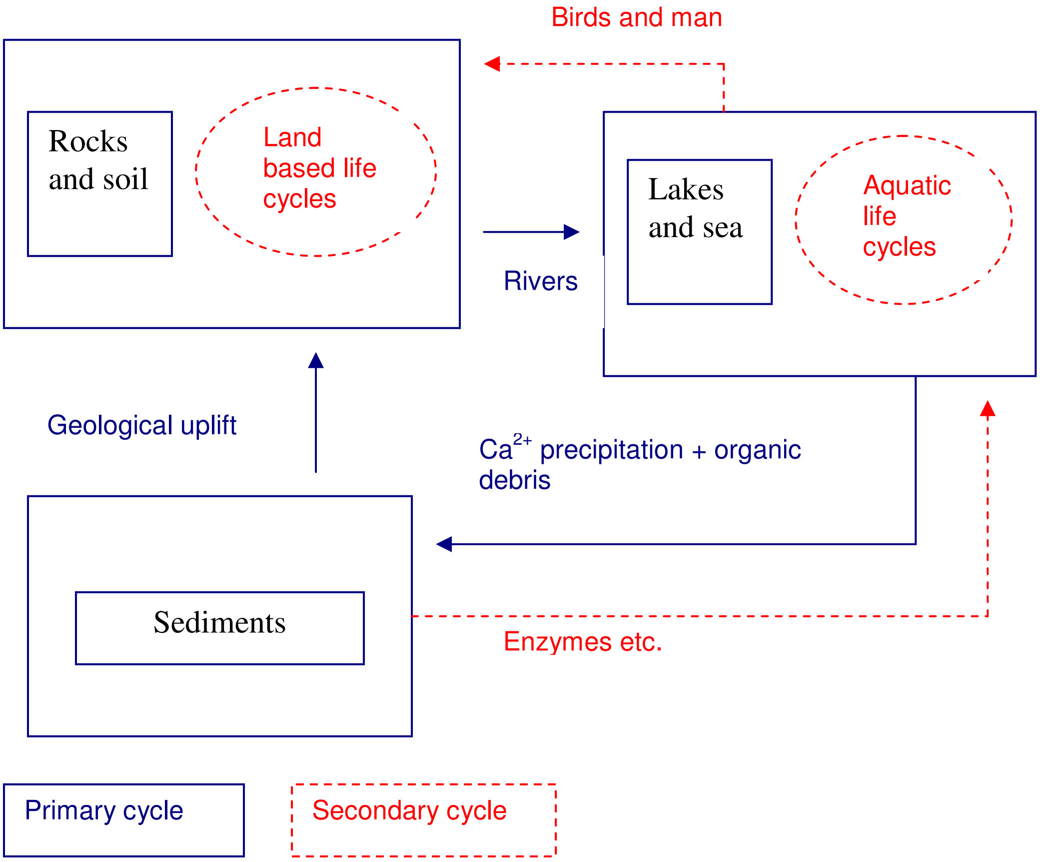


Figure 2.1 Primary and secondary phosphorus cycles (after Emsley and Hall 1976)

2.1.1 Industrial uses of phosphorus

The modern world has developed a demand for phosphorus which has led to its increased extraction from minerals and consequently its increased discharge into the environment. The industry with the largest demand for phosphorus is agriculture consuming 80-85% of total demand, the majority of this goes to the production of inorganic fertilizers with the remainder going into areas such as animal feed production. The second largest demand for phosphorus comes from the detergent industry where phosphorus is used as a “builder” which assists in softening the water and establishing optimum cleaning conditions. Other industries that require phosphorus include metal surface treatment, flame retardation, fruit and vegetable processing and paper production (Environment Agency 2011).

2.1.2 Phosphorus as a problem nutrient

Eutrophication is defined as the enrichment of water bodies by nutrients (Smoll 2008) the three nutrients typically associated with this are nitrogen, potassium and phosphorus. Watercourses will have natural background levels of nutrients and influxes of nutrients upset this natural balance. This idea can be traced back to the 1840’s and the work by Justus von Liebig who showed that if an element required by an organism is not sufficiently available, no matter how abundant other essential elements are, growth will be limited. This is known as Liebig’s law of the minimum (Smoll 2008). The nutrient that limits growth varies but in freshwater environments it is typically phosphorus (Mainstone and Parr 2002), Smith *et al.* (1999). Aquatic systems can be sensitive to phosphorus, the UK Environment Agency states that in rivers a level above 0.1mg/l of phosphorus is considered high and in 2008 51% of rivers in England were considered to have high levels of phosphorus (Environment Agency 2011 (b))

2.1.3 Effects of eutrophication

Where nutrient enrichment occurs one of the most common symptoms is enhanced growth of primary producers – plant life at the bottom of the food chain, this can take the form of blooms of blue-green algae (cyanobacteria) (Smoll 2008). The problems associated with these blooms include taste and odour problems. The algae also have the potential to produce toxins affecting the suitability of the water for consumption and making the water harder to treat, raising costs. These blooms will also reduce the penetration of light into the water affecting other plant life. Algal blooms can also have direct economic implications as they are unsightly and can thus affect tourism and property values Hilton *et al.* (2006).

Nutrient enrichment can lead to oxygen depletion in lakes due to bacterial respiration and decomposition of settling organic matter. Low dissolved oxygen levels will inhibit fish life and other biota (Smoll 2008). Enrichment will affect the competitive balance between species as they react differently to the influx of nutrients (Mainstone and Parr 2002) which can then have knock-on effects on other species.

2.1.4 Sources of phosphorus

Anthropogenic sources of phosphorous can be split into two categories, point and diffuse sources. Point sources are those that enter watercourses at a single point or discharge, these sources are typically water treatment works, but will also include discharges from industry (Mainstone and Parr 2002). Diffuse sources generally result from agricultural run-off where phosphorus from fertilizers and animal wastes can be washed into watercourses. The relative contribution from agriculture and domestic sewage to phosphorus in rivers varies depending on how urban or rural the catchment area is (Mainstone and Parr 2002). Although inputs from agriculture may be high the relative impact of these inputs may be lower that those from sewage treatment works as most of the agricultural load will enter the river during autumn and winter and under high river flows, so the phosphorus will be more dilute (Smoll 2008). Inputs from diffuse sources will also be lower during spring/ summer and these are the seasons where biological activity is at its highest Jarvie *et al.* (2006). This study is focused on treatment of point sources from sewage treatment works. Figure 2.2 shows the pathways of phosphorus from land to rivers and lakes, included in this figure are the anthropogenic sources such as sewage and agriculture.

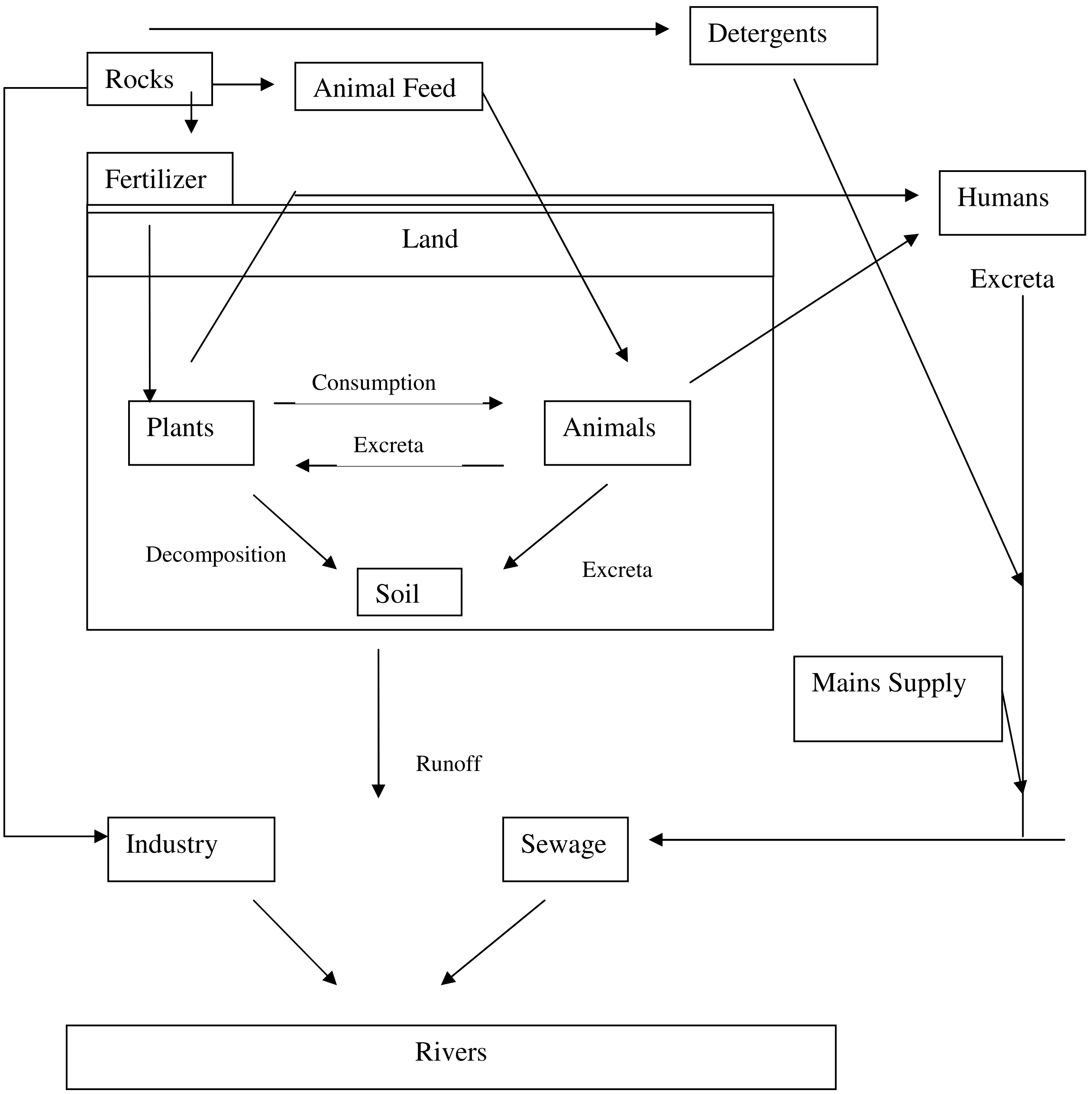


Figure 2.2 Pathways of phosphorus into rivers (After Mainstone and Parr 2002)

The various pathways of phosphorus into rivers are shown in Figure 2.2. Agriculture, the largest consumer of mined phosphorus results in both the diffuse input of phosphorus through runoff and also point inputs through human excreta. The inputs of phosphorus from industry and use in detergents are also shown.

This study focuses on point sources particularly those from sewage treatment works. Figure 2.3 shows the various sources of phosphorus into domestic wastewater

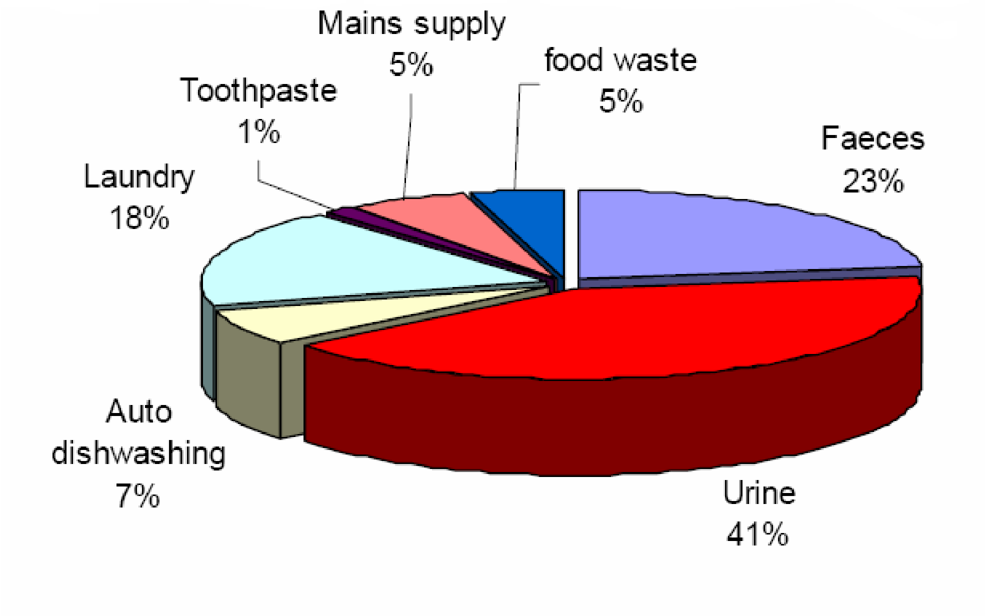


Figure 2.3 Breakdown of domestic sources of phosphorus in wastewater (DEFRA 2008)

The 5% mains supply segment is included in Figure 2.3 as phosphorus is dosed into the mains supply to retard lead entering the water supply from pipes and solder (Ofwat 2005).

2.1.5 Phosphorus Legislation

Phosphorus has been controlled under EU legislation since 1975 when standards for drinking water abstraction were drawn up. The 1991 Urban Waste Water Treatment Directive also contained controls for phosphorus as did the Directive for Integrated Pollution and Prevention Control (IPPC) (1996). The Water Framework Directive (WFD) is currently in the process of being implemented, this is a major piece of European legislation agreed in December 2000 and by December 2015 EU members should have achieved the main environmental objectives (2000/60/EC).

The WFD is based on a river basin management system, each river basin will have its own management plan which will be reviewed every six years. Under the WFD all watercourses will have to achieve a “good” status, this will be essentially as close to a natural status as possible, i.e. minimal anthropogenic influence. Rivers will be assessed under both ecological and chemical categories, phosphorus, as a key nutrient will be controlled under the WFD (2000/60/EC).

Where imposed currently WWTWs have phosphorus discharge consents of around 1-2mg/l (OFWAT 2005) under the WFD more WWTWs could have consents imposed or tightened. These potentially higher discharge limits will put higher strain on current phosphorus removal technology with which there are already issues, as is discussed in Section 2.1.6.

2.1.6 Current phosphorus removal techniques

Phosphorus removal at WWTWs first occurs with physical separation as some of the phosphorus will be bound up in the solid fraction, most however, is soluble and this is removed by incorporation into the solid fraction using chemical precipitation, biological removal, or a combination of the two.

Chemical precipitation can be carried out by lime or aluminium salts but ferric salts such as ferric chloride or ferric sulphate are generally used (Metcalf and Eddy 2003). Chemical dosing is quite a flexible technology and can be implemented throughout the WWTWs. It can be used to remove phosphorus with the primary sedimentation sludge, it can be used within the activated sludge process where it carries the phosphorus out with the secondary sludge (co precipitation) and it can also be used as a tertiary treatment i.e. as a polisher which has the drawback of producing a chemically rich tertiary sludge Morse *et al.* (1998).

Biological treatment can involve “luxury uptake” where the phosphorus is taken up in excess of that required for growth. An anaerobic/anoxic zone is established where the bacteria become “stressed” this is followed by an aerobic zone where this excessive “luxury uptake” occurs Morse *et al.* (1998)

There are issues relating to dosing of ferric (Fe III) salts. If phosphorus discharge limits are below 2mg/l then accurate and variable dosing is required. If the influent quality varies further operator input is required and the chance of overdosing increases which if happens can result in the ferric salts being discharged into the environment. Iron is a List 2 substance under the Dangerous Substance Directive (Dangerous Substances Directive 1967) and its use to remove phosphorus can result in iron discharge consents being implemented. Ferric chloride which is commonly used is corrosive and burns skin on contact and so there are many health and safety issues related to the use and storage of this chemical. The shortage of ferric salts has caused their price to rise (Ofwat 2005) and as the WFD is likely to put higher demands on this technology and so it will also put further strain on the already limited supply.

Biological treatments also have issues related to their operation, they often require a steady supply of carbon, such as brewery waste. It can be hard to consistently remove phosphorus to a low effluent concentration and therefore biological treatment is often run with chemical dosing as a backup, thus retaining the problems associated with this. Biological treatment can be temperamental and so it is hard to achieve consistently low effluent levels.

Both these favoured methods can require operator input which is particularly undesirable at smaller WWTWs that only serve small populations. These smaller plants have a much higher cost per kilogram of phosphorus removed (Ofwat 2005). This thesis therefore looks at providing a solution for phosphorus removal that is low cost, both in terms of capital and operating expenses, is easy to retrofit to existing works and has minimal demands in terms of operator hours.

2.2 Acid Mine Drainage

This section details the formation of Acid Mine Drainage (AMD) and the problems associated with this polluting waste.

2.2.1 AMD Formation

Exposure of minerals containing sulphur to water and oxygen can generate what is known as Acid Mine Drainage (AMD) or Acid Rock Drainage (ARD).
In natural conditions the exposure of such minerals to water and oxygen is minimal and so the generation of AMD is very slow, mining however exposes these rocks and generation is greatly accelerated. During operation mines are likely to go below the natural water table and so pumping is commonly used to stop the flooding of the mine's workings. After the mine or mine field is decommissioned the pumping may be stopped and the mine will flood thus exposing these minerals to water, exposure can also occur in tailing piles, ore stockpiles and open pit workings. The oxidation of pyrite (FeS_2) is the most commonly studied mechanism for the generation of AMD. The governing chemical reactions for this are shown below stoichiometrically and taken from Brown *et al.* (2002).

The first stage, the initiator reaction, involves the dissociation or oxidisation of pyrite ($Fe_{2(s)}$)

$$FeS_{2(s)} + 7/2\,O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad \text{Equation 2.1}$$

It can be seen that at this first stage the hydrogen ions released will cause a drop in pH.

The next stage is the propagation cycle which is the oxidation of Fe^{2+} to Fe^{3+} (ferrous to ferric) this stage requires contact with the atmosphere or dissolved oxygen in the water. The consumption of hydrogen ions can be seen on the left of the equation.

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad \text{Equation 2.2}$$

Ferric iron is insoluble in water at pHs above 2.3-3.5, this precipitates as ferric hydroxide ($Fe(OH)_3$) among many other forms. This forms the yellow red deposit often referred to as ochre that is shown in Figure 2.4. This step is capable of dramatically dropping the pH.

$$Fe3^{+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^{+} \qquad \text{Equation 2.3}$$

Ferric iron in solution can also react with the pyrite producing more ferrous iron and hydrogen ions

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^{+} \qquad \text{Equation 2.4}$$

Microbiological activity can have a large effect on the production on AMD generation, potentially affecting the rate of oxidation from ferrous to ferric iron by a factor of up to 10^6 Brown *et al.* (2002)

Figure 2.4 Example of AMD pollution (Coal Authority)

2.2.2 Effects of AMD on the Environment

Mines can have impacts on the environment centuries after closure Younger *et al.* (2004). The three major environmental impacts associated with AMD are reduction in pH, iron precipitates and trace metals.

Low pHs can results in watercourses failing to meet statutory requirements and often increase the solubility of trace metals. Typically as the pH of a watercourse decreases the number of species decreases Brown *et al.* (2002)

Ferric precipitates produce the scenario shown in Figure 2.4. The precipitates resulting from AMD pollution can smother life, reduce light penetration and potentially clog fish's gills. The precipitates are also unsightly and thus can reduce the recreational/commercial value of watercourses.

Trace metals can be toxic to life and include elements such as copper and lead Brown *et al.* (2002). The toxicity of these trace elements can be compounded through bioaccumulation Younger *et al.* (2004).

2.2.3 Treatment methods

AMD treatment can be split into two broad techniques, active and passive. Active treatment is often carried out by pH adjustment using materials such as lime or limestone Brown *et al.* (2002) these alkaline materials are used to raise the pH of the AMD which then results in the iron and other metals precipitating out of solution. Passive treatment is desirable due to the persistent nature of AMD, an example of this are constructed wetlands. These wetlands act as a buffer between the mine discharge and the aquatic environment Brown *et al.* (2002). The methods used to treat the particular materials used in this study are explored in the Chapter 5.

2.2.4 Disposal issues and costs

3.7×10^4 tonnes of AMD waste were produced from 49 sites in 2004 Hancock (2004). Dobbie *et al.* (2009) states a cost of £80-100 per tonne of AMD to be disposed. Therefore the total cost of AMD disposal could be in the region of £3.7 million. Landfill tax is currently £56 per tonne and set to rise to £80 per tonne by 2014 HM Revenue and Customs (2011). AMD could also be susceptible to reclassification which would impose further restrictions and therefore costs on its disposal. This leads to the situation of not only the amount of AMD being produced increasing but the cost of disposal also increasing Hancock (2004). It is clear why the Coal Authority is actively seeking uses for this waste (Coal Authority). The use of AMD solids suggested in this thesis will not consume the AMD solids, but could give this waste a commercial value. Options for reusing the ochre after being used to remove phosphorus are discussed in Section 3.6.

2.3 Chapter summary

This chapter identified and explored the problems that are the driving forces behind the work presented in this thesis. The problems associated with excessive release of phosphorus to the environment were stated. The limitations of current phosphorus removal technologies were shown along with discussion of the WFD and the extra strain that this may place on current techniques. The formation of AMD was explained as well as its impact on the environment and problems with its disposal.

3. Related Work

There has been a considerable amount of research carried out into alternative methods of phosphorus removal. This chapter reviews some of this work and draws out parts relevant to the current study. Firstly papers that investigate waste materials used for phosphorus removal are looked at, this includes concrete waste, animal wastes, fly ashes and slags. These papers proved useful in planning the experiments carried out in support of this thesis and there are other areas where parallels may be drawn, such as determining the dominant mechanism of phosphorus removal. Phosphorus removal by iron oxides is studied in depth as iron oxides are a major component of Acid Mine Drainage (AMD) solids. There have been studies into using solids from treated AMD to remove phosphorus, these are directly relevant to this study and will inform important areas of study so these are looked at in detail. Next other novel techniques that have been used at WasteWater Treatment Works (WWTWs) are discussed, these are other phosphorus removal methods that have the potential to replace current methods at WWTWs and could be considered as competition to the technology studied in the current thesis. Finally papers that have looked at the potential of recovering the removed phosphorus once it has been removed are reviewed.

3.1 Removal of phosphorus from water by waste materials

3.1.1 Phosphorus removal by concrete and concrete waste

A large part of this project involved looking at the pelletisation of AMD solids with cement, this section looks at work others have done investigating the phosphorus removal capability of cement and concrete.

Agyei *et al.* (2002) looked at the performance of Portland Cement on its own and also blended with fly ash and slag. The cement material studied had a mean diameter of 20.8 microns and was tested in 200ml batch tests with a solids concentration of 10g/l and initial phosphorus concentrations of 20-80mg/l. Cement on its own removed more phosphorus then when blended with fly ash or slag, removing up to 27mg/g total phosphorus. Its higher performance was attributed to it having the highest CaO content and the high levels of calcium ions released into solution, this correlation is indicative of calcium phosphate precipitation. The initial pH of tests was controlled through the addition of 0.1 M HCl and 0.1 M NaOH. Phosphorous removal was shown to have an inverse correlation with pH. This was suggested to be as a result of the surfaces gaining a positive charge and also due to the creation of acidic species which were then removed through deprotonation and then precipitated as $Ca_3(PO_4)_2$, these lower pHs are also likely to release more calcium into solution. The removal efficiency did rise slightly after a pH of 9 which Aygei *et al.* (2002). concluded was as a result of conditions more suited to calcium phosphate precipitation. Berg *et al.* (2005), Oguz *et al.* (2003), and Park *et al.* (2008) all concluded that calcium phosphate precipitation is a major removal mechanism by cement. Berg *et al.* (2005) used tobermorite-rich crushed gas concrete (0.6-13mm) as a seed for the precipitation of calcium phosphate. Both fixed bed and expanded bed tests were performed, the crushed concrete was found to removal more phosphorus than calcite. Oguz *et al.* (2003) also used gas concrete to remove phosphorus from water. Particles in the size range of 0.063-2mm were used in batch tests. Phosphorus removal was heavily correlated with rising pH with negligible removal at a pH of 2, 60-80% removal at a pH of 5.8 and essentially 100% removal at a pH of 11.5. This lead to the conclusion that calcium phosphate precipitation was the major removal mechanism It can thus be seen that pelletising AMD sludge with cement as carried out in tests for the current thesis could introduce calcium phosphate precipitation as a removal mechanism. There is a conflict between the conclusions of Aygei *et al.* (2002). and Oguz *et al.* (2005) in relation to the correlation of phosphorus removal and pH, the relationship between pH and removal is explored further in the subsequent sections of this chapter.

3.1.2 Phosphorus removal by animal wastes

Materials such as bones and shells can be viewed as calcium and hydroxide ion sources. These papers have been included in this literature review as they help further understand the ideal conditions for calcium phosphate precipitation.

Lee *et al.* (2009) studied the removal of phosphorus from water using pyrolyzed oyster shells. The waste shells were crushed to sizes below 1.4mm. In tests the pH of the influent quickly rose from the influent value of 7.2 up to 11.7. These high pH values and high calcium concentrations lead to the conclusion that precipitation was the dominant removal mechanism. It was thought that the likely precipitation end product was hydroxyapatite (HAP) ($Ca_5(PO_4)_3(OH)$), this is backed up by the findings of Yu *et al.* (2010) who also studied phosphorus removal by oyster shells. Due to the relatively high level of calcium in their influent Lee *et al.* (2009) viewed the oyster shells as a source of OH^-, the oyster shells providing 80% that calcium hydroxide would, but in an easier to handle form. The shells removed 98% of phosphorus within 30 minutes with an influent of 11.9mg/l and 6g/l of shells used.

Jang *et al.* (2002) looked at using cow bone to remove phosphorus. The bone was crushed and sub 0.5mm material was used in batch tests. The bone was envisaged as a seed for HAP precipitation as itself contains 57% HAP. Phosphorus removal was again shown to be highly correlated with increasing calcium ion concentration and pH.

These papers show again the effectiveness of calcium sources as phosphorus removers, in many ways mirroring the traditional method of phosphorus removal by lime dosing but avoiding the creation of a sludge. The end precipitation product was again generally concluded to be HAP.

3.1.3 Phosphorus removal by slags

A large amount of work has been carried out looking at the phosphorus removal capability of various slags. Slags are a waste generated in the steel industry and tend to contain oxides of calcium, magnesium, aluminium, silicon and iron. Their composition is variable depending on the process that produces them and the raw materials used for the steel production. The composition of slags studied in some of the papers discussed are shown in Table 3.1, only constituents representing above 1% by weight are shown.

Table 3.1 Examples of slag compositions

Reference	Drizo *et al.* (2006)	Xue *et al.* (2009)	Kostura *et al.* (2005)	Kim *et al.* (2006)	Shilton *et al.* (2006)
Slag type	Electric arc durance steel slag	Basic oxygen furnace slag	Blast furnace slag (crystalline)	Converter Slag	Steel slag
SiO_2 (% wt)	13.7	13.7	38.63	11.6	12.4
Al_2O_3 (% wt)	4.67	6.8	6.55	2.4	18.3
Fe_2O_3 (% wt)	34.7	17.8	-	25.9	2.61
MgO (% wt)	13.1	7.3	13.71	8.6	13.4
CaO (% wt)	30.4	45.4	38.02	40.5	15.9
TiO_2 (% wt)	0.68	-	-	-	35.3
MnO (% wt)	1.30	-	0.58	-	1.15

Table 3.1 shows that, in general oxides of calcium, iron, aluminium and silicon are dominant with CaO consistently forming a large fraction.

The phosphorus loading achieved by slags varies across the studies. Xue *et al.* (2009) found a highest removal of 41.6mg/g at 500mg/l equilibrium concentration, this contrasts with Xiong *et al.* (2008) who found a maximum capacity of 5.3mg/g. Kostura *et al.* (2005) found a saturation capacity of 19mg/g. These capacities will be affected by chemical composition, crystalline structure and test conditions amongst other factors.

The dominant removal mechanism varies, some studies found adsorption to be dominant, and others precipitation. Xue *et al.* (2009) studied a basic oxygen slag, tests on sub 0.6mm material found that the phosphorus adsorption capacity of the slag decreased from 4.97 to 3.71mg/g when the solution pH was increased from 2.0 to 13.0. This inverse relationship was concluded to show adsorption as a predominant mechanism as, when the pH increases it will eventually pass the point of zero charge for the slag whereafter the surface charge of the slag will change from positive to negative, thus inhibiting the adsorption of the negatively charged phosphate ions. Xue *et al.* (2009) also found decreasing levels of calcium, magnesium and aluminium ions in solution which lead to the conclusion that precipitation was also occurring. There therefore appears to be two competing removal mechanisms in operation with adsorption being concluded as the dominant one in this case.

Johansson and Gustafsson (2000) studied both a crystalline and an amorphous slag with particle sizes up to 4mm. Batch tests were carried out with initial concentrations from 5-25mg/l. Johansson and Gustafsson (2000) concluded that calcium precipitation, particularly in the form of HAP to be the dominating removal mechanism. This was indicated by a decrease in both dissolved calcium ions and pH with an increased dosing of phosphate. Johansson and Gustafsson (2000) state that a pH of above 9 and large amounts of soluble calcium are required for effective phosphate removal.

The apparent difference in dominant removal mechanism between Xue *et al.* (2009) and Johansson and Gustafsson (2000) could be attributed to the levels of soluble active ions that their materials released. Xue *et al.* (2009) found that their slag released 100µg/l Ca, 10µg/l Mg and 8µg/l Al, a total of 118µg/l. These values contrast with the 80mg/l Ca that Johansson and Gustafsson (2000) found. As Johansson and Gustafsson (2000) state, high levels of soluble calcium are required for efficient removal by calcium phosphate precipitation. Therefore this difference in concentrations of dissolved ions could explain the difference in dominating removal mechanism and correlation to pH.

Kostra *et al.* (2005) and Kim *et al.* (2006) both found a positive correlation between rising pH and higher phosphorus removal thus suggesting precipitation as the dominant mechanism, Kostra *et al.* (2005) found a correlation coefficient of 0.953 between saturation capacity and pH at equilibrium.

Kim *et al.* (2006) found a Ca:P molar ratio of 1.78 on the surface of the slag they studied and thus concluded that HAP was the most likely form of the precipitate as the ratio lies between 1.33 and 1.95 which they state as the range that HAP typically lies in, the stoichiometric ratio is 1.67. Johansson and Gustafsson (2000) found Ca:P ratios of 4 and 2.9 for their slags, they suggest the discrepancy between these values and that of HAP could be due to simultaneous precipitation of $CaCO_3$. Drizo *et al.* (2006) used XRD analysis to confirm HAP precipitation as the major removal mechanism.

It has been shown that various slags can be effective phosphorus sinks, in many cases the adsorption and precipitation mechanisms are in competition with large amounts of soluble ions and a pH above 9 seemingly important for efficient removal by precipitation and lower pH values favouring adsorption. Again HAP is suggested by several papers as the likely form of this precipitate.

3.1.4 Phosphorus removal by fly ashes

Fly ash is a by product from the combustion of coal in power stations, its chemical composition varies but they generally contain silicon, aluminium, iron, calcium, and magnesium in oxide forms, examples of compositions are shown in Table 3.2.

Table 3.2 Examples of fly ash composition

Reference	Lu *et al.* (2009)	Xu *et al.* (2010)	Oguz (2005)	Urgulu and Salman (1998)	Grubb *et al.* (2000)
SiO_2 (%wt)	49.51	56.8	50.56	33.5	31.3
Al_2O_3 (%wt)	31.12	23.4	25.34	14.45	17.8
Fe_2O_3 (%wt)	5.36	4.7	7.69	4.53	7.1
CaO (%wt)	5.44	9.3	11.57	25.32	31.9
MgO (%wt)	-	0.9	1.55	1.81	6.3
K_2O (%wt)	1.0	-	0.52	1.56	-
Na_2O (%wt)	0.3	-	0.31	0.27	-
P_2O_5 (%wt)	-	-	-	1.58	-
SO_3 (%wt)	-	-	1.84		3.1

Table 3.2 shows that as with slags, silicon and aluminium oxides often form a large constituent of fly ashes.

Fly ashes have been found with relatively high removal capacities. Oguz (2005) studied a fly ash with a maximum phosphorus capacity of 71.87(mg/g). Chen *et al.* (2007) found a maximum removal of 42.55mg/g. Lu *et al.* (2009) found removal up to 100mg/g at an equilibrium concentration of 40mg/l. Many of the studies agree that increasing phosphorus removal is related to increasing calcium content of the fly ash.

Lu *et al.* (2009) looked at this calcium correlation closely. In batch tests 68%-96% of total removal occurred within the first 5 minutes, they attributed this to fast removal by precipitation followed by a slower adsorption mechanism.
The pH and calcium concentrations were both monitored and found that both were decreased with the addition of phosphorus. Lu *et al.* (2009) suggest that this shows calcium phosphate precipitation as the major removal mechanism. The difference in performance between fly ashes studied was linked to their calcium content and pH. Fly ashes were acid treated in order to isolate the adsorption and precipitation mechanisms, this showed a contribution by adsorption of 30-34%. Ugurlu and Salman (1998) also concluded that calcium dissolution was mostly responsible for the phosphorus removal with the calcium concentration and pH again dropping with phosphorus addition. The fly ash studied by Ugurlu and Salman (1998) contained 338.3 g/kg CaO and when 0.2g was shaken in 50ml of water for 3 hours 880mg/l calcium was found in solution. Chen *et al.* (2006) studied 15 different fly ashes and the influence their composition had on phosphorus removal. Chen *et al.* found that found that phosphorus removal was strongly correlated to both calcium content and iron content (correlation coefficient, $r = 0.9836$ and 0.8049 respectively) this could indicate that in this case both precipitation and adsorption are important.

Can and Yidliz (2006) describe two situations at low pH and high pH. At low pH lots of calcium was released into solution but the pH was too low to form insoluble compounds. At high pHs the dissolution of calcium was reduced and so the removal of phosphate was retarded, a neutral pH was therefore decided to be the most advantageous. Chen *et al.* (2007) also describe the importance of pH showing that even though large amounts of dissolved calcium were present the pH was the limiting factor to phosphate removal. Thus reinforcing Johansson and Gustafsson's (2000) conclusions discussed above that pH values of 9 and above is generally required for efficient calcium phosphate precipitation. As to the form that any calcium phosphate precipitation may take, as in the previous sections of this chapter Can and Yidiz (2006) state that HAP is the likely end form of the precipitate as do Chen *et al.* (2007), Lu *et al.* (2009) and Ugurlu and Salman (1998).

These studies on fly ashes show the importance of high calcium concentrations and elevated pH values for calcium phosphate precipitation. The competition of adsorption and precipitation was also highlighted, showing that ideal conditions for one are likely to reduce the impact of the other.

3.2 Phosphorus removal by iron oxides

Solids resulting from the active treatment of AMD are predominately composed of iron oxides. This section looks at the performance of iron oxides and at the mechanism of phosphorus removal by these.

Chitrakar *et al.* (2006) looked at goethite (α-FeOOH) and akaganeite (β-FeOOH) in adsorption studies with phosphorus spiked seawater. A phosphorus loading of 10 mg/g at an equilibrium phosphate concentration of 0.3 mg/l was found for both materials. Kang *et al.* (2003) looked at synthetic ferrihydrite, goethite, and hematite, ferrihydrite performing by far the best, removing 20mg/g at an equilibrium concentration of 1mg/l. At the same equilibrium concentration goethite removed 3mg/g and haematite 1mg/g. Zeng *et al.* (2004) who looked at iron oxide tailings from a mineral processing industry found they removed 7mg/g at an equilibrium of 20mg/l. Torrent *et al.* (1990) studied goethites differing in crystal morphology and found removals ranging from 1.8 to 8.9mg/g at an equilibrium phosphorus concentration of 6mg/l showing the structure of these materials has an impact on their removal.

Chitrakar *et al.* (2006), Geelhoed *et al.* (1997), Li and Stanforth (2000) and Zeng *et al.* (2004) found that phosphorus removal by iron oxides was inversely correlated to increasing pH. This is the expected pattern for adsorption of anions, At higher pHs the oxide surfaces will become more negatively charged and therefore repulse the negatively charged phosphate ions.

Bastin *et al.* (1999) tested a synthetic compound made up of iron oxide and gypsum, thus combing a source of calcium from the gypsum with the adsorptive properties of the iron oxide. The material was produced by dissolving $Fe_2(SO_4)_3 \cdot$

$n$$H_2O$ and $Ca(OH)_2$ in distilled water. This mirrors tests presented in the current thesis where cement was used to pelletise AMD solids, thus the cement will act as a source of calcium in addition to the adsorptive properties of the AMD solids. Bastin *et al.* (1999) found phosphorus removal in batch tests at a pH of 4-8 was constant at around 15mg/g from a solution originally containing 10mg/l P. Between a pH of 9-11 the removal increased to over 30mg/g, this ties in with the conclusions reached by Johansson and Gustafsson (2000) in Section 3.1.3 above who state that pHs above 9 are ideal for calcium phosphate precipitation. Most of the calcium contained in the iron oxide-gypsum compound was found to dissolve thus providing the calcium ions required for calcium phosphate precipitation.

The roles of adsorption and precipitation are also identified by Kang *et al.* (2003), tests were carried out using both synthetic water containing only phosphorus and secondary wastewater which contained a variety of other ions. For the synthetic water an increase in pH reduced the removal from 80% at a ph of 5 to 5% removal at a pH of 13 following the expected pattern for anionic adsorption. Conversely when the secondary wastewater was used the removal rose from 80% at a pH value of 5 to nearly 100% at a pH of 13, this rise was attributed to interactions with the calcium and magnesium ions present in the secondary effluent, this behaviour is as expected with chemical precipitation. These results therefore again show pH to be instrumental in the determination of the dominant removal mechanism.

The Freundlich and Langmuir isotherms are both commonly used in the papers presented. Chitrakar *et al.* (2006) found the Freundlich isotherm fitted their data better than the Langmuir isotherm. Boujelben *et al.* (2008) found the two isotherms to perform similarly. Kang *et al.* (2003) used the Freundlich isotherm and Genz *et al.* (2004) used the Langmuir. Both isotherms therefore seem to describe phosphate adsorption by iron oxides to a similar accuracy.

It can be seen that phosphate adsorption by iron oxides is well researched and is established knowledge. It was shown that, as with waste materials described in the sections above, when other ions such as calcium are present, adsorption and precipitation reactions occur in competition, their dominance being affected by pH.

3.3 Phosphorus removal by ochre

Two centres where research has been carried out into phosphorus removal by AMD are focused on. Firstly research carried out at Newcastle and Edinburgh universities headed by Kate Heal are discussed. The second centre is headed by Paul Sibrell who has also researched the potential of this technology and has papers published plus a relevant American patent. Wei *et al.* (2008) have also released a thorough paper on the subject.

3.3.1 Research by Edinburgh and Newcastle universities

Heal *et al.* (2004) looked at two sources of AMD, from two minewater treatment plants in Scotland named Polkemmet and Minto. The AMD from Polkemmet dries to a coarse texture, and that from Minto to a fine. These sludges are viewed to be used as a wetland substrate or dosing system at wastewater treatment works. Their potential use in drainage ditches to control agricultural runoff was also considered.

The phosphorus removal capacities of these sludges were determined in batch tests. Polkemmet solids removed a maximum of 26 mg/g and the Minto sludge removed 30.5 mg/g. From the Freundlich isotherm provided, it can be calculated that these loadings were achieved at equilibrium concentrations of 67.4 and 8.2mg/l respectively. Phosphorus removal by the Polkemmet solids occurred within an hour, by the Minto solids within minutes. pH was shown not to have significant effect, this was hypothesised to be due to the buffering effects of the ochre however only initial pHs were reported. Long term removal was also investigated by pumping phosphorus spiked water onto a trough containing Polkemet ochre for 9 months. After the 9 month period the ochre was still removing the phosphorus from 20mg/l influent to below 1mg/l. Heal *et al.* (2004)

compared the performance of the ochres to other wetland substrates the best performing of which was zeolite at 1mg/g.

A considered limitation to the implementation of these AMD solids is cited as their engineering properties, these solids being vulnerable to erosion and difficult to handle, therefore a more granular form that doesn't detract from the phosphorus removing properties is considered as ideal, it is suggested this could be achieved through pelletisation using Portland cement. The current thesis is predominantly focused on AMD pelletised with cement.

In Dobbie *et al.* (2009) two experiments were carried out at WWTWs to asses the performance of both granular ochre and ochre-cement pellets, 6.4-9.5mm in diameter. The granular ochre is the Polkemmet ochre as reported on in Heal *et al.* (2004). The first test was carried out at Leitholm a WWTWs in South East Scotland, some of the effluent from the biological filter was diverted into a trough which at first contained granular ochre, this was replaced by ochre pellets during the second half of the experiment. The second experiment was carried out at Windlestone WWTW in North-East England. This experiment only tested the ochre-cement pellets again by diverting effluent into a trough.

The ochre-cement pellets showed higher removal, believed to be due to their superior contact with water as batch tests showed that pellets had a lower saturation capacity than the unpelletised solids (26 vs. 22 mg/g). The ochre-cement pellets removed the equivalent of 0.49mg/g after 1000 hours of operation. Retention time was found to be important with above 15 minutes recommended. This report shows that these AMD solids and pellets can be used in “real world” situations and offer long term removal of phosphorus.

3.3.2 Research Headed by Paul Sibrell

In Adler and Sibrell (2003) treated AMD solids are used to remove/control phosphorus in water, soil and manure. AMD sludge was neutralised and the resulting floc crushed to pass a 1mm sieve. In batch tests, phosphorus removal from water up to 20mg/g at 1mg/l phosphorus equilibrium was found and the Freundlich isotherm was used to describe the data. The AMD solids were also used as an addition to soil and manure to stop soluble phosphorus leaching out. In soil 70% of soluble phosphorus was contained, in manure 90% was. This paper shows that AMD is effective at controlling phosphorus in a variety of situations.

Sibrell (2007) describes the pelletisation of waste with an affinity for phosphorus, AMD is particularly cited as a suitable material. Various cement additions and other admixtures were tested but for ideal strength and resistance to abrasion 30% addition of cement was found to be the optimum, pellets were produced in the range of 1-4mm using a pan pelletiser. The unpelletised AMD solids studied were found to remove 3mg/g at an equilibrium concentration of 0.3mg/l. It was stated that using the pellets in two columns so that one can be rested whilst the other is in use “tremendously” increases the removal capacity.

Sibrell *et al.* (2009) looked at six different AMD sludges, in batch tests lasting two hours, the highest performing removed nearly 24mg/g at an equilibrium concentration of 1mg/l, the worst 1.8mg/g at the same equilibrium concentration. The Freundlich isotherm was again used to describe the data of all materials, The sludge with the lowest performance had large amounts of silicates present, thus diluting the active iron and aluminium oxides. This shows how the performance of these AMD sludges from various sources can vary.

3.3.3 Other centres of research

Wei *et al.* (2008) looked at an AMD sludge from West Virginia USA. Batch tests results were well fitted by the Freundlich isotherm, this showed that the sludge removed from 9.89 to 31.97mg/g phosphorus at an equilibrium phosphorus concentration range of 0.21 to 13.61mg/l. The effects of pH and temperature on these batch studies were investigated, pH was found to have a large effect on removal, tests in the range of pH 5-8.5 were investigated and the final phosphorus concentration rose from 2.5 – 7mg/l in this range. This is consistent with the expected effect of pH on anionic adsorption.

Continuous stirred tank reactor (CSTR) experiments were carried out by Wei *et al.* (2008) on three different waters a synthetic wastewater, river water and secondary effluent from a treatment works. AMD sludge and the influent water were both pumped into the reactor and the hydraulic retention times was controlled to be either 1 or 2 hours. Removal was very similar for all three waters, showing that the presence of other ionic species had little effect on phosphorus removal.

Han *et al.* (2005) deposited AMD solids onto chipped juniper wood which was then used as a phosphorus adsorbent. Batch tests found a removal capacity of 2.3mg/g in equilibrium with 4mg/l. Column tests with an influent concentration of 30mg/l were performed and removal reached 3-4mg/g however some of the deposited iron was lost from the column, which could be an issue for implementation.

Simmons (2010) investigated how AMD pollution of a river may increase its phosphorus buffering capacity and therefore how higher control of AMD pollution could lead to further phosphorus related problems such as eutrophication. The interaction of phosphorus with metal hydroxides typically found in AMD was looked at (Fe, Al, Mn) as well as samples of actual AMD. The iron hydroxides removed by far the most phosphorus. Field trials were carried out by analysing river water for phosphorus both up and downstream of AMD inputs, this showed reductions of between 50 and 90%. On a similar vein Tate *et al.* (1995) looked at how both iron sediments and algae removed injected phosphorus from a river polluted by AMD.

AMD solids are clearly capable phosphorous sorbents but this capability can vary dramatically with the source as shown by Sibrell *et al.* (2009). Dobbie *et al.* (2009) have successfully pelletised AMD sludge, but have found through batch tests the pellets perform worse that the AMD solids (26 vs. 22 mg/g) however in pilot plant tests the pellets seemed to outperform the sludge. Sibrell has also pelletised these sludges and although the effect on performance is unclear a resting phenomenon is described to enhance longevity of removal. It seems that full understanding of the performance and removal mechanism of these pellets is not yet completely understood.

As with the papers investigating phosphorus removal by iron oxides reviewed in Section 3.2 the Freundlich and Langmuir isotherms were commonly used to describe the removal of phosphorus by AMD solids. In Adler and Sibrell (2003), Sibrell *et al.* (2009) and Wei *et al.* (2008) the Freundlich isotherm was favoured whereas Heal *et al.* (2004) found the Langmuir fitted their data better than the Freundlich.

3.4 Other novel phosphorus removal techniques

There are novel phosphorus removal techniques that are established and have been used in full scale applications. Virofilter is a simple flow through filter from the company Virotec. It is stated as offering many advantages over conventional biological removal and chemical dosing especially when removing phosphorus at small plants in remote locations. The material is made from red mud, a waste product from aluminium processing. The red mud goes through the Basecon™ process which involves mixing the red mud with seawater and solid/liquid separation, the end results being known as the Bauxsol material This consists of predominantly hematite (Fe_2O_3), boehmite (g-AlOOH), gibbsite ($Al(OH)_3$), sodalite ($Na_4Al_3Si_3O_{12}Cl$) and quartz (SiO_2). Depending on application demands this material can be pelletised with cement. Two publications on Bauxsol reviewed in the current thesis are a 6 month independent review by the Water Research Council (WRC) Lowrie and Dee (2005) and one regarding a pilot plant at a Yorkshire water treatment works Wood *et al.* (2007). Lowrie and Dee (2005) carried out a pilot plant test and found Bauxsol to have a phosphorus capacity of at least 14mg/g while complying with a discharge consent of 2mg/l. Wood *et al.* (2007) state that Bauxsol costs £23-£27 per kilogramme of phosphate removed at small To medium-sized WWTWs, this compares favourably with chemical dosing costs at similar sized works where prices are quoted as costing up to £146 per kg of phosphate removed. Bauxsol is presented as an ideal solution for small, unmanned works due to its low power and maintenance demands. When pelletised with cement, it is suggested that the technology is unsuitable for neutral to alkaline wastewaters as it raises the pH to an undesirable level and Virotec are looking at other binders to overcome this problem. The pelletising of AMD with cement for this thesis could therefore also encounter similar problems.

The Dutch company DHV have developed a crystallisation technology known as the crystalactor, this takes the form of a vertical reactor. The influent water to the reactor must be pH adjusted and a reagent is dosed. Inside the reactor crystals such as calcium and magnesium phosphates grow up to around 1mm diameter and drop to the bottom of the reactor where they can be removed. Thus highly pure and dry pellets (5-10% moisture content) are produced, these pellets can then be used directly as a fertiliser or take the place of a raw material Giesen (1999).

In 1997 Morse published a paper reviewing phosphorus removal technology available at the time, this included the Crystalactor and a myriad of other technologies covering genus such as crystallisation, biological removal and tertiary filters among others. Phosphorus is viewed as a resource opportunity rather than a problem with technologies offering the potential to replace large amounts of raw material extraction.

3.5 Performance comparison

The adsorption isotherms from a selection of the papers discussed in this chapter are presented in Figure 3.1

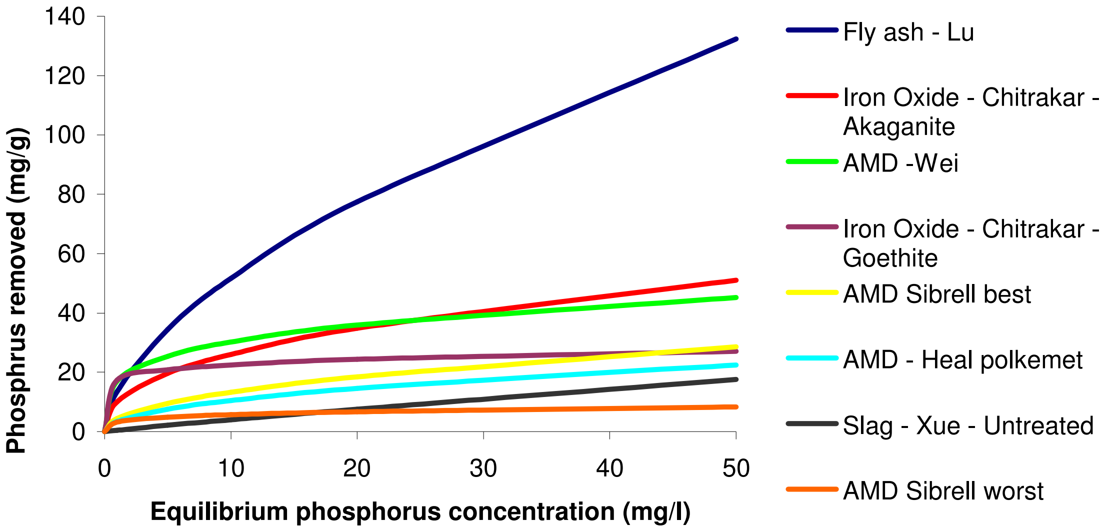


Figure 3.1 Comparison of select adsorption isotherms from literature review

Figure 3.1 shows the phosphorus removal capability of various materials from papers reviewed in this chapter. There is clearly one material outperforming the others, this is the fly ash studied by Lu *et al.* (2009). Lu *et al.* (2009) concluded that adsorption formed 30-34% of the removal, with calcium phosphate responsible for the remainder. The higher performance by this fly ash could highlight the higher effectiveness of calcium phosphate precipitation. The other results plotted in Figure 3.1 are ones where adsorption was reported as the dominant removal mechanism. Sibrell *et al.* (2009) studied a variety of AMD solids. Figure 3.1 shows that the material studied by Sibrell *et al.* (2009) represent the lowest performing and near joint second best performing. The materials studied in this thesis, particularly those of an AMD origin, could be expected to perform in a similar manner to those studied by Sibrell *et al.* (2009).

3.6 Phosphorus recovery

The term “peak phosphorus” is becoming more common, based on the idea of peak oil. It is believed that peak phosphorus may occur as soon as 2030, with current global phosphorus reserves being depleted in 50-100 years Cordell *et al.* (2009). Phosphorus rock is a finite resource and thus focus is increasing on removing phosphorus from wastewater in such a way that it may be recovered. The technology typically takes one of two routes, either the phosphorus is sorbed onto a substrate type material which then has the potential to be applied directly to land as a fertilizer or, the phosphorus is removed in such as a way that the material produced can be used as a source of phosphorus, as a raw material. Phosphorus recovery is not possible using the currently favoured technology at WWTWs.

Moriyama *et al.* (2001) looked at precipitating calcium phosphate, namely HAP and then looked at its potential as a fertiliser, it was found that this was a good source of plant available phosphorus. This chapter has shown that HAP is a likely end form of calcium phosphate precipitation and therefore there may be potential for the recovery of phosphorus using the pelletised materials studied in this thesis.

Dobbie *et al.* (2009) built on the work carried out by Heal *et al.* (2004) as discussed in Section 3.3 and looks specifically at the use of phosphorus saturated AMD solids directly a fertilizer, this involved monitoring the release of both plant available phosphorus and also any heavy metals which would inhibit its potential use. The Polkemmet ochre was used and was saturated with phosphorus before use, this was then used in tests in both greenhouse and fields trials to compare its performance in relation to that of traditional fertilizers. The plants grown were barley and grass which were then harvested and analysed. It was found that phosphorus saturated ochre performed as well as conventional fertiliser in the short term. Only 4% of the total sorbed phosphorus was released immediately, this slow release has its advantages as it reduces the rate of need for reapplication and also reduces problems with the surface runoff of phosphorus. No significant release of heavy metals was found, but the authors did urge caution that this could well vary between sources of AMD. Another benefit of the application of AMD was that it provided a slight liming effect which is often desirable in agriculture.

3.7 Chapter Summary

This chapter has discussed papers in the field of phosphorus removal and picked out points that are particularly relevant to this study. There has been a large amount of research on various waste materials with many showing a good phosphorus removal capacity. Some papers found adsorption as a dominating phosphorus removal mechanism, others found calcium phosphate to dominant, many stating HAP as a likely end product. In general, low pHs were found to favour adsorption and high pHs and large amounts of soluble calcium to favour precipitation. The waste iron oxides studied in this thesis are expected to remove phosphorus through adsorption. Once pelletised with cement however it seems likely that a calcium phosphate precipitation mechanism will be introduced. The correlation of phosphorus removal with pH and soluble calcium levels, as described by many of the papers reviewed, will help identify the dominant phosphorus removal mechanism.

Papers that have looked directly at the use of AMD solids to remove phosphorus were reviewed, this included some which further looked at their pelletisation with cement. The difference in removal mechanism between the pelletised and unpelletised cement is not fully explored by any paper and so will form an area of investigation of this thesis. Long term column/wetland studies have been performed on materials similar to those studied in this thesis. This thesis will attempt to link the removal mechanism of pellets with their performance in a column situation.

4. Theory

This chapter presents the theoretical background to concepts used in this thesis. Firstly the theories relating to the materials studied in Chapter 6 are presented, this includes adsorption theory and the theory behind adsorption isotherms. Theories relating to the pellet tests presented in Chapter 7 are then discussed, namely cement theory and the basics of precipitation. The theoretical background to the column studies are shown next, this involves the classic adsorption column theory and other models used to present column test results. Finally the methods of calculation for the statistics used are presented.

4.1 Theories relating to the adsorption studies

4.1.1 Adsorption

Adsorption can be defined as the enrichment of a substance at a boundary layer between two phases. This study focuses on the interaction between the solid and liquid phases. Adsorption occurs due to interactions between the adsorbent solids and the adsorbate molecules in the liquid phase. As an adsorbate molecule encounters the solid surface, the intermolecular attractive and repulsive forces will reach a balance.

Adsorption can take the form of either physisorption or chemisorption. Physisorption involves Van der Waals forces, it is a general form of adsorption with little specificity. The sorbed molecules retain their identity and can return to their original state through desorption. Chemisorption involves the exchange or sharing of electrons, thus is dependant upon the reactivity of the adsorbent and adsorbate. Chemisorption only produces a monolayer and the sorbed molecules lose their identity.

4.1.2 Adsorption Isotherms

Adsorption data is often presented as an adsorption isotherm. The amount that a material can adsorb is constant at a constant equilibrium concentration and temperature. Therefore tests at a constant temperature, of a known volume, initial concentration and mass of adsorbent can be performed and once the final, equilibrium concentration is determined, the adsorption isotherm can be plotted. These isotherms can then be used to compare adsorption behaviour in different systems. There are many equations that have been developed to describe this adsorption behaviour, the two most commonly used are the Freundlich and Langmuir equations. Many studies reviewed in Chapter 3 of the current thesis used these equations to describe the adsorption of phosphorus.

4.1.2.1 The Freundlich isotherm

The Freundlich isotherm is the simplest of the theoretical isotherms, it was derived empirically and takes the form;

$$\frac{x}{m} = KC^{n}$$

Equation 4.1

Where x/m is the loading in mg/g, C is the equilibrium phosphorus concentration and K and n are constants (Langmuir 1997)

This can be put into a linear form by taking the logarithms of both sides resulting in

$$\log\frac{x}{m} = \log K + n\log C$$

Equation 4.2

This linear form can then be plotted to determine the coefficients, this is shown in Figure 4.1.

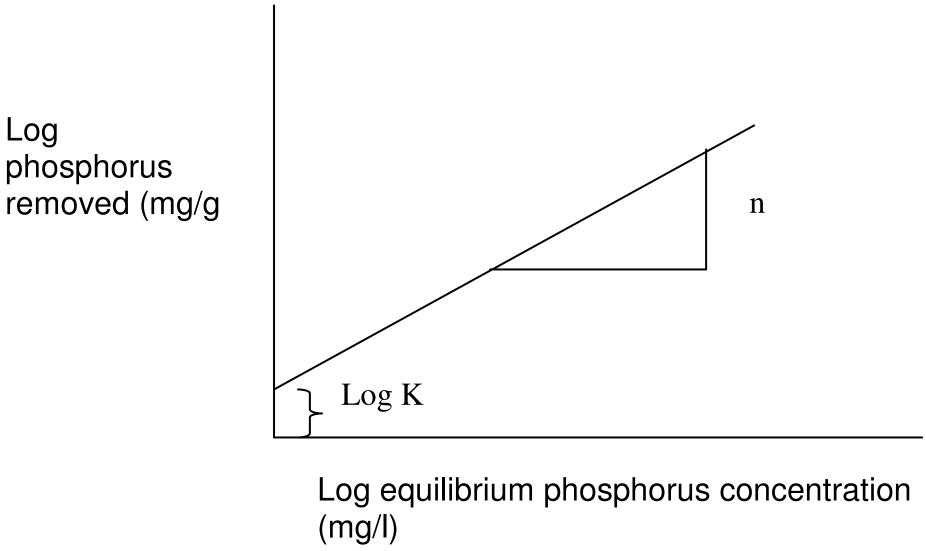


Figure 4.1 Linear form of the Freundlich isotherm

n is determined from the gradient and K can be determined from the inverse log of the intercept.

4.1.2.2 The Langmuir isotherm

The second isotherm used in this study is the Langmuir isotherm, its derivation was based upon a number of assumptions as follows

- There are a fixed number of adsorption sites on the adsorbent, all with the same energy
- Adsorption is reversible
- Equilibrium is achieved when the rates of adsorption d desorption are balanced
- There is no interaction between adsorbed molecules

The Langmuir isotherm takes the form

$$\frac{x}{m}=\frac{aC}{1+bC}=\frac{bCN_{\max}}{1+bC} \qquad \text{Equation 4.3}$$

Where x/m and C are as previously defined, a and b are constants and N_{max} is the maximum loading on the solid, representing monolayer coverage (Langmuir 1997).

The best method of linearisation, so as to avoid any induced correlation is through inversion of all terms

$$\frac{1}{x/m}=\frac{b}{a}+\frac{1}{aC}=\frac{1}{bCN_{\max}}+\frac{1}{N_{\max}} \qquad \text{Equation 4.4}$$

Therefore a plot of the inverse of the phosphorus loading against the inverse of the equilibrium concentration will allow the coefficients to be determined, this is shown in Figure 4.2

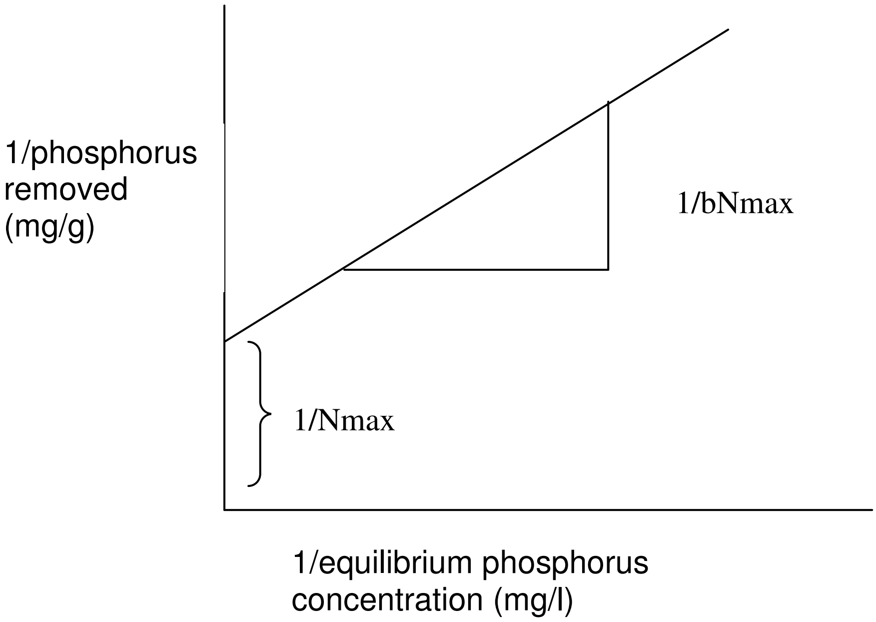


Figure 4.2 Linear form of the Langmuir isotherm

The coefficient Nmax can be determined through the inversion of the intercept which then allows b to be calculated from the gradient.

4.2 Theories relating to the pellet study

4.2.1 Cement theory

Due to the use of Portland cement in the pelletisation of the solids from Horden it is important to have a grasp of the basic conditions governing the reactions occurring. The water/cement ratio is a determining factor upon the strength of the cement, this is shown in Figure 4.3

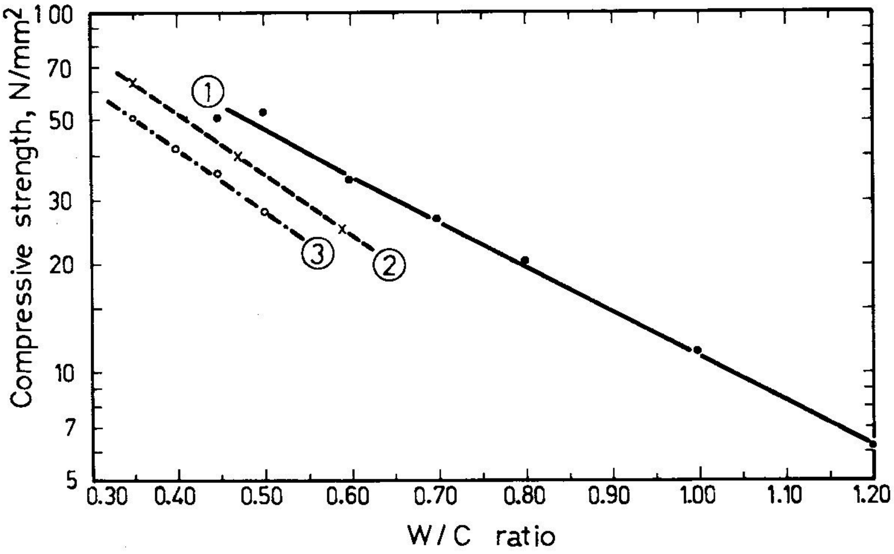


Figure 4.3 effect of water/cement ratio on the compressive strength of concrete the encircled 1, 2 and 3 represent findings from separate studies (Soroka 1979)

For the production of pellets, Portland cement was added so as to form 30% of the final blend, the moisture content of the sludge from Horden was 33% which therefore resulted in a water/cement ratio of 0.73. From the widest ranging study in Figure 4.3 this ratio would result in a compressive strength of 25N/mm^2 this compares to the highest value of 60N/mm^2 represented in Figure 4.3, therefore a ratio of 0.73 seems reasonable. Another important factor is the aging of the cement, Figure 4.4 shows how the strength of cement progresses with age.

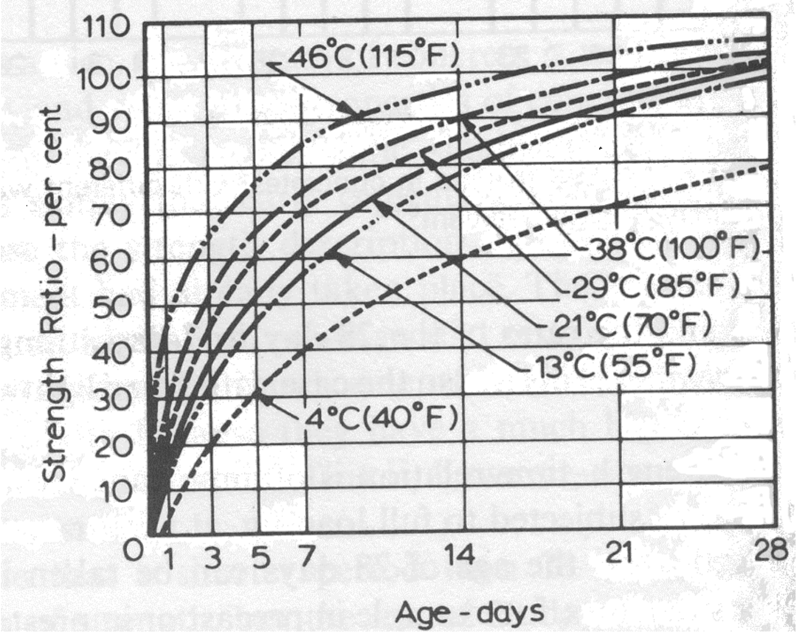


Figure 4.4 the development of concrete strength with age (Neville 1995)

For the majority of the tests involving pellets, the cast blocks were allowed to cure for 7 days at room temperature, Using the 21°C line from Figure 4.4 this suggests that 60% of the final strength will have been achieved by this point. For the column tests, the pellets were allowed to cure for a month before crushing and were over 3 months old before use in the column tests, this was to ensure that there would be no recementation inside the column which would affect the flow. Figure 4.4 shows that essentially all of the cementitious reactions should have occurred within 28 days.

4.2.2 Precipitation/crystallisation

It is shown that through the use of cement to pelletise AMD solids a calcium phosphate precipitation mechanism is introduced, therefore a brief outline of the precipitation/crystallisation process is outlined here. Precipitation is generally considered as a fast process resulting from high levels of supersaturation and forming amorphous products, whereas crystallization can be a slower process resulting in more ordered structures.

There are typically three stages of crystal growth, the first is nucleation, this is the creation of centres where spontaneous growth can happen it is assisted by the presence of solid particles and high shear rates within the fluid. Homogenous nucleation is that which occurs within the bulk fluid phase with no solid interaction. Heterogeneous nucleation is that which occurs in the presence of foreign solids. Secondary nucleation occurs due to the presence of the crystallisation material itself. The next stage is crystal growth where material is deposited onto the nucleation centres. A third stage known as ripening may also occur where large crystals are formed. The relationship between the concentration of the substance which is precipitating from solution and time classically follows the pattern shown in Figure 4.5.

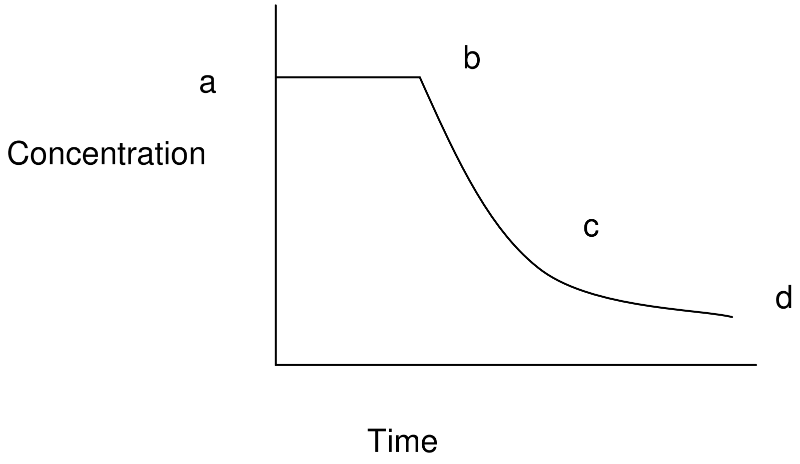


Figure 4.5 Relationship between soluble concentration and time for a precipitating substance (After Khomskii 1969)

In Figure 4.5 the period a-b represents the induction period where nucleation occurs, at high levels of supersaturation this period can be very short. The period b-c represents the rapid formation of crystals and c-d represents slow crystallisation.

4.3 Column Theory

This section discusses the theoretical background to the column tests, much of this is based upon adsorption theory but maybe be analogous to the columns of pellets studied in Chapter 8 although precipitation is thought to be the major mechanism. Firstly the classic column theory is presented and then models for the up scaling of laboratory data are presented

4.3.1 Classic column theory

This section details the underlying theory of adsorption columns. The classic theory is based upon the idea of a Mass Transfer Zone (MTZ) which is the area where the majority of the removal is occurring. The results for column experiments are typically presented as a “breakthrough curve” this plots the effluent concentration leaving the column against the volume of fluid treated. Figure 4.6 shows the progression of the MTZ through a column where the fluid is introduced at the bottom as is the case with the columns used in tests in Chapter 8. The breakthrough curve for this column is also presented, the diagram of the MTZ ties in with the progression of the breakthrough curve.

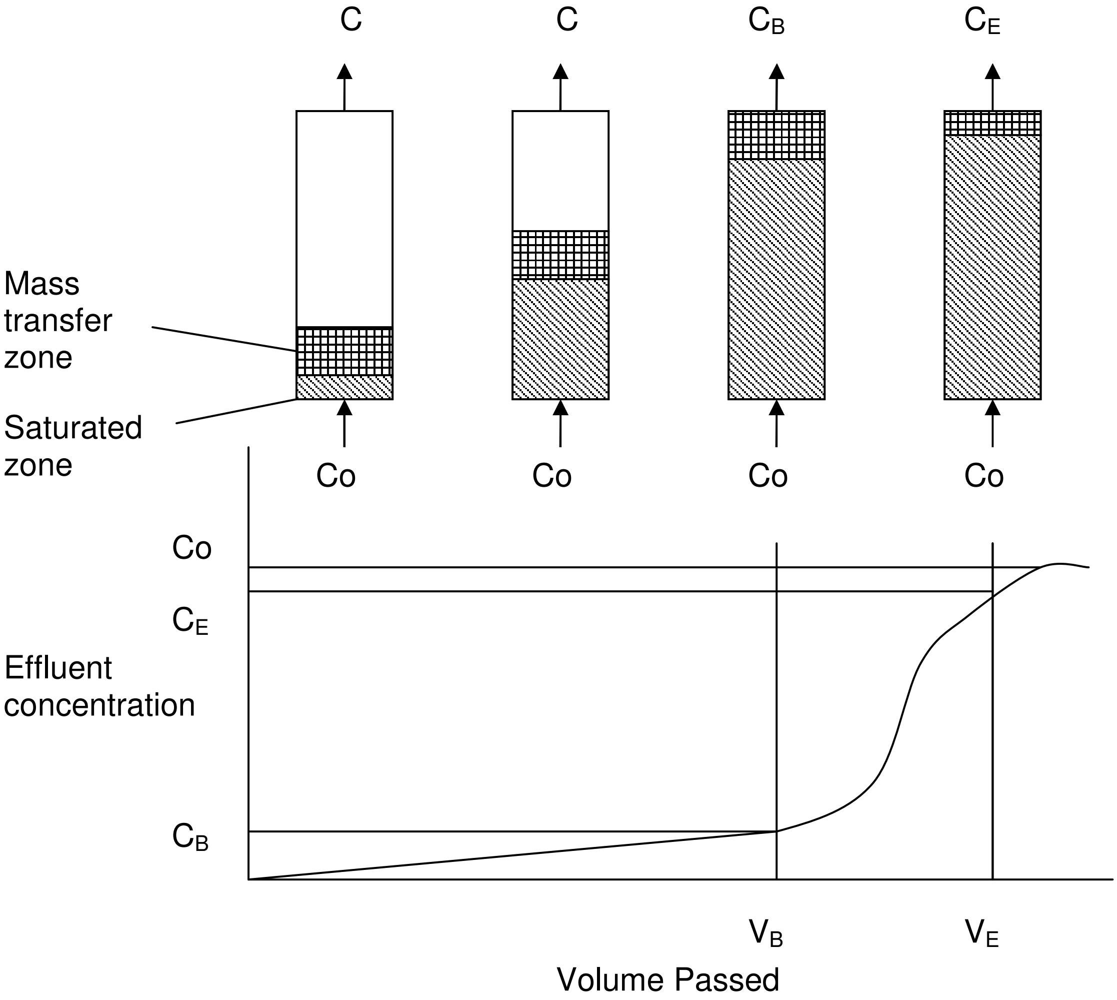


Figure 4.6 The progression of the Mass Transfer Zone (MTZ) through the column and the resultant breakthrough curve (After Sundstrom and Klei 1979)

Figure 4.6 shows the classic adsorption column theory. The contaminated fluid is introduced, in this case, at the bottom of the column with an initial contaminant concentration of Co. The majority of the removal occurs within the mass transfer zone which gradually moves up the column during the test. Behind the MTZ is the saturated zone, here the material is at equilibrium with the influent concentration and no further removal occurs within this zone. As the MTZ nears the outlet of the column, the effluent concentration will begin to rise until it reaches the breakthrough concentration (C_B). This is the chosen maximum effluent concentration which is considered acceptable, for phosphorus at WasteWater Treatment Works (WWTWs) this is likely to be 1mg/l. After the breakthrough point has been reached, the effluent concentration typically quickly rises. The exhaustion point (C_E) is arbitrarily chosen and is typically around 95% of the influent concentration.

4.3.2 Column result models

There are several models that are used for the design of fixed bed adsorbers from laboratory data. Whilst the actual dominant mechanism believed to be in operation here is precipitation, not adsorption, these models may still be used to gain an insight into the up scaling of the lab based column tests.

4.3.2.1 Empty Bed Contact Time (EBCT)

Perhaps the simplest method is the Empty Bed Contact Time (EBCT). Three or more column lengths are used which represent differing contact times. The breakthrough volume for each column length is obtained from the breakthrough curve as shown in Figure 4.6. Knowledge of the mass of material in the column allows the usage rate to be determined in terms of unit weight of material used to treat unit volume of water e.g. kg/m^3. The second value that needs to be calculated is the EBCT, this is done by dividing the bed volume by the flow rate. Once both these values are known the usage rate is plotted against the EBCT as shown in Figure 4.7. This plot thus allows the optimization of the design and a compromise to be achieved between lowering the EBCT and the resultant increase in material usage rate.

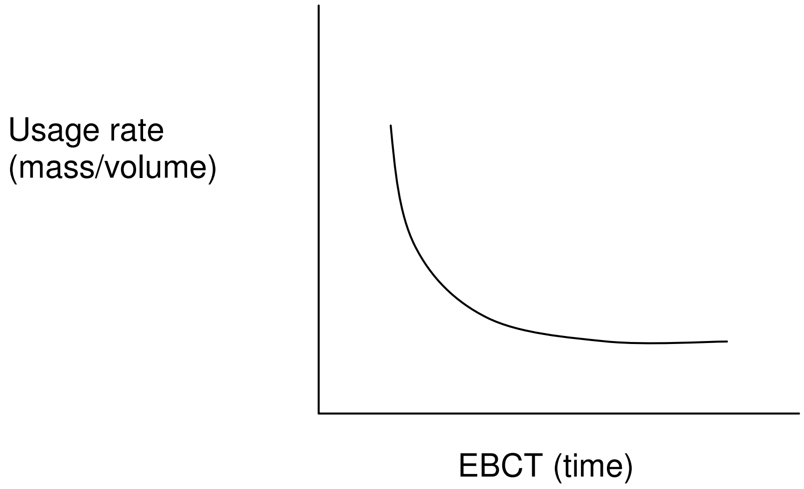


Figure 4.7 EBCT plot (After Crittenden and Thomas 1998)

4.3.2.2 Bed Depth Service Time (BDST)

This method is based upon the Bohart-Adams method but is simplified and requires data from only three column lengths. This theory is based on the plot of the time until breakthrough versus the column depth as shown in Figure 4.8. It is assumed that the adsorption rate is proportional to the residual adsorbent capacity and then remaining adsorbate concentration. The relationship between the two variables, service time, t and bed length, L is given below.

$$t = \frac{N_o}{C_o u}\left[L - \frac{u}{kN_o}\ln\left(\frac{C_o}{C_b} - 1\right)\right] \qquad \text{Equation 4.5}$$

t= service time (time until breakthrough) u = linear velocity, L = bed depth, k= rate constant, No= adsorptive capacity (mass per unit volume), Co = influent concentration, Cb= concentration at breakthrough (Crittenden and Thomas 1998)

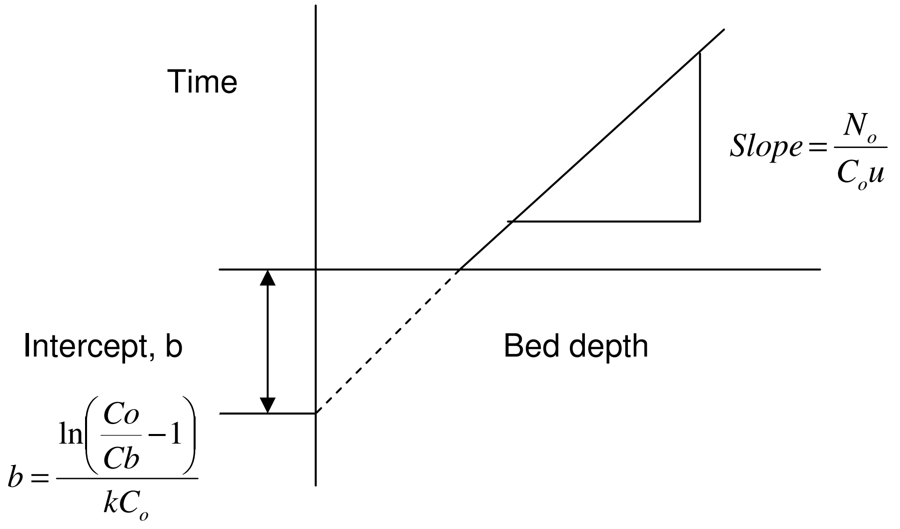


Figure 4.8 BDST plot and significance of the gradient and intercept (After Crittenden and Thomas 1998)

The Mass Transfer Zone Length (MTZL) can be determined through substituting t=0 into equation 4.5, thus

$$MTZL = \frac{u}{kN_o}\ln\left(\frac{C_o}{C_b} - 1\right) \qquad \text{Equation 4.6}$$

4.4 Statistics

Statistics have been used throughout this study to quantify the spread of data, to fit lines of best fit to data and to quantify the wellness of fit of these lines. These calculations have all been carried out automatically using Excel, the underlying theories are presented here.

The standard deviation is a measure of the spread of data around the mean. It is used in this thesis to quantify the variation of results for repeated tests. The standard deviation is calculated from the below equation.

$$s = \sqrt{\frac{1}{n-1}\sum (x_i - \bar{x})^2}$$ Equation 4.7

Where x_i is the value, $\bar{x}$ is the mean and n is the number of observations. (Stroud and Booth 2001)

Throughout this thesis Microsoft Excel has been used to produce linear lines of best fit to data, Excel calculates these lines through the least squares method. This method ensures the vertical distances from the data points to the line are a minimum. The equation of the line is determined from equations 4.8 – 4.10.

$$an + b\sum x = \sum y$$ Equation 4.8

$$a\sum x + b\sum x^2 = \sum xy$$ Equation 4.9

where

$$y = a + bx$$ Equation 4.10

(Stroud and Booth 2001)

From the calculation and summation of the values x,y,xy and x^2 the coefficients and therefore the equation of the line can be calculated.

The coefficient of determination, R^2 quantifies how well the least squares line fits the data, this is equal to the regression sum of squares divided by the total sum of squares, this can be expressed as;

$$R^2 = \frac{S_{xy}{}^2}{S_{xx} S_{yy}}$$ Equation 4.11

Where

$$S_{xy} = \sum xy - \frac{\sum x \sum y}{n}$$ Equation 4.12

$$S_{xx} = \sum x^2 - \frac{\left(\sum x\right)^2}{n}$$ Equation 4.13

$$S_{yy} = \sum y^2 - \frac{\left(\sum y\right)^2}{n}$$ Equation 4.14

(Swift 1997)

Further to the use of the coefficient of determination, R^2, to analyse how well the theoretical isotherms describe the data the chi squared test was also used to quantify the wellness of fit of the plotted theoretical isotherms to the plotted data. The chi squared test takes the form of;

$$X^2 = \sum_{i=1}^{n} \frac{(O_i - E_i)^2}{E_i}$$ Equation 4.15

(Moore 1995)

Where X^2 is the chi squared value, O is the observed value, i.e. my data and E is the expected value i.e. the value predicted by the isotherm. The chi squared test thus allows the wellness of fit of isotherms across the same data range to be directly compared.

4.5 Chapter summary

This chapter has described the theories behind the concepts used in support of this thesis, this included theories relating to adsorption and precipitation as well as the background to the continuous column tests. The methods of calculation for the statistics used to describe the data presented in this thesis were also described.

5. Materials and methods

This chapter describes the materials that were used in the experimental part of this thesis and lays out the experimental procedures and equipment used. The nature and origins of the materials used in the batch adsorption studies are discussed and their chemical compositions and surface areas presented. The experimental procedures used for experiments on these materials are then shown. Next the pellets produced from the addition of cement to the sludge from Horden minewater treatment plant are discussed. The method of pellet production is described as is the resultant pellet composition. Scanning Electron Microscope (SEM) micrographs of the pellets are presented to allow an assessment of their morphology and the surface area and pore details are given. The experimental procedures used for the batch tests on the pellets are then laid out and finally in this chapter, the details of column tests on pellets are presented. Firstly the design of the columns used is shown; this is followed by the design of the rig used. The method of pellet production of these tests is discussed and then the operational details of the column test are presented.

5.1 Materials used in the adsorption studies

This section describes the materials used in batch adsorption studies, their chemical composition, surface area and the procedures used in these tests.

5.1.1 Materials description

This section describes all four materials used in the batch adsorption experiments presented in this thesis, discusses their origins and presents photographs of each.

5.1.1.1 Solids from Horden minewater treatment plant

The principal material used in the experimental part of the current thesis was the solids from the treated effluent of the Horden minewater treatment plant, located near Durham in the UK. The treatment plant actively treats the mine effluent, caustic soda is dosed which raises the pH and causes the precipitation of contaminants, this then allows the water to be safely discharged. This material was received in large batches of 10-80 kilos in sealed boxes or barrels. The material was received in its wet state, the solids forming a dense cake at the bottom of the storage container with water on top of this. This material was stored at room temperature in these sealed containers. This sludge is a dark orangey-brown colour, as can be seen in Figure 5.1 which shows the residual sludge as it leaves the centrifuge at the treatment plant.

Figure 5.1 Photograph showing the treated sludge form Horden minewater treatment plant as it is discharged from the centrifuge at the treatment plant.

Through both air drying until weights were constant and drying in an oven at 100°C overnight, a moisture content of 33% was found for this material.

5.1.1.2 Filter cake from a water treatment plant

The second material studied was an iron rich filter cake from a water treatment plant based in South-East Wales, this material is shown in Figure 5.2. This material was received in sealed sample bags and in a wet state with all water retained within the solids, it was stored in sealed bags, in the fridge at 4°C. Its moisture content was determined in a 100°C oven overnight and was found to be 80%. The individual flocs shown in Figure 5.2 have dimensions in the order of 5cm.

Figure 5.2 Photograph showing the filter cake from a water treatment plant

5.1.1.3 The commercial phosphorus adsorbent, Rowaphos

Rowaphos is a commercial phosphorus adsorbent, primarily targeted at use for phosphorous removal for home aquariums. It has also been used in large applications such as the treatment of a lake in Berlin and also to control phosphorus at the Beijing Olympics (D-D The Aquarium Solution).
Rowaphos is akaganeite (βFeO-OH) (Jekel and Genz) with a moisture content of 35%. It was stored in its sealed packaging in the fridge at 4°C. Rowaphos is a

very dark brown granular material with a particle size of around 3mm it is shown in Figure 5.3.

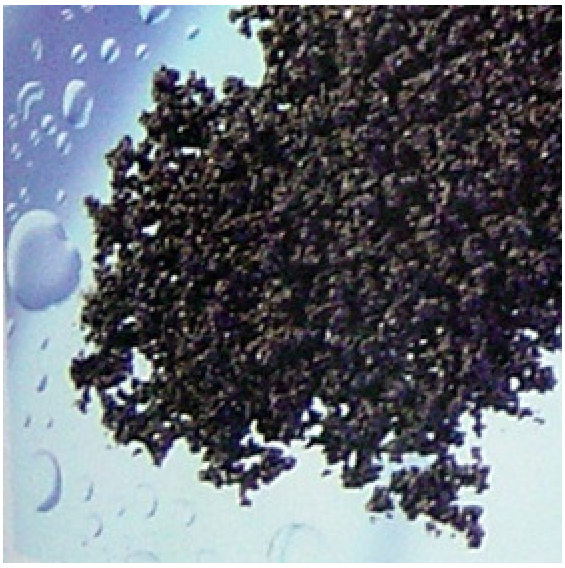


Figure 5.3 Photograph of the phosphorus adsorbent Rowaphos (D-D The Aquarium Solution)

5.1.1.4 Solids from the Dawdon minewater treatment plant

Solids from the minewater treatment plant at Dawdon, Durham, UK were also obtained but at a much later stage in the study. The Dawdon plant uses a High Density Sludge (HDS) process to actively treat the mine effluent, using lime as a pH elevator (Coal Authority). The solids were received in a dry state and were similar to the solids from Horden when dried. This material was received in chunks in the order of 5-10cm composed of fine material and was stored in the laboratory in sealed bags. The solids from Dawdon are shown in Figure 5.4, the blocks shown have dimensions in the order of 5cm.

Figure 5.4 Photograph of the solids from the Dawdon minewater treatment plant

A fifth material was initially studied, this was another AMD sludge from the Parys Mountain copper mine, located in North-East Anglesey, UK. This material was not used in the adsorption studies due to its chemical composition, as explained in Section 5.1.2

5.1.2 Chemical composition and surface area.

The chemical compositions of the four materials were determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). This was carried out through digestion of the sample. 0.1g of dry sample was weighed on a balance accurate to 0.0001g. The samples were digested in a Perkin Elmer p1200 microwave using 10ml of aqua regia made from 1 part HNO_3 to 3 parts HCl. The fully digested sample was then analysed for the presence of 12 elements (aluminium, barium, calcium, copper, iron, potassium, magnesium, manganese, sodium, titanium, zinc and tungsten). Total carbon and sulphur concentrations were determined on 1 g samples of dry powdered material using a SC144DR Leco furnace. The solids from the Dawdon minewater treatment plant were not included in the chemical or surface area analysis as they were received much later on in the study. The percentage content by weight for the four samples is shown in Figure 5.5, only the elements that were found to have concentration above 1% are included.

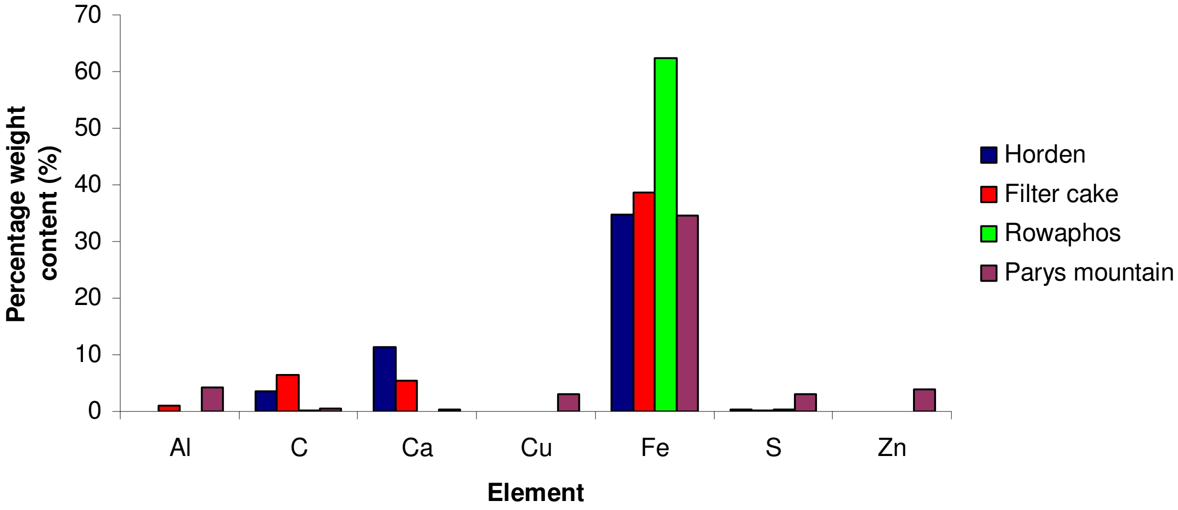


Figure 5.5 Elemental concentrations of materials studied.

The solids from Parys Mountain were discounted from the adsorption studies due to the levels of undesirable contaminants. These solids were found to have an Aluminium concentration of 4.2%, copper of 3%, sulphur of 3% and zinc of 3.8%. It was felt that this composition could be a block towards its use at WWTWs and therefore this material was not used in any phosphorus removal studies.

The solids from Horden were found to contain 35% iron by weight with 11% calcium and 4% carbon also present. Both the solids from Parys Mountain and the filter cake from the water treatment plant contain similar amounts of iron to the solids from Horden. The filter cake also contains 6% carbon, 5% calcium and 1% aluminium.

Rowaphos is reported as being pure βFeO-OH (akaganeite) by Jekel and Genz, iron represents 62.8% of that equation by weight, the value found in Figure 5.5 was 62.4% thus showing good agreement with the expected value.

5.1.3 Surface area

Surface area is an important factor in adsorption, the higher the surface area, the more adsorption sites being available. Brunauer Emmett Teller (BET) analysis was carried out in collaboration with Cardiff University's School of Chemistry. Dried samples were provided as requested by the School of Chemistry. The BET method uses the adsorption of nitrogen and the BET isotherm to determine surface area. The results of this analysis are shown in Table 5.1.

Table 5.1 Surface areas of materials studied

Material	Specific surface area (m^2/g)
Solids from Horden	64
Filter Cake	13
Rowaphos	34

Adler and Sibrell provide the surface area of three AMD flocs, these are in the range 85.4-119m^2/g. Geelhoed *et al.* (1998) studied phosphorus sorption onto a goethite with a specific surface area of 96.4m^2/g. These values higher but comparable to the solids from Horden, the other two material studied in the current thesis were found to have relatively low surface areas.

5.1.4 Methodologies for batch adsorption tests

The test methods for batch adsorption tests on the materials described in Section 5.1.1 fall into two categories, firstly the initial kinetic tests carried out upon the solids from Horden and secondly the batch equilibrium adsorption tests, which followed the same pattern for all materials. The stock solution used in these and all following tests was prepared by dissolving 4.3871g analytical grade KH_2PO_4 in 1 litre of deionised water to create a stock solution of 1g/l as total phosphorus.

5.1.4.1 Kinetic test methodology

The steps used in performing the experiments to determine the rate of phosphorus uptake by the solids from Horden are as follows:

1. Two 1l glass vessels were soaked overnight in a solution prepared from Decon 90, a phosphate free cleaning agent. In the morning the vessels were thoroughly rinsed with tap water and then with deionised water. 800ml of deionised water were then measured into these vessels
2. 8 ml of 1g/l stock solution was prepared from KH_2PO_4 and was added to each of the 800ml solutions to produce an initial concentration of 10mg/l
3. Both a 2g and a 3g sample of powdered, dry Horden solids were weighed out on a balance capable of accuracy to four decimal places. When added to the 800ml solutions these resulted in 1.25 and 3.75g/l solids concentrations
4. These solids were added to the phosphorus solutions, the flocculator stirring paddles lowered into the solutions and their rotation started at 180rpm. The flocculator used is shown in Figure 5.6
5. At the appropriate time the glass vessel was removed from the flocculator and approximately 30ml of solution poured into a vacuum filter. 0.44μm cellulose nitrate membrane filters were used. The glass vessel was then returned to the flocculator as soon as possible.
6. The vacuum filter setup was washed through with a plug of approximately 30ml of deionised water between the filtering of each sample to avoid contamination. This was particularly important as, unavoidably, the samples were filtered in the order of high concentrations to lower concentrations.
7. After the conclusion of the hour long tests the pH of all filtered samples was determined. This was performed with a Severn multi mettler Toledo with an expert pro pH probe, this was capable of a precision of three decimal places
8. The samples were then stored in the fridge at 4^oC until analysis by the ICP-OES for phosphorus, this was carried out within a week of the test

and was determined at a wavelength of 213.617nm, the ICP-OES was calibrated at 0.1,1 and 10 mg/l.

Figure 5.6 Photograph of the flocculator used for the kinetic tests on the solids from Horden

5.1.4.2 Equilibrium batch test methodology

The batch equilibrium adsorption tests for all four materials were carried as detailed below.

1. 0.5g of solids was weighed out on a balance capable of a precision up to 0.0001g. This was carried out for each test
2. Each 0.5g of solids were placed in a 60ml polypropylene sample pot
3. The appropriate volume of deionised water for dilution was pipetted into the sample pot
4. The appropriate volume of 1g/l as total phosphorus stock solution was pipetted into the sample pot. The initial concentrations ranged from 28-

560mg/l, apart from the tests on the solids from Dawdon where the initial range was 50-150mg/l.

5. For an initial concentration of 25mg/l the solution would have contained 39ml of deionised water and 1ml of stock solution
6. The sample pots were then fixed horizontally on the orbital shaker table shown in Figure 5.7. The shaker table was set at 180rpm to ensure good mixing and started
7. After the 16 hours the samples were removed from the shaker table and vacuum filtered using 0.44µm cellulose nitrate membrane filters
8. Samples were filtered in the order of lowest concentration to highest concentration so as to avoid contamination. Around 10ml of sample was also passed through the filter before the full sample was filtered to further avoid contamination
9. The pH of the filtered samples was carried out using a Severn multi mettler Toledo meter with an expert pro pH probe which is capable of a precision of three decimal places
10. The samples were stored in the fridge until analysis by the ICP-OES for phosphorus, this was carried out within a week of the test completion. Phosphorus concentrations were determined at a wavelength of 213.617nm and the ICP-OES was calibrated at 1,10 and 100 mg/l for most tests and at 0.1,1,10mg/l for the tests on the Dawdon solids.

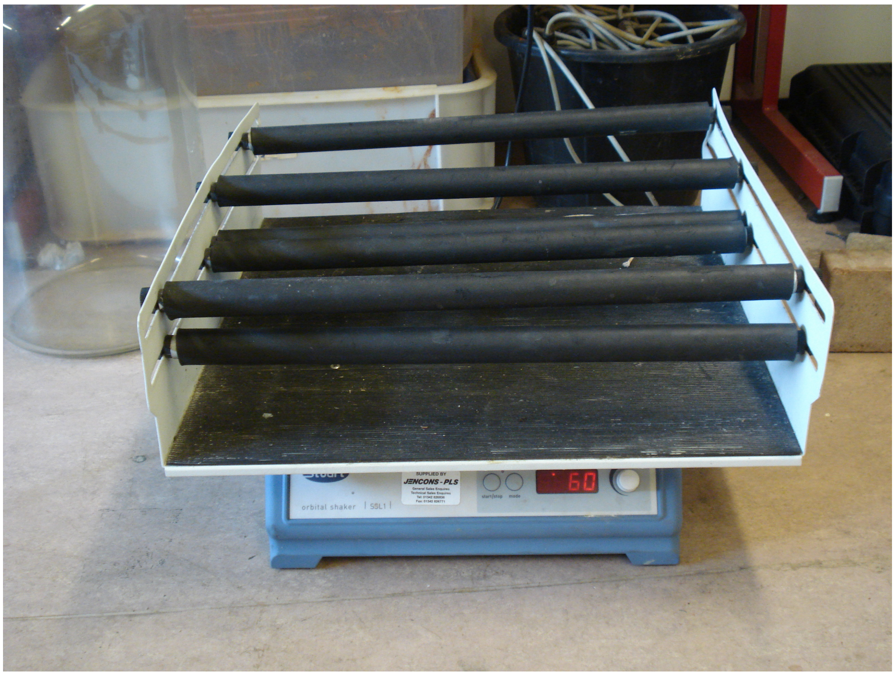


Figure 5.7 Photograph of the shaker table used in the batch experiments

5.2 Pellet study: batch tests

This section describes the methods of production of the pellets produced from the sludge from Horden minewater treatment plant. The composition of the pellets, their surface area and pore details are then presented. The morphology of the pellets is investigated through Scanning Electron Microscope (SEM) photographs and finally the methodologies used for batch tests involving these pellets are presented.

5.2.1 Pellet production

5.2.1.1 Pellets produced from Horden solids and cement

Pellets were produced through the addition of Portland cement to the sludge from Horden so as to form 30% by weight of the total blend. The addition of cement at 30% was decided upon following the work of Sibrell and initial tests carried out by the author showing this to produce solid pellets. This blend was cast into a block, allowed to cure for seven days and then crushed into pellets, the details of this process are shown below.

1. A large sample in the order of 3kg of the wet sludge from Horden was homogenised in a dough type mixer, as shown in Figure 5.8
2. A small sample of this sludge in the order of 100g was taken for moisture content determination, this was determined through the air drying of the sample until the weight was constant.
3. 2100g of the homogenised sludge and 900g of Portland cement were separately weighed out and then mixed together with the mixer set to its highest rate. The mixer was occasionally stopped to allow the material stuck to the side of the bowl to be scrapped off to ensure a complete mix.
4. After 5 minutes of mixing, the blend was completely homogenous and was transferred into 250x50x50mm steel cast
5. The blend was added a small mass at a time to the cast and well compressed using a palette knife so as to form a solid, cohesive block
6. The cast was then well wrapped with Clingfilm to minimise the loss of moisture and left to cure for six days
7. After six days the block (example shown in Figure 5.9) was removed from the cast and well crushed with a hammer
8. The small particles (pellets) were then sieved through the appropriate sized sieves on a vibrating separator, shown in Figure 5.10
9. The pellets were dry sieved until all the fines were separated, this was assisted through the brushing of the pellets across the sieve.
10. The pellets were then stored in sealed plastic sample bags until the next day, when they were 7 days old and were ready to be used in tests. The pellets were aged for 7 days to allow the majority of the cementations reactions to have occurred (see Figure 4.4).

The produced pellets were found to be robust, after the longest test length studied, three weeks the pellets were still found to be solid with no fines released into solution.

Figure 5.8 Photograph of the dough type mixer used for the mixing of cement and the sludge from Horden minewater treatment plant

Figure 5.9 Photograph of a cast block after 6 days curing produced from the addition of cement to the sludge from Horden. The block is 250mm long and 50mm square.

Figure 5.10 Photograph of the vibrating siever used to separate the pellets into the desired size fractions.

5.1.1.2 Pellets produced without the solids from Horden

Two sets of pellets were produced without the solids from Horden. Pellets were produced where the solids from Horden were replaced by crushed sand. To produce these a volume of sharp sand was obtained from the concrete laboratory at Cardiff University's School of Engineering. The sand was dried and then crushed to fine. The water cement ratio was kept the same as for the pellets containing the solids from Horden and the pellets were produced in the same manner as detailed in Section 5.1.1.1.

Pellets were also produced from a concrete sample obtained from the concrete laboratory at Cardiff University's School of Engineering. This was a cured concrete sample that had been used in an unconfined compression test. This sample was crushed using a hammer and pellets produced as per step 9 and onwards in Section 5.1.1.1.

5.2.2 Pellet composition

The sludge received from Horden had a constant moisture content of 33%. Cement was added so as to form 30% by weight of the final mix, this lead to the pellet composition shown in Figure 5.11

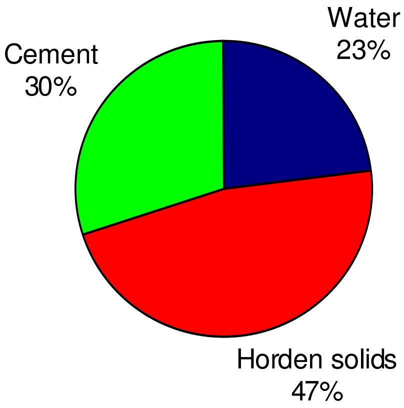


Figure 5.11 Composition of pellets produced from sludge from Horden minewater treatment plant and cement. Percentages are on a mass basis.

This composition results in a water to cement ratio of 0.77. Figure 4.3 suggests that this is a reasonable ratio in terms of strength with a ratio of 0.77 giving a strength of 25N/mm^2, at the mid point of strengths reported in Figure 4.3.

The pellets produced with the solids from Horden replaced by sand, the results for which are shown in Section 7.9 had exactly the same composition as shown in Figure 5.11 but with the Horden solids directly replaced by crushed sand.

No details are known of the composition of the concrete block obtained from the concrete laboratory at Cardiff University's School of engineering which was crushed to make pellets.

5.2.3 Pellet surface area, pore volume and pore diameter

As with the raw materials described in Section 5.1 the 45-63 and 63-125 micron pellets were sent for BET analysis. This was again carried out in conjunction with the Cardiff University School of Chemistry. Along with the specific surface area (m^2/g) the pore volume (cubic centimetres per gram) and the average pore diameter (Ångströms) were also determined. The results for this analysis are shown in Table 5.2

Table 5.2 BET analysis on pellets produced from Horden sludge and cement

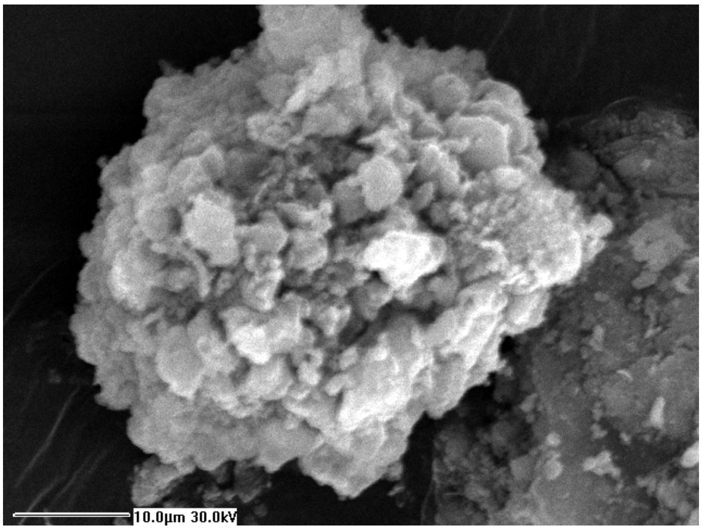
Pellet Size (μm)	Surface Area (m^2/g)	Pore Volume (cc/g)	Average Pore Diameter (Å)
45-63	1.768	0.07852	177.7
63-125	2.922	0.11374	188.1

Å = Ångström = 0.1nm

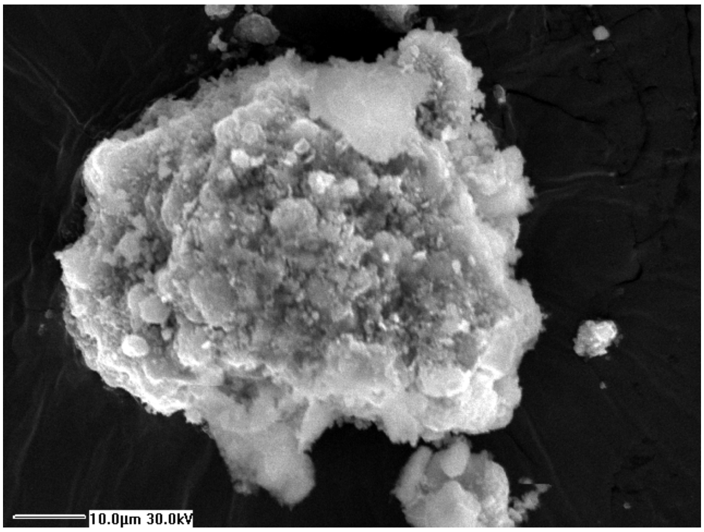
Table 5.2 shows that surprisingly it was found that the smaller pellets in fact were found to have the lower surface area by almost a factor of two, the larger pellets were found to have a larger pore volume. Both pellet sizes essentially have the same average pore diameter. The BET analysis on the solids from Horden shown in Section 5.1.4 found a specific surface area of 64 m^2/g. Pelletisation has therefore resulted in between a 22 and 36 fold reduction in surface area. Agyei *et al.* (2002) studied blends of fly ash, slag and Portland cement, mean particle diameters range from 20.8-31.4 microns and the specific surface areas 1.29-1.42m^2/g. Both the pellet size and specific surface areas of the materials studied by Agyei *et al.* (2002) are therefore comparable to those of pellets studied in this thesis.

5.2.4 Pellet morphology

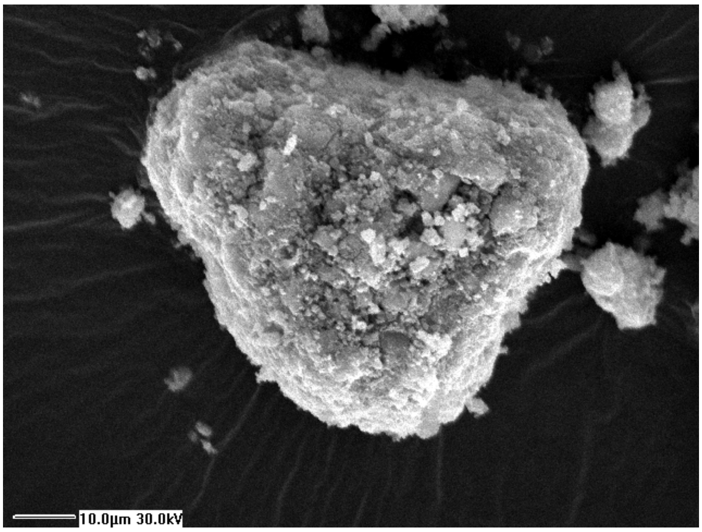
The morphology and appearance of the pellets produced was studied using a Scanning Electron Microscope (SEM). This analysis was carried out at the Cardiff University School of Engineering by the author with the assistance of a laboratory technician. Micrographs are presented of both 45-63μm and 63-125μm pellets in Figure 5.12.



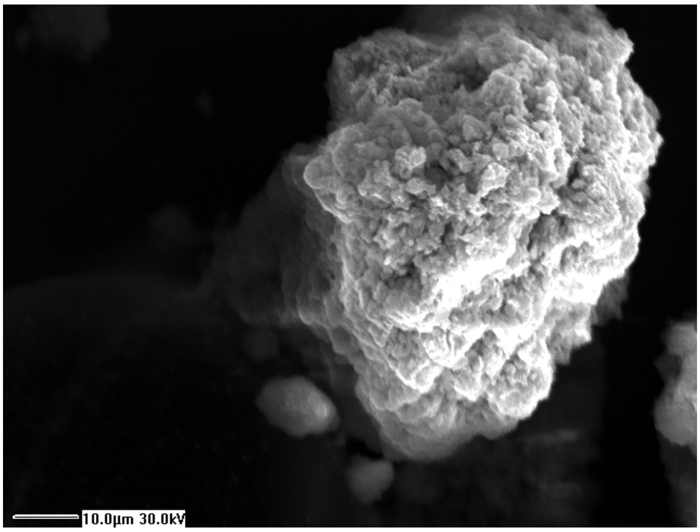
(a) 45-63μm pellet



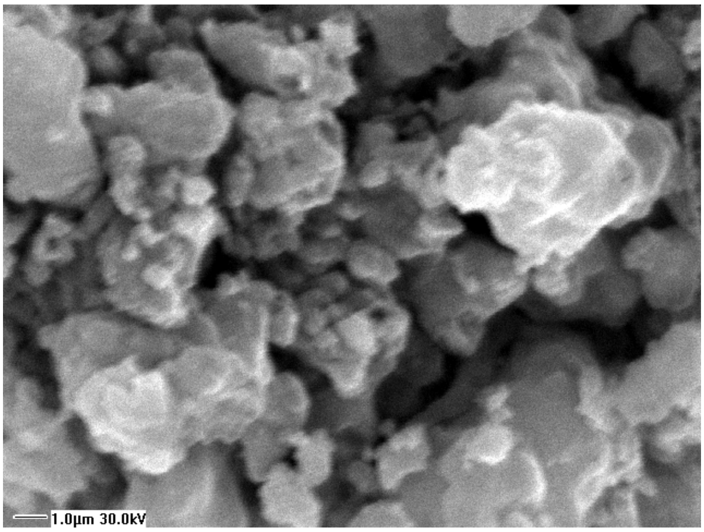
(b) 45-63μm pellet



(c) 63-125µm pellet



(d) 63-125µm pellet



(e) close up on surface of pellet shown in (a)

Figure 5.12 SEM micrographs of pellets (a,b) 45-63 micron pellets, (c,d) 63-125 micron pellets, (e) close up of surface of pellet shown in (b).

Both pellet sizes were found to have similar, rough, surfaces this being quite rough. The close up of the pellet's surface shown in Figure 5.12 (e) shows the pellet surface to be composed of particles in the order of 1 micron. There are valleys in the pellets surface which will assist in the contact of the pellet with the water.

5.2.5 Methodologies for kinetic pellet tests

The kinetic tests lasting one hour were carried out in a similar fashion as the kinetic tests detailed in Section 5.1.5.1. Three such tests were performed, two on 45-63µm pellets (0.3g and 0.4g) and one test on 63-125µm pellets (0.3g). The weight of material was the only difference to the methods used in Section 5.1.5.1 and so this methodology is not repeated here.

5.2.6 Methodologies for batch pellet tests

This section details the procedures used for the majority tests involving the pellets produced from the addition of cement to the sludge from Horden minewater treatment plant.

1. 0.1g of seven day old pellets were weighed out on a balance capable of a precision of four decimal places, these were placed in a 60ml polypropylene sample pot
2. The appropriate volume of deionised water for dilution was pipetted into the sample pot
3. The appropriate volume of 1g/l as total phosphorus, KH_2PO_4 derived stock solution was added to the deionised water
4. The sample pot was then fixed horizontally on the rotary shaker table (shown in Figure 5.7) which was set at 180rpm so as to ensure good constant mixing. The samples were left on the shaker table or the required time (up to three weeks)
5. After the appropriate time the samples were removed from the shaker table and vacuum filtered using 0.44µm cellulose nitrate membrane filters
6. Samples were filtered in the order of lowest concentration to highest concentration so as to avoid contamination. A small volume (5-10ml) of sample was passed through the filter before the sample was filtered so as to further eliminate any contamination.
7. The pH of the filtered samples was then measured using a Severn Multi Mettler Toledo meter with an expert pro pH probe, this is capable of a precision of three decimal places
8. The samples were stored in the fridge at $4^{o}C$ until analysis by the ICP-OES for phosphorus and calcium. Analysis was carried out within a week of the samples being filtered Phosphorus was determined at a wavelength of 213.617nm and the ICP-OES was calibrated at 0.1,1 and 10 mg/l for the tests with lower concentrations and 1,10 and 100mg/l for the higher. Calcium was determined at a wavelength of 317.933 and the ICP-OES was calibrated at 1,10 and 100mg/l

The above describes the method employed for the majority of phosphorus removal tests on pellets. Kinetic tests lasting 16 hours were carried out, these followed the above method with 0.1g of pellets used in 40ml solutions. Six tests were started with an initial concentration of 130mg/l a test was removed and filtered after 0.5,1,3,5,8 and 16 hours. The initial appreciation batch tests were carried out in the same manner as described here except 0.5g of pellets was used and the total volume was 100ml, the results for these tests are in Section 7.1. The tests where the weight of pellets were varied whose results are shown in Section 7.8 were carried in exactly the same fashion as described above, the only variation being the change in pellet weight to between 0.0044 and 0.008g and the initial concentration was maintained at a constant 11mg/l.

5.3 Pellet study: continuous column tests

This section presents the details of the column tests carried out. The design of the columns and rig used are shown and the procedures of the production of the pellets and the operational details of the columns are then presented

5.3.1 Column details

A schematic of the columns used is shown in Figure 5.12. The total length of the columns was 40cm. Starting from the bottom, after the inlet there was a 5cm gap, this was included to ensure the water was distributed across the whole cross-section of the column. Next was a 1cm deep plastic filter, this was perforated with 5mm holes, the job of this filter was to support the 2cm bed of sand which in turn supported the pellets. The total depth of pellets was 30cm and every 10cm after the start of the pellets there was a sampling port. Attached to this was a 5cm long, 3mm internal diameter pipe which reached into the centre of the column, this ensured samples were taken from the centre of the column. This 3mm tubing had a small amount of glass wool inside it to filter out any pellets that may have otherwise flowed out of the column.

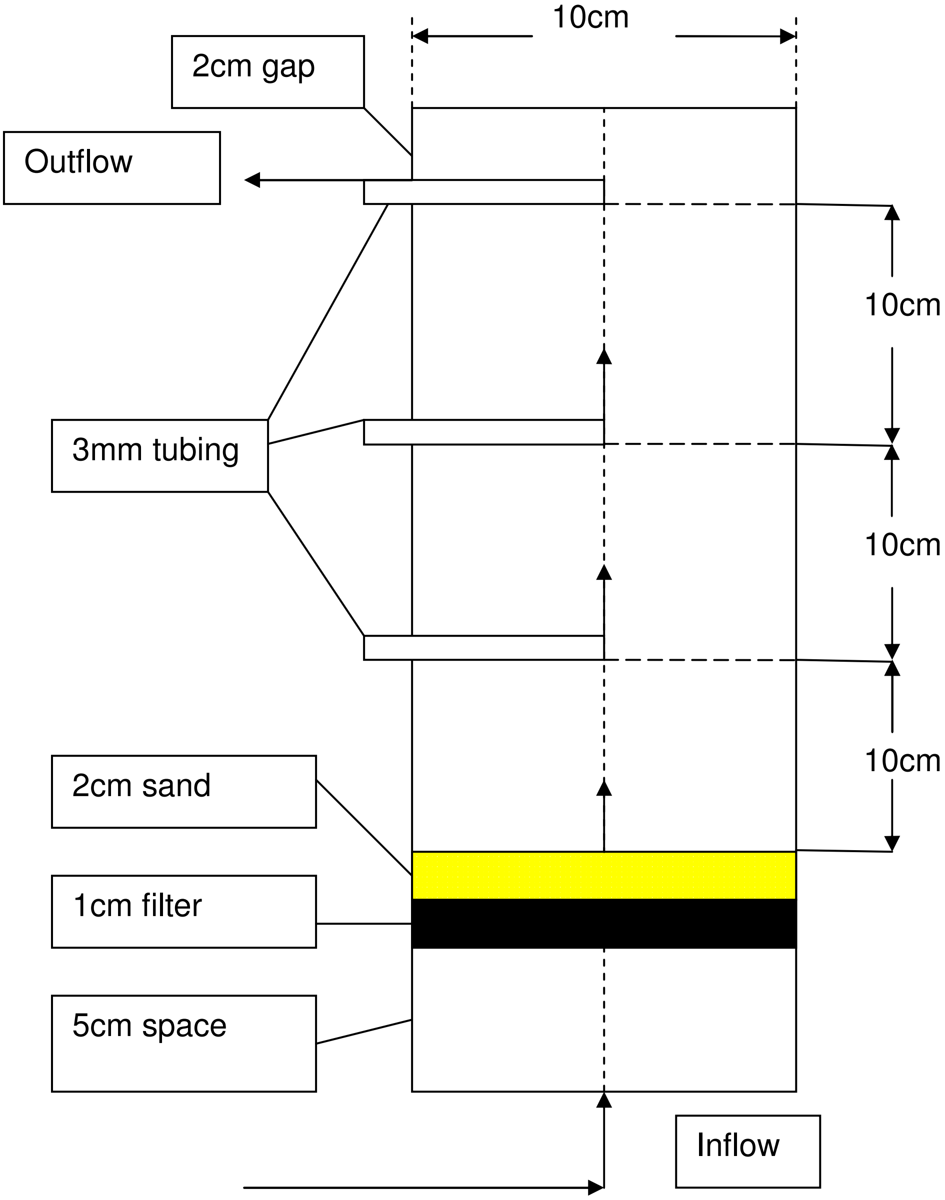


Figure 5.12 Schematic of the column used in continuous phosphorus removal tests

5.3.2 Column test rig design

The design of the column test rig was based upon the idea of a re-circulating main from which, through a manifold, the flow to the columns could be controlled through the use of pinch valves. The piping used had an internal diameter of 7mm. The manifold was constructed using three T-pieces which allowed the flow to be split. Two Intermediate Bulk Containers (IBC's) were used as influent and effluent reservoirs, these both had a capacity of 1m^3. A peristaltic pump was used to pump the water, this allowed flow to be drawn from the top of the influent IBC. The columns were placed on top of the receiving IBC and a spirit level was used to ensure that they were level. A schematic of the rig design is shown in Figure 5.14 and an annotated photograph of the setup is shown in Figure 5.15. A close up of the manifold is shown in Figure 5.16 and a picture of the outflows in Figure 5.17.

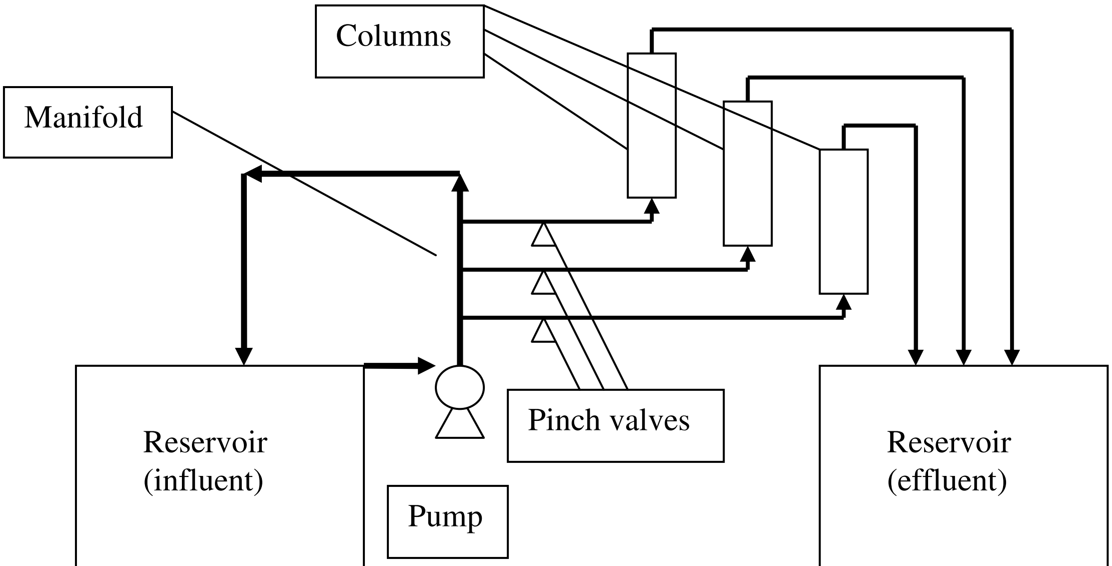


Figure 5.14 Schematic of the rig design for the column tests

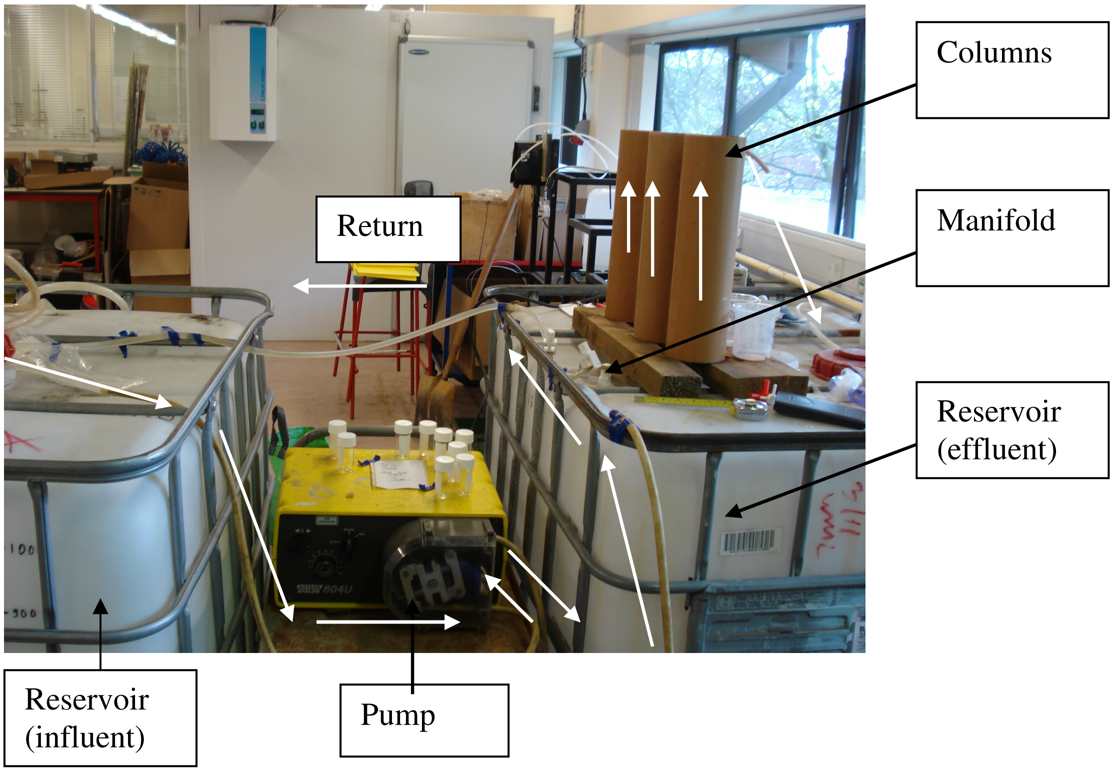


Figure 5.15 Annotated photograph of the rig setup for the column tests

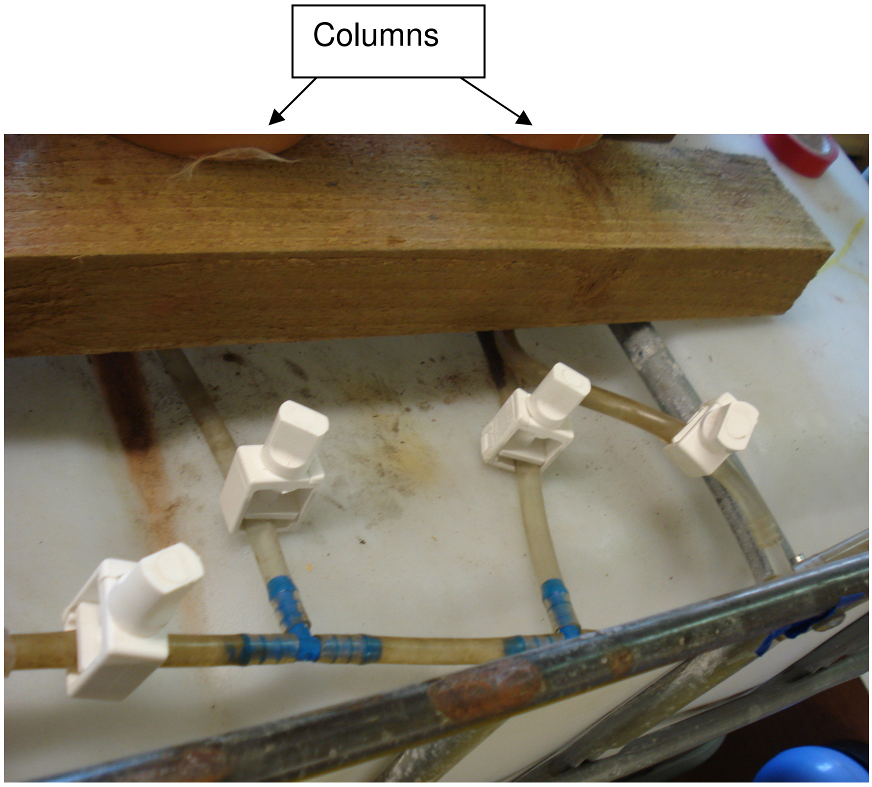


Figure 5.16 Photograph of the manifold and flow controlling pinch valves

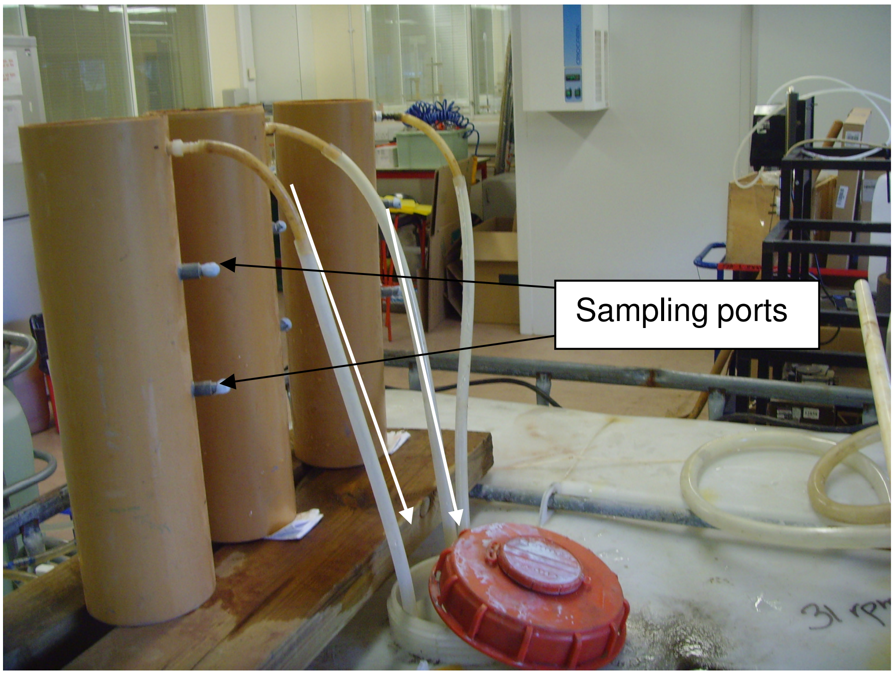


Figure 5.17 Photograph of the outflow from the columns into the receiving reservoir

5.3.3 Column pellet production

The method of pellet production for the column tests varied from the previous methods due to the larger batches produced. The cast blocks were allowed to cure for 28 days rather than 7 days so as to avoid any potential of re-cementation inside the column. The method of production is detailed below.

1. A linear drum mixer with a capacity of 163kg was used to enable pellet production on a larger scale, this can be seen in Figure 5.18.
2. Pellet production was based upon using a 25kg sack of Portland cement representing 30% of the final mix therefore 58.3kg of the sludge from Horden was weighed out and placed in the drum mixer. The sludge was mixed to homogenise the sludge and a small sample was taken for moisture content determination.
3. The 25kg sack of Portland cement was added to the homogenised sludge and the drum mixer restarted

4. The mixing was regularly paused to scrape material out of the edge to ensure complete mixing and after 10 minutes the mixture was completely homogenous
5. The mixture was then transferred to two plastic storage containers, a plasters' trowel was used to compact the sludge into the storage containers
6. The lids of the storage containers were then taped onto the containers which were then wrapped in cling film to ensure a tight seal and the cast blocks were allowed to cure for 28 days
7. After 28 days the blocks removed from the containers and the two blocks were initially crushed with a hammer to chunks with dimensions in the order of 10cm
8. These pieces were then placed in a ball mill for 2 hours, this is shown in Figure 5.19. The ball mill was approximately one third full of ball bearings with a diameter of 5cm and one third full of the 10cm chunks. The final third was left empty to ensure enough space for the crushing to take place
9. After two hours the contents of the ball mill were tipped into the grid shown in Figure 5.19 to remove the pellets from the ball bearings
10. The pellets were then dry sieved on the sieving apparatus shown in Figure 5.10, the sieve sizes used were 1180, 840, 500, 300, 212, 125 and 63µm
11. Once the majority of the fines were removed from the pellets, they were wet sieved. The dry followed by wet sieving was carried out to minimise the washing of the pellets and therefore the leaching of the active hydroxide ion and calcium content. The pellets were washed until the water ran clear
12. The pellets were then laid out and allowed to air dry
13. The dry pellets were then weighed in their size fractions to determine the particle size distribution, this is shown in Figure 5.21
14. All pellets were then laid onto a concrete mixing base and carefully blended using a trowel, this is shown in Figure 5.20. The fully mixed pellets were then ready to be introduced into the column.
15. The pellets were three months old at the start of the column tests due to the time taken to crush them and other factors delaying the start

Figure 5.18 Linear drum mixer used for column pellet production

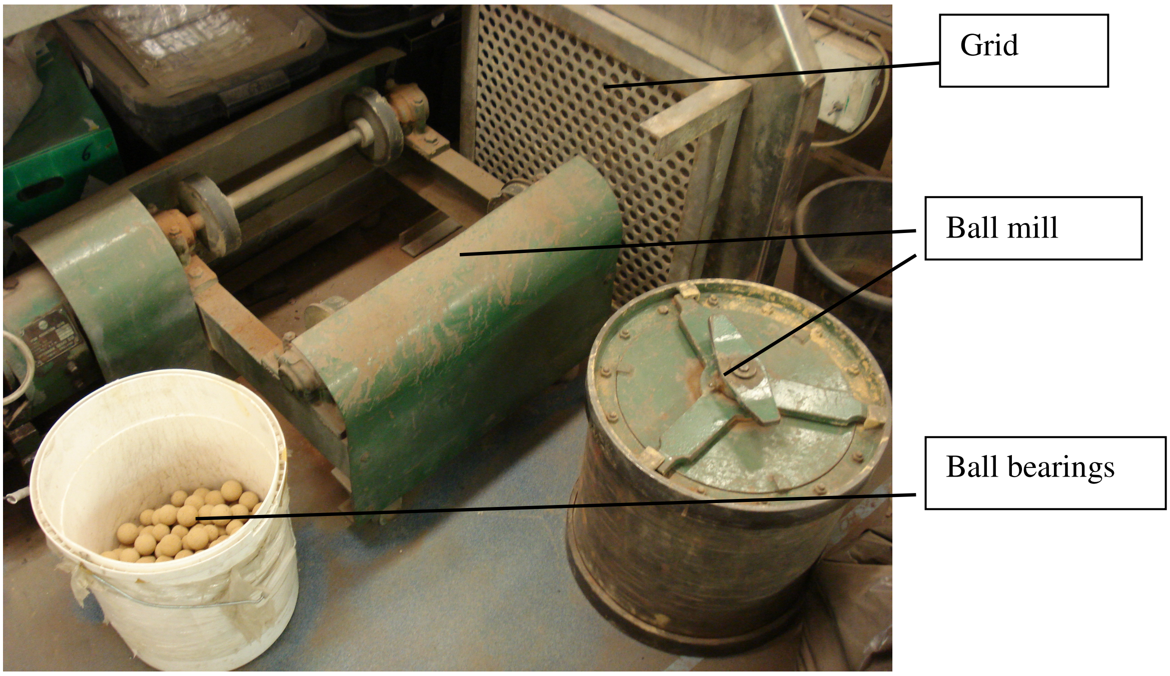


Figure 5.19 Ball mill used to crush material down to suitably sized pellets

Figure 5.20 Blending of the various pellet sizes

5.3.4 Particle size distribution

Once the pellets had been sieved into its fractions, washed and dried the weight of each size fraction was determined. This particle size distribution is shown in Figure 5.21 where the percentage passing the sieve size is potted against the sieve size.

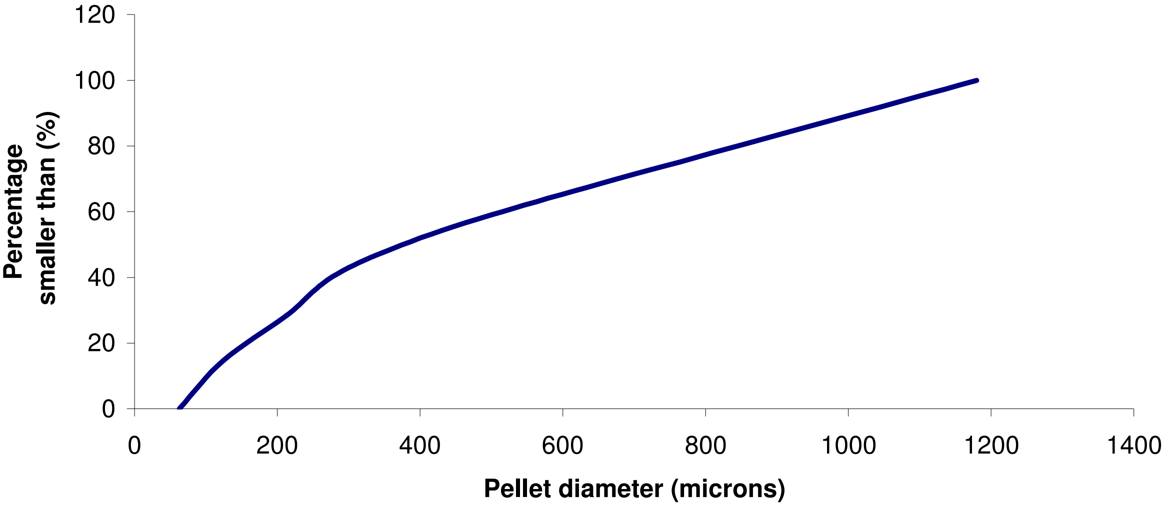


Figure 5.21 Particle size distribution of pellets used in column tests (sieve sizes used were 63,125,212,300,500,1180µm)

Figure 5.21 shows that the size fraction most studied in the pellet study (63-125µm) represents 15% of the total weight of pellets used. The d_{50} value for this distribution is 320 microns, therefore 50% of the pellets by weight are smaller than this size and 50% are larger. The particle size distribution is quite linear, particularly for particles above the 212µm size. A larger range of pellet sizes were used in the column tests due to the difficulty in producing large amounts of small pellets.

5.3.5 Column filling

All three columns were filled at the same time and in the following manner.

1. A volume of sharp sand was obtained from the Cardiff University concrete lab this was thoroughly washed using the sieving machine shown in Figure 5.10 until the passing water ran clear
2. The appropriate volume of sand was then measured out so as to form a 2cm deep bed. This sand was then poured into the column and each column was then weighed

3. The mixed pellets were placed into the columns, each column was filled up to just below the top effluent point
4. Each column was then reweighed, the difference representing the mass of pellets within, the packed bed density could then be determined from this and the known bed volume. The average packed bed density was found to be 1.129kg/l, the standard deviation was 0.03 and so the average value was used for all three columns.

5.3.6 Pore volume determination

The pore volumes of the filled columns were determined so that the flows required for certain residence times could be known, the pore volumes were determined as detailed below.

1. The columns were completely filled with water and then allowed to completely drain, the columns were then weighed
2. All outflows of the columns were blocked and the columns were slowly filled from the top, allowing all the air to escape
3. These saturated columns were then weighed, the difference between this weight and that found in step 1 is the pore volume

5.3.7 Column operation

Once the rig was completely setup as shown in Figure 5.15 the column test was carried out as described below

1. The influent reservoir was filled with 1000l of Cardiff tap water
2. 43.87g of KH_2PO_4 was fully dissolved in a volume of water which then formed part of the final 1000l, this is the required dosage for a target initial concentration of 10mg/l

3. The pump (Watson Marlow 604U peristaltic pump) was set to 20% of its power, this provided plenty of flow with the majority flowing back through the re-circulating main and did not strain the pump.
4. The flow passing through the columns was determined by measuring the volume passed in 2.5 minutes
5. The flow rates were altered by varying the tightness of the pinch valves, these were adjusted until the desired flow rates were achieved.
6. Column 1 was sampled twice weekly, column 2 thrice weekly and column 3 every weekday
7. Before any samples were taken the flow rates through each column was determined and noted down
8. For each column the top outlet was sampled first, followed by the middle and then the bottom
9. Once the samples had been taken, the flow through the top outlet was allowed to re-establish and the flow rates re-measured again and readjusted if necessary
10. The pHs of the sample were then determined out using a Severn Multi Mettler Toledo meter with an expert pro pH probe which is capable of a precision of three decimal places
11. The samples were stored in the fridge until analysis by the ICP-OES for phosphorus and calcium. Analysis was carried out weekly. Phosphorus was determined at a wavelength of 213.617nm and the ICP-OES was calibrated at 0.1,1 and 10 mg/l. Calcium was determined at a wavelength of 317.933nm and the ICP-OES was calibrated at 1,10 and 100mg/l

After three weeks of operation the columns were drained and allowed to stand for a week to investigate the potential of the rejuvenation mentioned by Sibrell (2007) and Drizo (2002). The columns were then operated for a further three weeks in the same manner as above. During this break both the IBCs were drained and the influent IBC refilled in the manner described in steps 1 and 2 above.

5.4 Chapter summary

This chapter has described the materials used for the experimental side of this thesis and the manner in which they were used. Firstly the raw materials were described and their use in adsorption studies was described. The method of producing pellets from the Horden solids used was then outlined. These pellets were then characterised and the methods used in their testing outlined. These pellets were also used in column tests. The columns and the rig used were described as were the operational procedures of the column tests.

Chapter 6 Phosphorus adsorption by AMD solids and other iron oxyhydroxides: results and discussion

This chapter presents the results for the batch experiments on the raw materials as described in Section 5.15. Firstly results appertaining to the solids from the Horden minewater treatment plant will be presented. The preliminary kinetic tests carried out to gain an initial appreciation of the performance of this material are shown, these then informed more targeted tests. The results of batch adsorption experiments are presented and both the Freundlich and Langmuir isotherms are calculated and compared to those for materials from select papers from the literature review. Similar batch results are presented for the other three materials investigated: a filter cake from a water treatment plant, the commercial iron based phosphorus adsorbent Rowaphos and finally a second source of AMD solids from the Dawdon minewater treatment plant.

6.1 Kinetic tests on treated AMD solids from Horden mine water treatment plant

The initial tests comprised of kinetic tests on the solids from Horden minewater treatment plant. These tests were carried out to get both an idea of the removal performance of these solids and the time frame of these removals. Two tests were carried out at room temperature using a flocculator (see Figure 5.6) with 1 and 3 grams of dried Horden solids (1.25 and 3.75 g/l solids concentration respectively). Both tests had an initial phosphorus concentration of 10mg/l and a total volume of 800ml. Samples were removed and filtered at the appropriate times and analysed with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) as described in Chapter 5. The variation of phosphorus concentration with time is presented in Figure 6.1. The elapsed time is plotted on the x-axis and the corresponding phosphorus concentration upon the y-axis

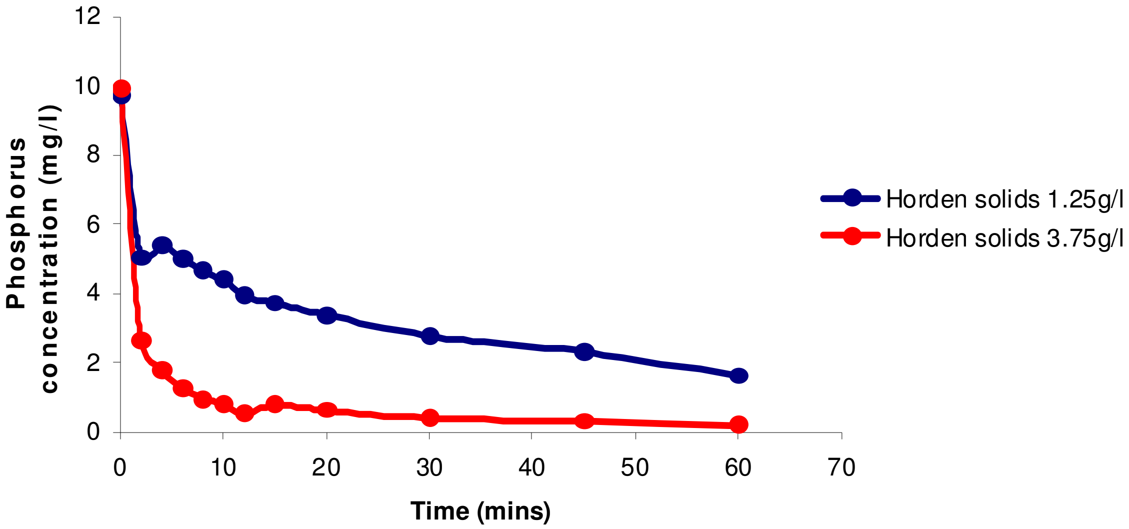


Figure 6.1 Variation of phosphorus concentration with time for the kinetic tests with solids from Horden minewater treatment plant

It can be seen that for both tests, particularly the test with 3.75g/l solids concentration, the rate of removal is particularly high for the initial few minutes. For the 1.25g/l test, within the first 10 minutes the phosphorus concentration had been reduced from 10mg/l to 4.39mg/l, the final concentration after 60 minutes was 1.62mg/l. The test with a solids concentration of 3.75g/l reduced the initial 10mg/l to 0.81mg/l after 10 minutes with a final concentration of 0.19mg/l again showing a high initial rate of removal. These results fit in with those of Heal *et al.* (2004) who found rapid phosphorus removal by AMD solids, one material achieving equilibrium within an hour another within minutes. Wei *et al.* (2008) also found that for the AMD solids studied equilibrium was reached within one hour. The percentage removal for the results in Figure 6.1 is shown in Figure 6.2 where the cumulative percentage of phosphorus removed is plotted against time.

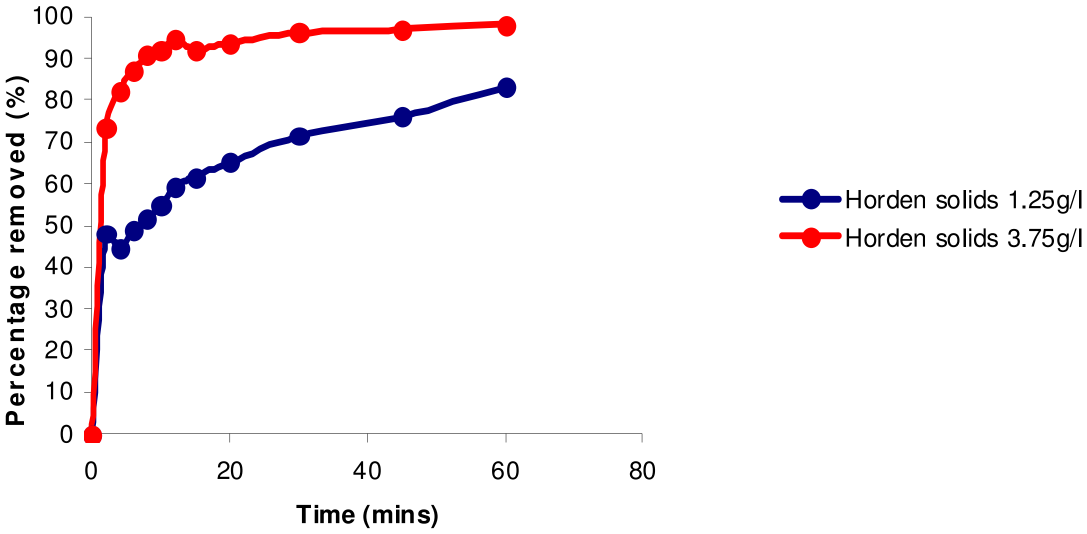


Figure 6.2 Cumulative percentage of phosphorus removal for the kinetic tests on the solids from Horden.

After the first 10 minutes Figure 6.2 shows that the test with 1.25g/l of solids has removed 50% of the initial phosphorus, this rises to 83% after 60 minutes. The 3.75g/l test removed 90% after 10 minutes and 98% after the hour. Both tests show a rapid period of removal lasting a few minutes followed by a slower rate lasting up to the hour.

After 60 minutes the 1.25g/l test had removed 6.4mg of phosphorus and therefore 6.4mg per gram of dry Horden solids at a final concentration of 1.62mg/l. The 3.75g/l test removed 7.8mg equivalent to 2.6mg/g at a concentration of 0.19mg/l. This shows that although the 3.75g/l test removed more phosphorus after 60 minutes, in terms of the usage rate of the Horden solids, the 1.25g/l test was a more efficient use of the material. In Sibrell *et al.* (2009) six sources of AMD solids were tested. For the range of 0.19-1.62mg/l equilibrium concentrations these removed between 2.0 and 5.5mg/g for the highest performing and 2.2-3.7mg/g for the lowest. This shows that the loadings achieved by the solids from Horden are comparable to those found by other studies on similar materials. Full comparisons are shown in Section 6.2.1.

This section has presented the kinetics of removal for the solids from Horden minewater treatment plant. It has been shown that, as with studies by Heal *et al.*

(2004) and Wei *et al.* (2008) the phosphorus removal by these solids is rapid. This is especially true for the test with the higher solids concentration where 90% removal was achieved within 10 minutes. The two tests finished with phosphorus concentrations of 0.19 and 1.62mg/l where phosphorus loadings were 2.6 and 6.4 mg/g respectively, these loadings at these final concentrations are comparable to those reported by Sibrell *et al.* (2009).

6.2 Batch phosphorus adsorption tests on treated AMD solids from Horden mine water treatment plant

This section details the results for the equilibrium batch tests on the solids from Horden minewater treatment plant. This involved two sets of tests in order to get a good resolution of data across a wide range of equilibrium concentrations. The data are used to calculate the Freundlich and Langmuir isotherms which then allow direct comparisons to results from select papers from the literature review.

6.2.1 Phosphorus adsorption by AMD solids from Horden mine water treatment plant – wide range of concentrations

Eight tests were carried out in triplicate with a wide range of initial concentrations (28-560mg/l) so as to get a good overall picture of the performance of the Horden solids at a wide range of equilibrium concentrations. The volume of each batch test was 40ml and 0.5g of dried Horden solids was used, the tests were carried out at room temperature. These tests lasted 16 hours to ensure that equilibrium was reached. The concentration of solids was much higher for these tests (12.5g/l) compared to 3.75g/l for the 3 gram test from Section 6.1. The results from Section 6.1 show that higher solids concentrations achieve equilibrium faster and so a 16 hour test at this higher solids concentration should achieve equilibrium even for these higher initial concentrations. The equilibrium phosphorus concentrations found are plotted against their initial concentration in Figure 6.3. Error bars for the y-axis represent ± 1 standard deviation.

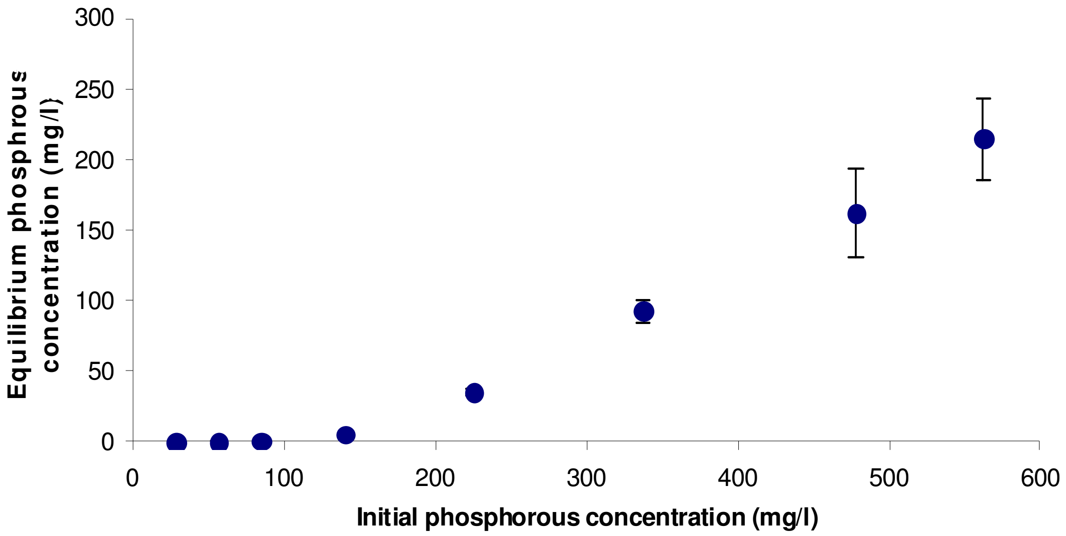


Figure 6.3 Results for the 16 hour batch adsorption test on the solids from the Horden minewater treatment plant. The solids concentration was 12.5g/l.

Up to an initial concentration of 85mg/l in this test the solids still removed phosphorus down to a 0.5mg/l equilibrium concentration. The lowest initial concentration of 29mg/l was reduced to 0.26mg/l and the highest of 560mg/l was reduced to 214mg/l. As stated in Chapter 2 WWTWs typically have influents in the order of 10mg/l. This test has only four data points that have an equilibrium concentration below this value, therefore further tests are required to give a good resolution in this area of particular interest.

These tests become more meaningful if the data are processed to provide an adsorption isotherm plot, the nature of these plots is described in Section 4.1.2. This allows the phosphorus removed in terms of milligrams of phosphorus (as milligrams of total phosphorus removed per gram of dry Horden solids) to be plotted against the relevant equilibrium concentration. Whereas Figure 6.3 is specific only to the conditions used for that test, Figure 6.4 is a more general form allowing comparison to other materials and studies. As before error bars represent ± 1 standard deviation

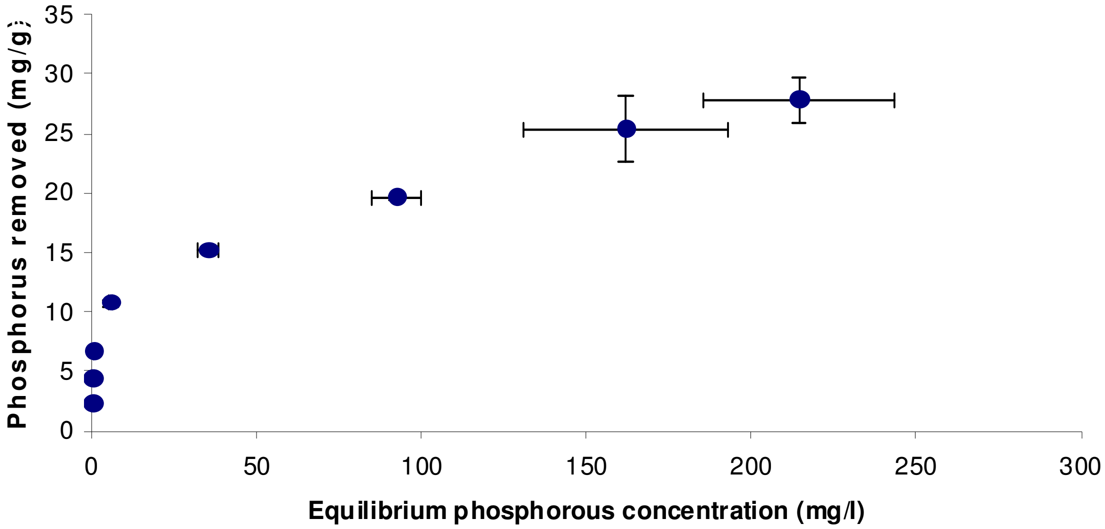


Figure 6.4 Adsorption isotherm data for batch tests on the solids from the Horden minewater treatment plant

The results shown in Figure 6.4 are taking the classic adsorption isotherm shape with the increase in phosphorus loading tailing off towards a maximum value. It shows that the maximum phosphorus removal found by these tests is 27.9mg/g but this dramatically drops off as the equilibrium concentration approaches zero. This maximum value of 27.9mg/g is comparable to those values found for other AMD solids by Heal *et al.* (2004) (26 and 30.5mg/g) and Wei *et al.* (2008) (31.97mg/g). However Wei *et al.* (2008) found this level of loading at an equilibrium concentration of only 13.61mg/l whereas this test the maximum was found at an equilibrium concentration of 215 mg/l. A direct comparison of the results for the Horden solids to that of AMD solids tested by others is shown in Figure 6.15. The removal capacity of this material at specific equilibrium concentrations will become easily quantifiable once the theoretical adsorption isotherm equations are calculated in Section 6.2.3.

As discussed in Chapters 3 and 4 pH can have a large effect on adsorption, the pH was not controlled in tests, but was monitored. Figure 6.5 plots the variation of the initial pH with the initial phosphorus concentration. The initial pH was measured before the solids from Horden were added to the phosphorus solutions.

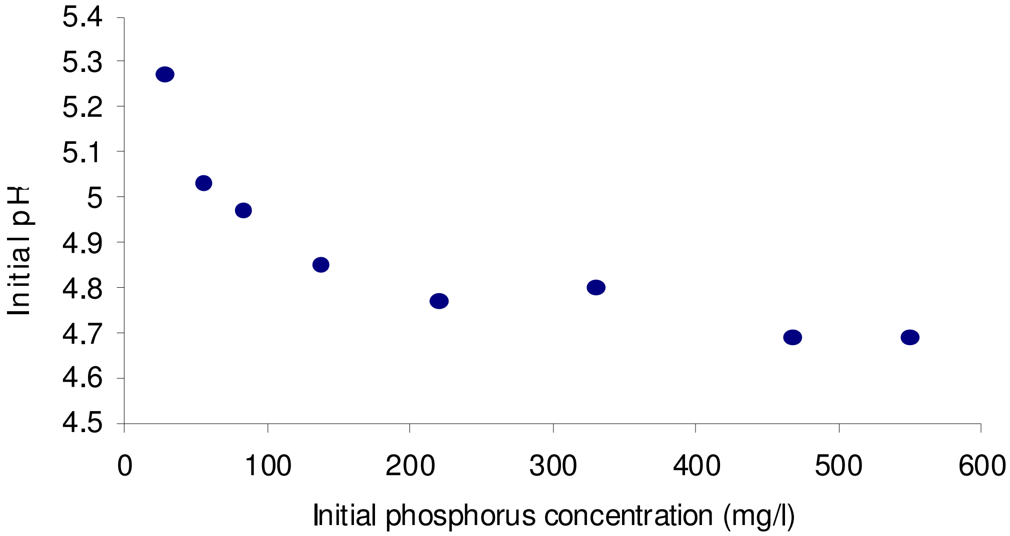


Figure 6.5 Variation of initial pH with initial phosphorus concentration.

The initial pHs ranged from 4.69 to 5.27, the initial pH drops as the initial concentration increases due to the acidic nature of the KH_2PO_4 stock solution. These low pH values could be considered as preferential for anionic adsorption as they will create a more positive surface charge on the solids as discussed previously in Chapter 3. The variation of final pH with initial pH is shown in Figure 6.6. The final pH was determined once the solution had been filtered, error bars represent ± 1 standard deviation.

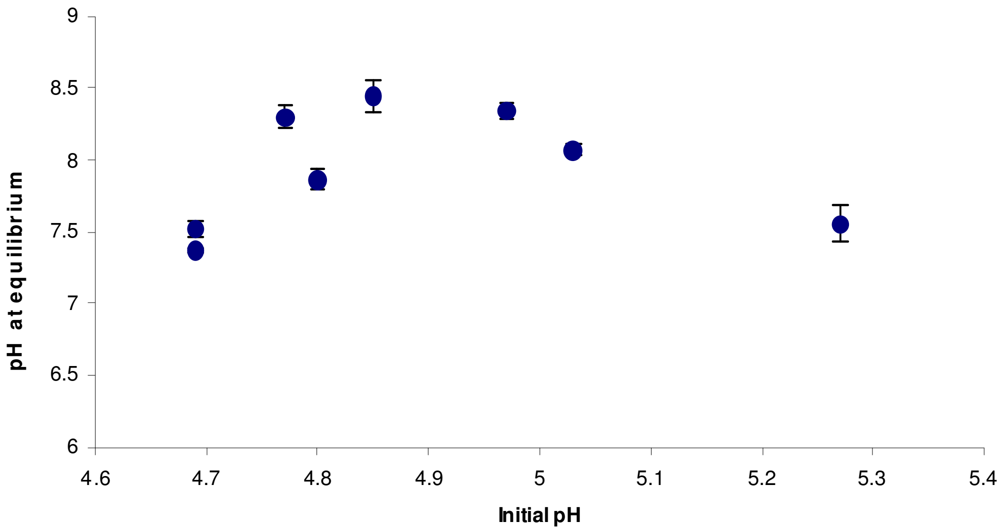


Figure 6.6 Variation of pH at equilibrium for batch adsorption tests on the solids from Horden minewater treatment plant.

The pH values at equilibrium are in the range 7.47 to 8.44, this increase in pH is likely be as a result of the alkaline treatment methods used at the Horden treatment plant. The final pHs are showing a peak at the median initial pH with the final pH dropping off either side. The range of final pHs is relatively small yet the pattern is clear, this pattern could be as a result of calcium found in the Horden solids (11.32%) becoming involved in removal and thus confusing the pH relationship with some consumption of hydroxide ions as a result of calcium phosphate precipitation. Cornell and Schwertmann (2003) state the range of the point of zero charge for a variety of iron oxides, these all fall in the range of 6.3-9.5. It can be seen then that these higher, final pHs may not be ideal for anionic adsorption. The variation of phosphorus loading (mg/g) with final pH is shown in Figure 6.7.

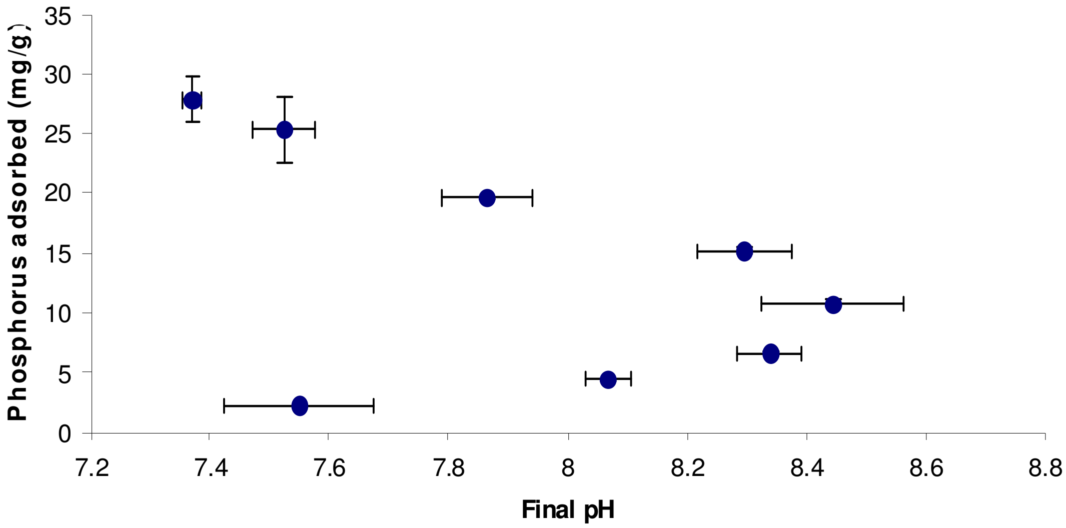


Figure 6.7 Variation of phosphorus removed with final pH

Figure 6.7 reflects the same pattern in Figure 6.6. The variation of final pH for these tests is unlikely to have a large impact on phosphorus loading compared to the impact of the large range of initial concentrations. Both Chitrakar *et al.* (2006) and Zeng *et al.* (2004) studied phosphorus adsorption by iron oxides and found an inversely proportional relationship between pH and removal, this pattern is not shown in Figure 6.7, perhaps as a result of the interaction of the calcium in the Horden solids with the phosphorus in solution.

6.2.2 Phosphorus adsorption by AMD solids from Horden mine water treatment plant – focus on lower concentrations

This section reports on the test which looked to produce results that would give more detail at the lower equilibrium concentrations. Eight tests with initial concentrations of 65 -200 mg/l were prepared over eight tests compared to the eight tests over the range 28-560 used in the tests in Section 6.2.1. Again the batch volume was 40ml, 0.5g of dried Horden solids was used and the tests were carried out at room temperature, for 16 hours and in triplicate. Figure 6.8 shows the initial and corresponding final concentrations from this test.

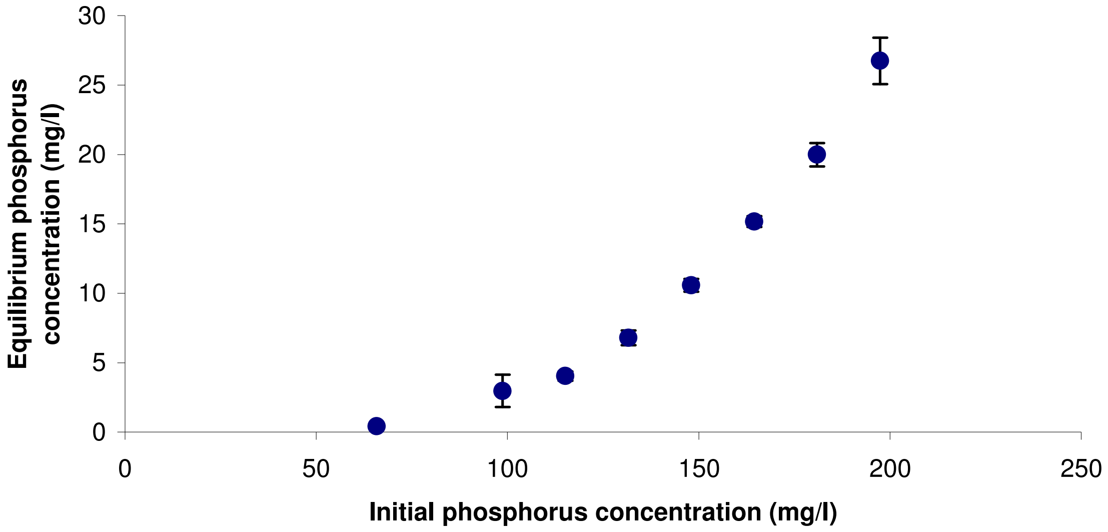


Figure 6.8 Results for the second batch adsorption test on the solids from the Horden minewater treatment plant

Figure 6.8 shows that this test has produced results within the desired range of lower equilibrium concentrations, all results being in the range 0-30mg/l. This data can then be used to provide better resolution of data at the lower equilibrium concentrations. Firstly the data in Figure 6.8 is converted into the adsorption isotherm form in Figure 6.9.

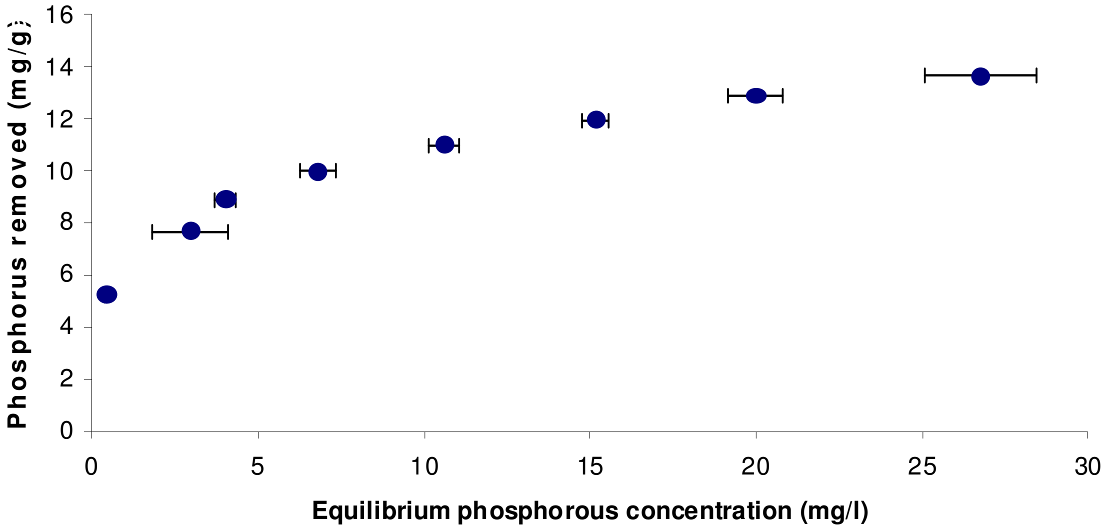


Figure 6.9 Adsorption isotherm data for batch tests on the solids from Horden minewater treatment plant – focused at low concentrations

In the range of equilibrium concentrations of particular interest (0-10mg/l) the material is removing 5-11mg/g, compared to the maximum loading of 28mg/g found by the tests in Section 6.2.1. It is now possible to combine the two data ranges from Figure 6.5 and Figure 6.9 to get a full data range with a good number of data points at the lower equilibrium concentrations. The data covering the full range of equilibrium phosphorus concentrations are shown in Figure 6.10.

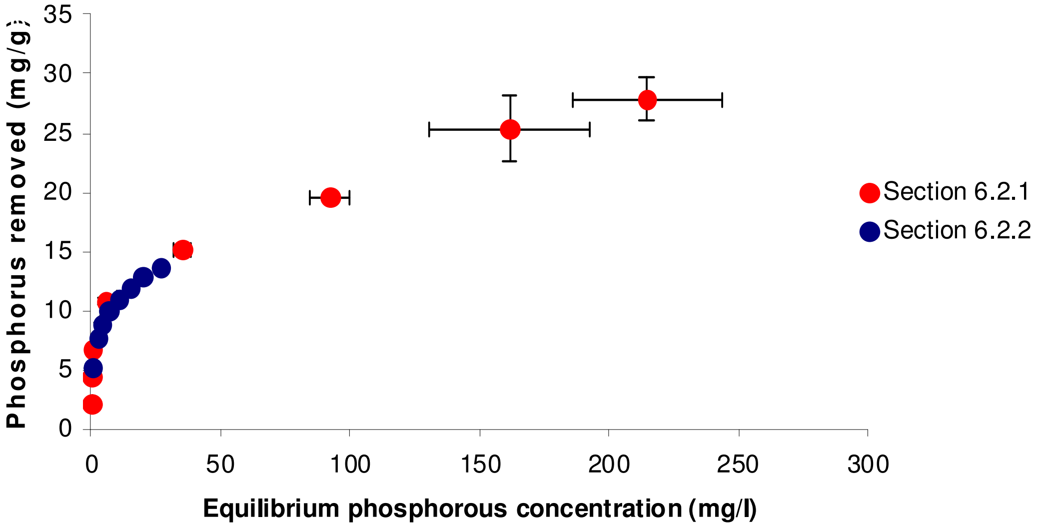


Figure 6.10 Adsorption isotherms for both batch tests on the solids from Horden minewater treatment plant

Both data sets lay directly on top of each other, highlighting the repeatability of these tests. It is now possible to confidently combine these into one data set from which it will be possible to calculate the theoretical isotherms.

6.2.3 Calculation of theoretical isotherms

The Freundlich isotherm takes the form of Equation 6.1.

$$\frac{x}{m} = KC^{n}$$

Equation 6.1

Where x/m is the loading in mg/g, C is the equilibrium phosphorus concentration (mg/l) and K and n are constants

This can be converted to a linear form by taking the logarithms of both sides resulting in Equation 6.2

$$\log\frac{x}{m} = \log K + n\log C$$

Equation 6.2

This linear form can then be plotted to determine the coefficients K and n from the slope and intercept of the line of best fit. This linear form is shown in Figure 6.11

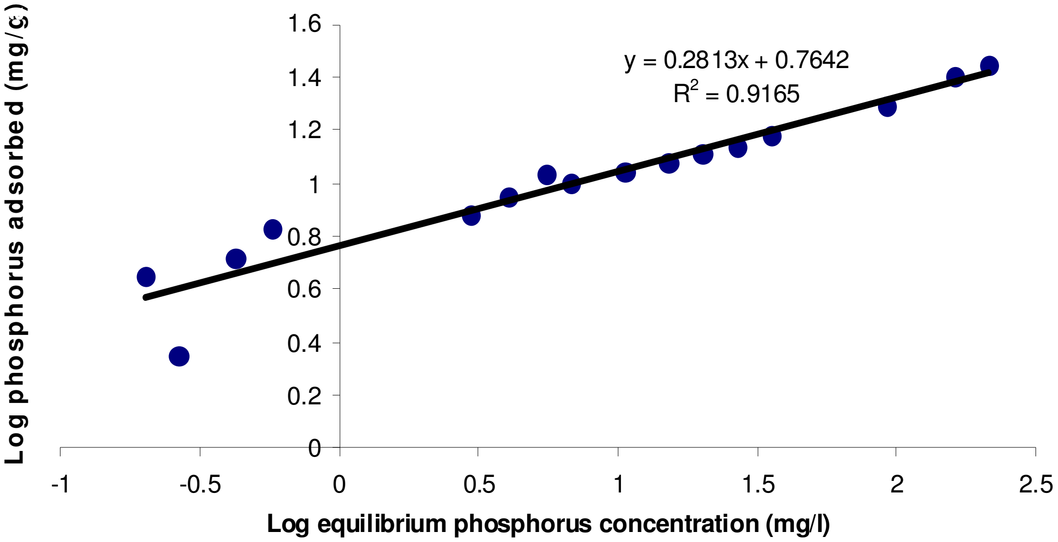


Figure 6.11 Linear plot of the Freundlich isotherm for the adsorption data for the solids from Horden minewater treatment plant.

Figure 6.11 results in a value of 5.81 for K and 0.2813 for n providing a Freundlich equation of

$$\frac{x}{m} = 5.81C^{0.2813} \qquad \text{Equation 6.3}$$

Figure 6.11 shows the line of best fit has a coefficient of determination value of 0.9165, with a value of 1 showing perfect correlation this shows the Freundlich isotherm to provide a good fit to the data.

The Langmuir isotherm takes the form

$$\frac{x}{m} = \frac{aC}{1+bC} = \frac{bCN_{\max}}{1+bC} \qquad \text{Equation 6.4}$$

where x/m and C are as previously defined, a and b are constants and N_{max} is the maximum loading on the solid, representing monolayer coverage.

The best method of linearisation, so as to avoid any induced correlation is through inversion of all terms

$$\frac{1}{x/m} = \frac{b}{a} + \frac{1}{aC} = \frac{1}{bCN_{\max}} + \frac{1}{N_{\max}} \qquad \text{Equation 6.5}$$

Therefore a plot of the inverse of the phosphorus loading against the inverse of the equilibrium concentration will allow the coefficients to be determined. This is plotted in Figure 6.12

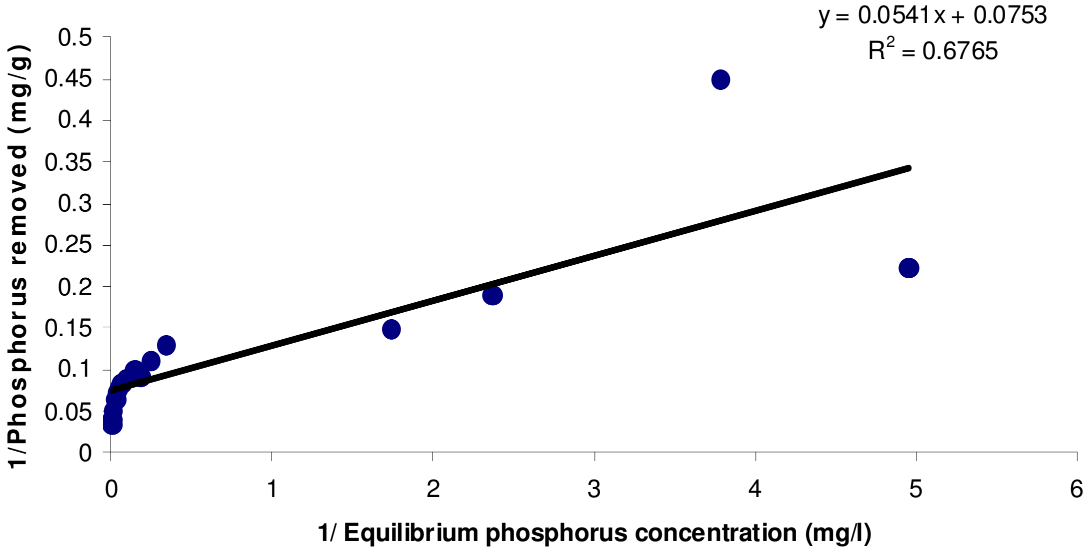


Figure 6.12 Linear plot of the Langmuir isotherm for the solids from Horden minewater treatment plant.

Thus the Langmuir isotherm takes the form

$$\frac{x}{m} = \frac{1.39 * C * 13.28}{1 + (1.39 * C)} \qquad \text{Equation 6.6}$$

Figure 6.12 shows the linear form of the Langmuir isotherm has a R^2 value of 0.6765, significantly lower than that found for the Freundlich isotherm. The

Freundlich isotherm therefore offers a superior fit to the data than the Langmuir for the Horden solids.

Now that the theoretical isotherms have been calculated they can be plotted alongside the experimental data. The data is represented by the blue points in Figure 6.13, the Freundlich isotherm as a red line and the Langmuir as a green.

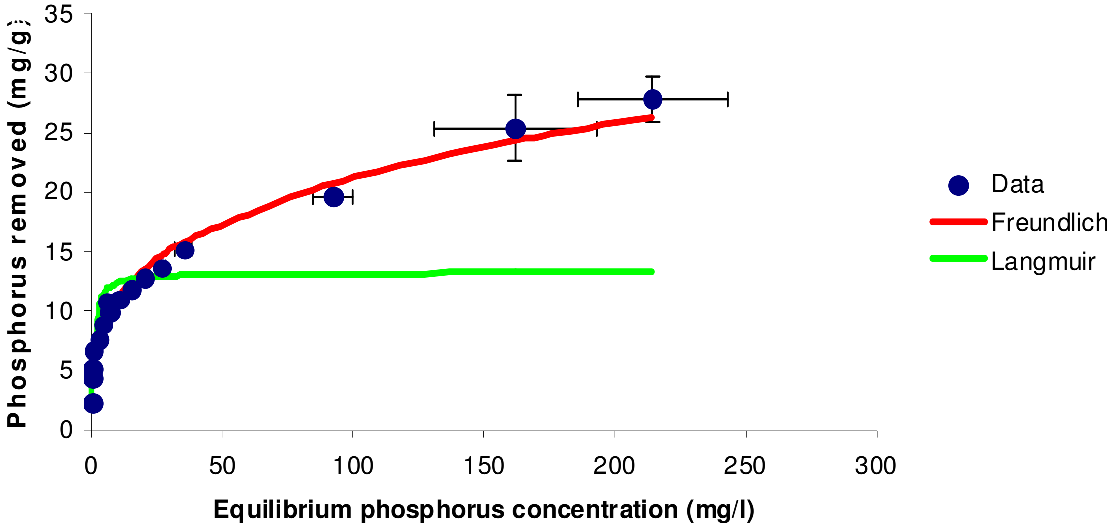


Figure 6.13 Freundlich and Langmuir isotherms alongside the adsorption data for the solids from Horden minewater treatment plant

As expected from the lower R^2 value from its linear form, the Langmuir model has a visibly poorer fit to the data than the Freundlich, The Freundlich isotherm fits well over all equilibrium concentrations whereas the Langmuir appears to be reasonable over low equilibrium concentrations but shows a predicted maximum removal of 12mg/g after which it predicts no increase in removal. The goodness of fit can be quantified by using the chi squared test, this takes the form.

$$X^2 = \sum_{i=1}^{n} \frac{(O_i - E_i)^2}{E_i} \qquad \text{Equation 6.7}$$

where X^2 is the chi squared value, O is the observed value, i.e. the experimental data and E is the expected value i.e. the value predicted by the isotherm.

A lower chi squared value represents a better fit to the data, it is relative to the values in the data set and so can only be compared to the same data set. A value of 2.2 for the Freundlich isotherm and 34.2 for the Langmuir isotherm was found. This quantifies the wellness of fit to allow comparison and again shows the Freundlich isotherm to be a far superior fit. Section 3.4 reviewed other papers that looked at phosphorus removal by AMD. Of these Adler and Sibrell (2003), Sibrell *et al.* (2009) and Wei *et al.* (2008) also used the Freundlich isotherm to describe their data. Heal *et al.* (2004) was the only study that found the Langmuir isotherm to offer a better fit to their data.

As discussed above in terms of use at WWTWs it is the lower equilibrium concentrations that are of the most interest therefore data within the range of 0-20mg/l equilibrium concentrations are plotted alongside the Freundlich isotherm in Figure 6.14.

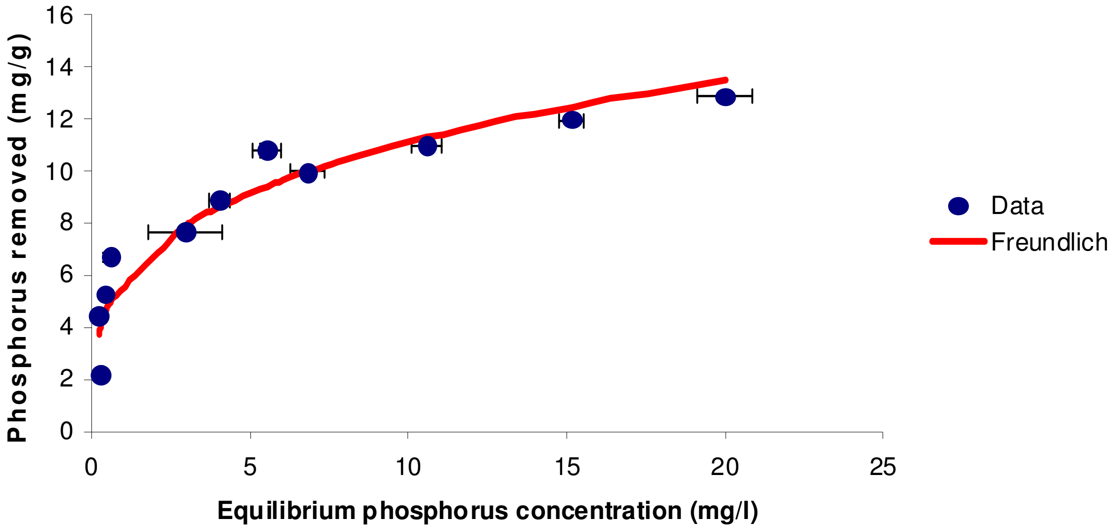


Figure 6.14 Freundlich isotherm and adsorption data for solids from Horden minewater treatment plant. Focused at the lower equilibrium concentrations

Figure 6.14 gives a clearer picture of the adsorptive performance of Horden sludge at the lower equilibrium concentrations. In the range of 0-20mg/l equilibrium Horden solids are removing 4-13mg/g of phosphorus. The kinetic tests from Section 6.1 found 6.4mg/g removed at 1.62mg/l for the 1.25g/l test and 2.6mg/g at 0.19mg/l for the 3.75g/l. The Freundlich isotherm from Figure 6.13 gives phosphorus loadings of 6.6mg/g at 1.62mg/l and 3.6mg/g for 0.19mg/l, the tests presented in this section tests are therefore finding results very similar to those from Section 6.1 suggesting that the majority of removal found after 16 hours occurred after 1 hour and that equilibrium has been reached.

6.2.4 Comparison of adsorption performance to materials from the literature review

The Freundlich isotherm for the solids from Horden is plotted alongside adsorption isotherms for other AMD solids from the literature review in Figure 6.15 as way of a comparison. The isotherms used as comparisons are taken from Heal *et al.* (2004), Wei *et al.* (2008) and Adler and Sibrell (2003).

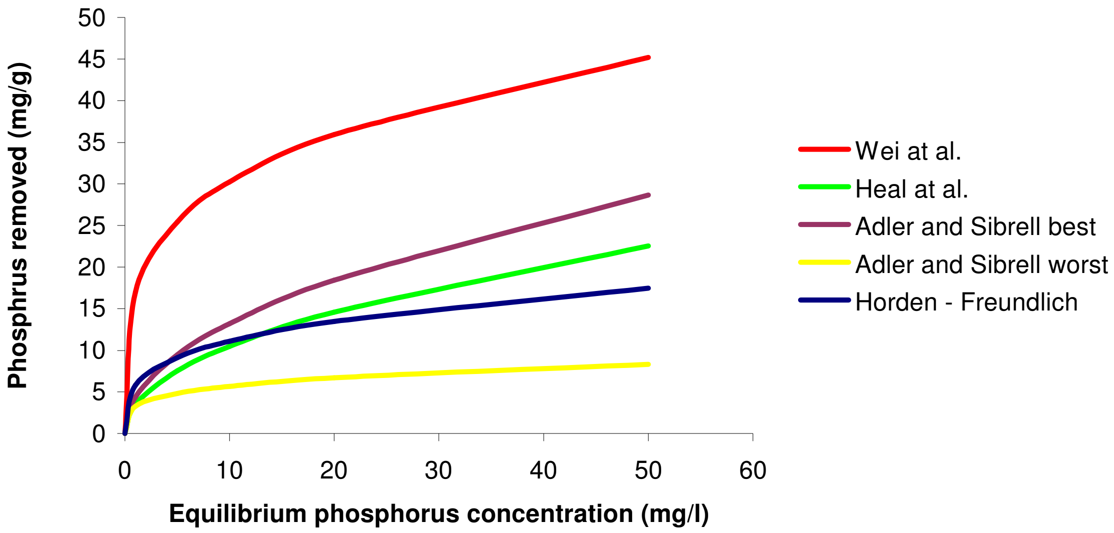


Figure 6.15 Comparison of the Freundlich isotherm for the solids from Horden to other AMD's from the literature review

Figure 6.15 shows that the solids from Horden are performing to a standard comparable to that of AMD solids tested by others. Of the four other isotherms shown the solids from Horden has the second lowest maximum phosphorus loading but at the lower equilibrium concentrations it is removing the second highest amount of phosphorus. The material is clearly performing in a similar manner to comparable materials that others have studied. The material studied by Wei *et al.* achieves significantly higher phosphorus loadings than the other materials.

This section has provided a full adsorption data set for the solids from Horden mine water treatment plant and the Freundlich and Langmuir isotherms were calculated for the data. Linear regression and the chi squared test showed that the Freundlich isotherm has the superior fit to the data. Finally the Freundlich isotherm was compared to isotherms for similar materials from other studies, this showed the solids from Horden to have an average phosphorus capacity for materials of its ilk.

6.3 Adsorption performance of filter cake from a water treatment plant

This section details the results found from adsorption tests using solids from a filter cake from a water treatment plant as described in Section 5.1.1.2. The results presented will mirror those presented in Section 6.2 for the solids from Horden. Firstly the results are presented and from these the theoretical isotherms calculated. The adsorptive performance of this material is then compared to that of the solids from Horden and materials from the literature review.

6.3.1 Phosphorus adsorption by of filter cake from a water treatment plant

The raw results from batch adsorption tests with a wide range of initial concentrations are presented. As with the tests in Section 6.2.1 the initial concentrations ranged from 28-550mg/l, the batch volume was 40ml and 0.5g of wet filter cake (80% moisture content) was added. This is a solids concentration of 2.70g/l compared to 12.5g/l for the test in Section 6.2. The filter cake was added in its wet form as drying left the material in hard granules which could thus affect the contact with the water and therefore adsorption performance.

Again all tests were carried out in triplicate with error bars representing ± 1 standard deviation. These results are presented in Figure 6.16 with the equilibrium phosphorus concentrations plotted against the relevant initial concentrations.

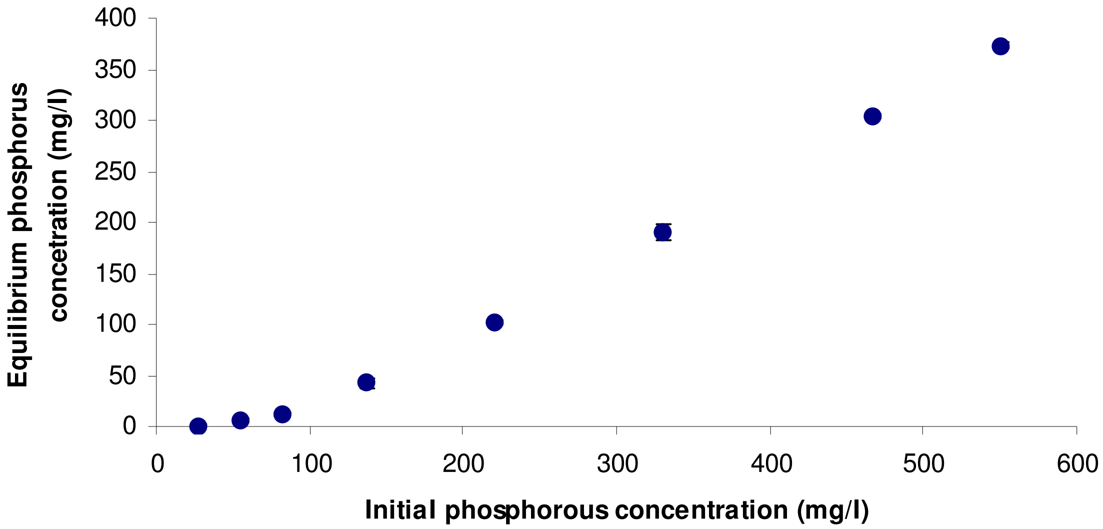


Figure 6.16 Results for batch adsorption tests on solids from the filter cake from the water treatment plant

The lowest initial concentration of 27.5mg/l was reduced to an equilibrium concentration of 0.88mg/l and the highest initial concentration of 550mg/l was reduced to 370mg/l. These results are converted to the adsorption isotherm form in Figure 6.17 with the phosphorus removed per gram of dry solids plotted against the equilibrium concentrations. Comparisons with the Horden solids and other materials are made once the theoretical adsorption isotherms are calculated.

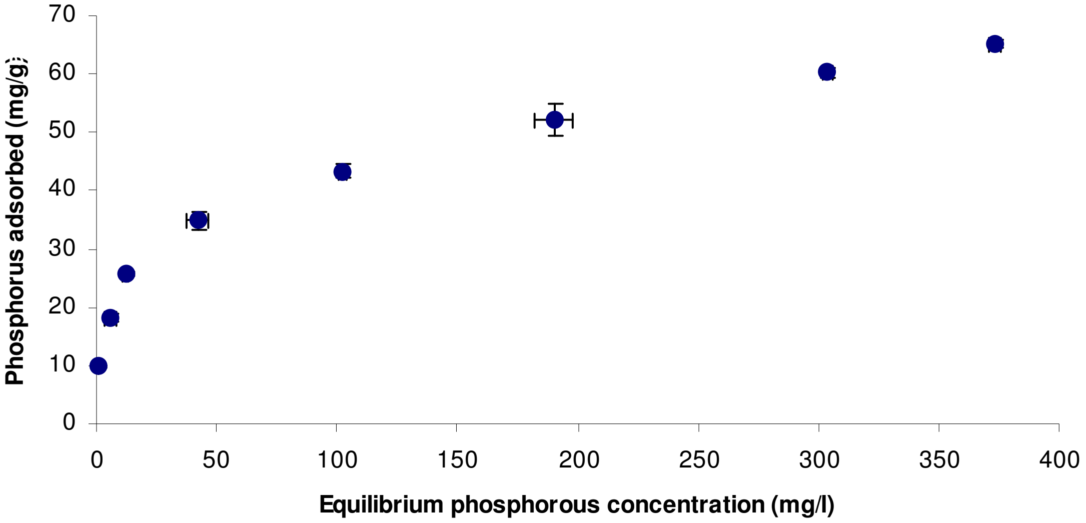


Figure 6.17 Adsorption data for the solids from the filter cake from the water treatment plant

Figure 6.17 shows that this filter cake is a good phosphorus sorbent able to remove 65mg/g at an equilibrium concentration of 370mg/l this drops to 10mg/g at an equilibrium of 0.88mg/l. At both high and low equilibrium concentrations this filter cake is outperforming the Horden solids, a full comparison is shown in Figure 6.24. The adsorption isotherm form however also has its limitations as there is no consideration of moisture content. The filter cake has a moisture content of 80% and therefore in terms of weight of active material the filter cake is more diluted then the Horden sludge at 33% moisture. This is fully explored in Figure 6.42.

The same initial concentrations as those in Section 6.2.1 were used and so the relationship between initial concentration and initial pH was the same as shown in Figure 6.5. The relationship between initial and final pH for the tests reported on in this section is shown in Figure 6.18.

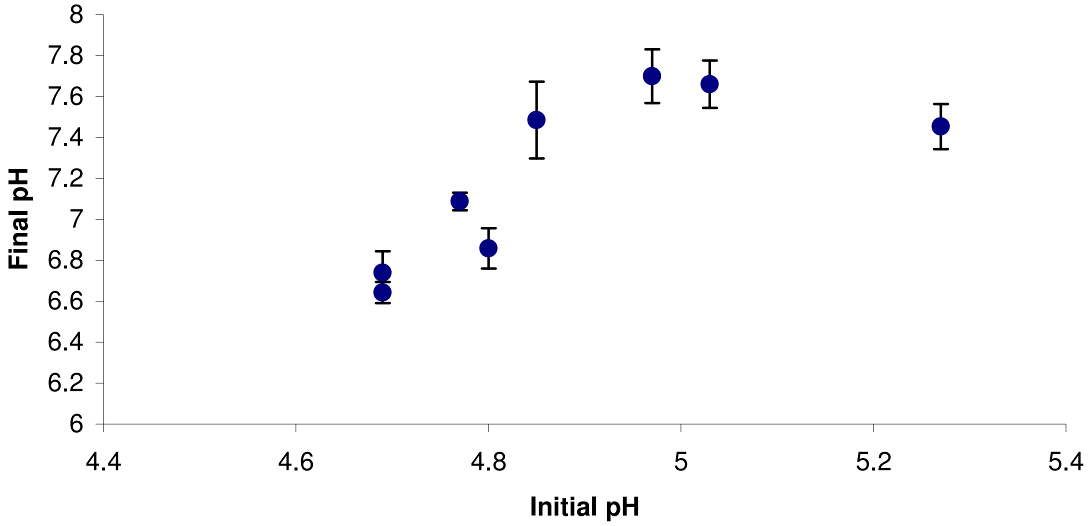


Figure 6.18 variation of final pH with initial pH

The final pH values in Figure 6.17 range from 6.64 to 7.70, the solids from Horden resulted in final pHs in the range of 7.47-8.44. The lower pHs found for the filter cake may be more preferential towards anionic adsorption. The results shown in Figure 6.18 are following a similar pattern to those of Figure 6.6 where the final pHs are rising with initial pH and then dropping slightly. As with the solids from Horden the filter cake was found to contain calcium (5.47%) and so again this may becoming involved in removal. The phosphorus removed by the filter cake is now plotted against the final pH in Figure 6.19.

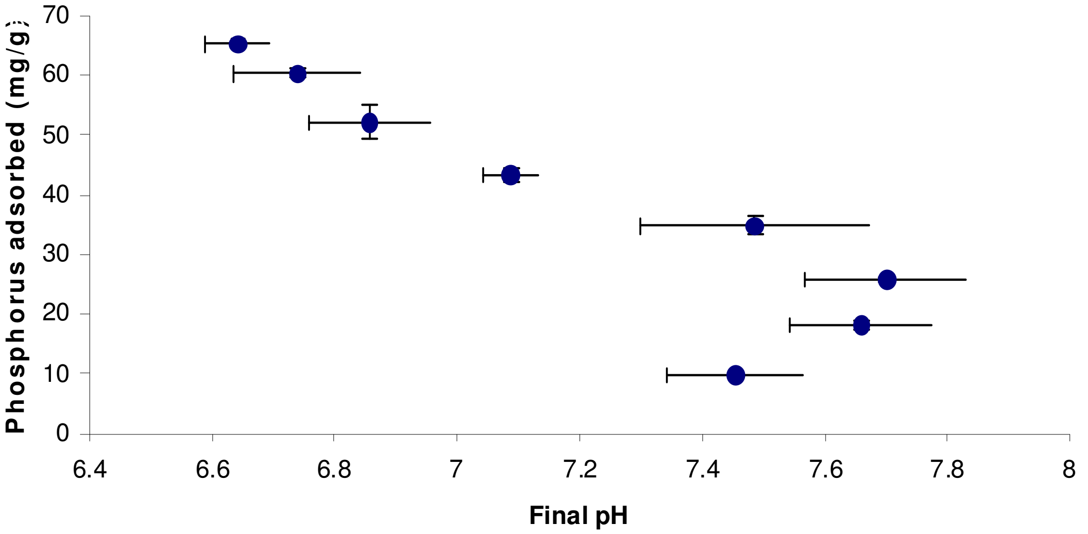


Figure 6.19 Variation of phosphorus removed with final pH.

Figure 6.19 shows a general trend of higher phosphorus removal at lower final pHs which is as expected for the adsorption of anions. However the large range of initial concentrations used is likely to have had a more profound effect.

6.3.2 Calculation of theoretical isotherms

As with the data for the solids from Horden from the Section 6.2 the Freundlich and Langmuir isotherms have been determined by plotting their linear forms. Firstly in Figure 6.20 the logarithms of the results in Figure 6.16 are plotted as to enable to calculation of the coefficients for the Freundlich isotherm.

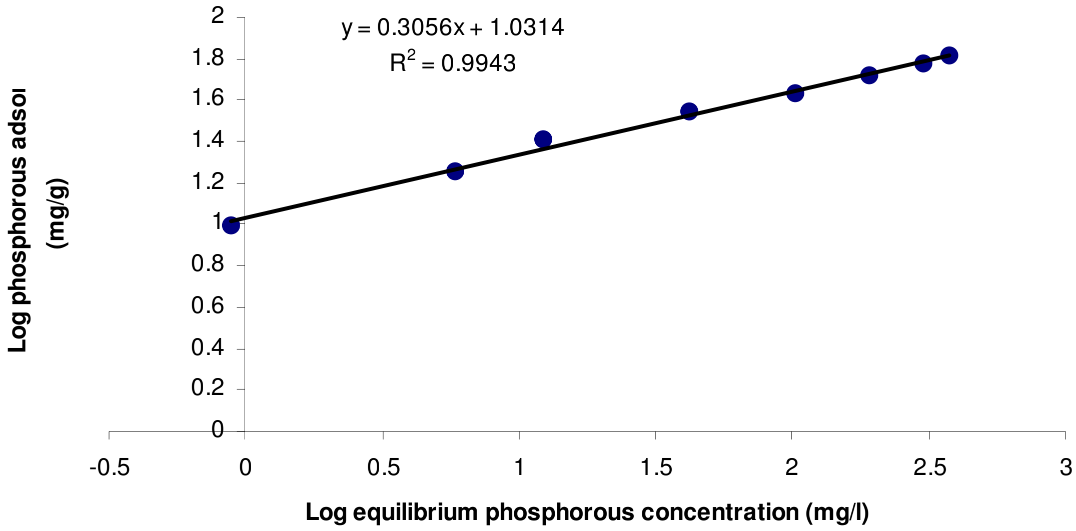


Figure 6.20 Linear form of the Freundlich isotherm for the filter cake from a water treatment plant. The equation and R^2 value of the line of best fit is also shown.

Figure 6.20 yields the equation of

$$\frac{x}{m} = 10.75C^{0.3056} \qquad \text{Equation 6.7}$$

The coefficient of determination (R^2) was 0.9943, therefore as with the Horden solids the Freundlich isotherm is showing an excellent fit to the data.

Figure 6.21 shows the linear plot for the determination of the coefficients for the Langmuir isotherm. This plot is achieved by taking the inverse of the values plotted in Figure 6.17.

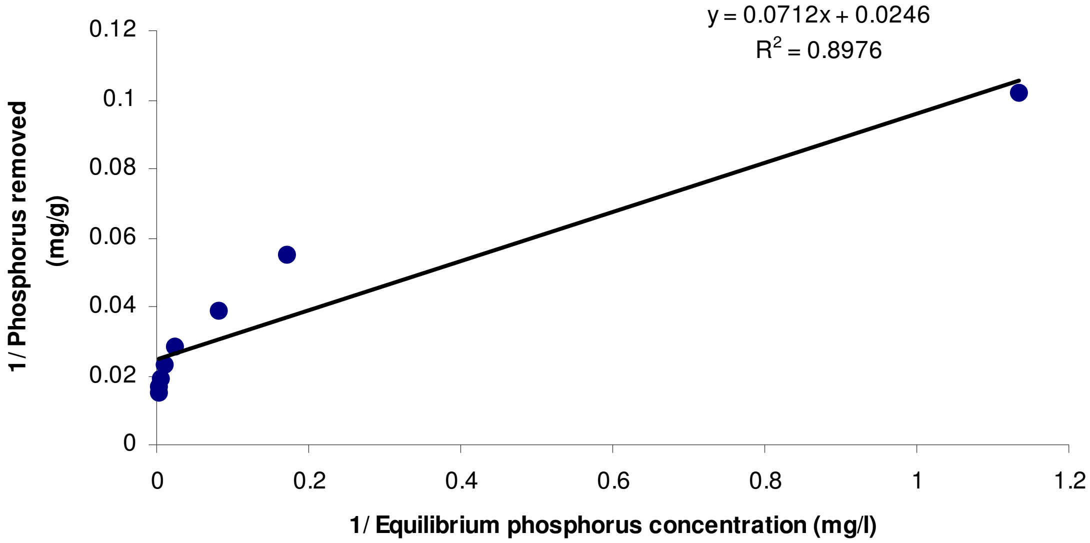


Figure 6.21 Linerisation of the Langmuir isotherm for the filter cake from the water treatment plant. The equation and R^2 value of the line of best fit is also shown.

Figure 6.21 results in a Langmuir equation of

$$\frac{x}{m} = \frac{0.345 * C * 40.65}{1 + (0.345 * C)} \qquad \text{Equation 6.8}$$

The line of best fit had a R^2 value of 0.8976 which suggests good correlation yet is still lower than that for the Freundlich equation.

The isotherms have been plotted along side the adsorption data in Figure 6.22.

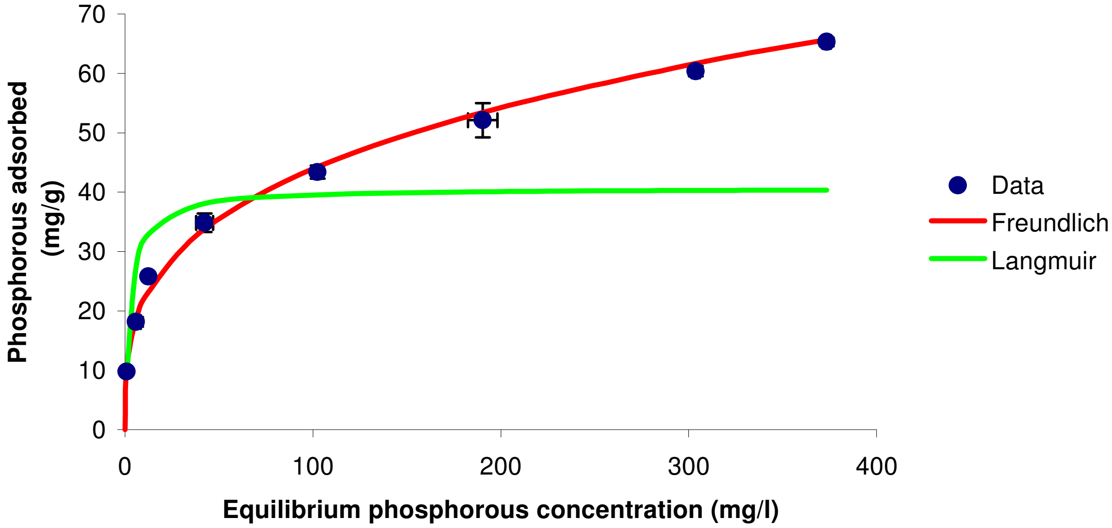


Figure 6.22 Freundlich and Langmuir isotherms alongside the adsorption data for the filter cake from the water treatment plant.

As with the results for the solids from Horden from Section 6.2, Figure 6.22 shows the Freundlich isotherm to fit the data well across all equilibrium concentrations whereas the Langmuir shows a rather poor fit and again reaches a plateau, in this occasion at 40mg/g. The Freundlich follows the data right to the limit of these tests where the solids are removing 65mg/g.

As before the wellness of fit can be quantified using the Chi-squared test. In this case the Freundlich isotherm gives a value of 0.4 and the Langmuir 34.4 so again it can be seen that the Freundlich is by far the more representative of the data.

Figure 6.23 focuses on the lower equilibrium concentrations from Figure 6.22 as these lower equilibrium concentrations are the ones of most import. The data is plotted alongside the Freundlich isotherm.

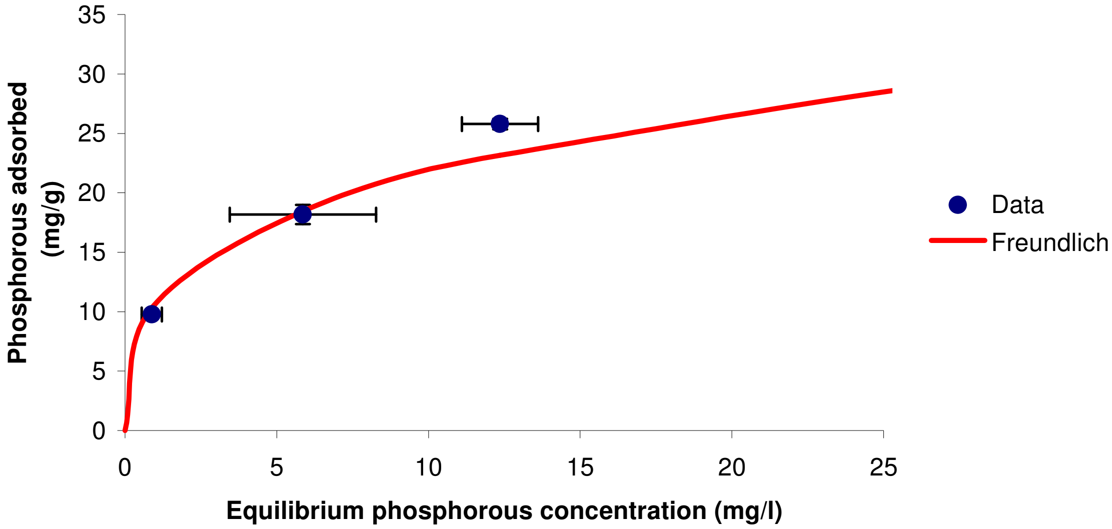


Figure 6.23 Freundlich isotherm and adsorption data for solids from the filter cake from the water treatment, focused on the lower equilibrium concentrations

Figure 6.23 shows that in the equilibrium concentration range of 0-20mg/l this filter cake is removing between 5 and 16mg/g, in this range the solids from the Horden minewater treatment plant removed 4-13mg/g. A direct comparison is shown in Figure 6.24.

6.3.3 Comparison of adsorption performance to materials from the literature

The Freundlich isotherm for the water treatment solids has been added to the comparative chart (Figure 6.15) from Section 6.2 to provide comparison to that of the solids from Horden and other studies from the literature review.

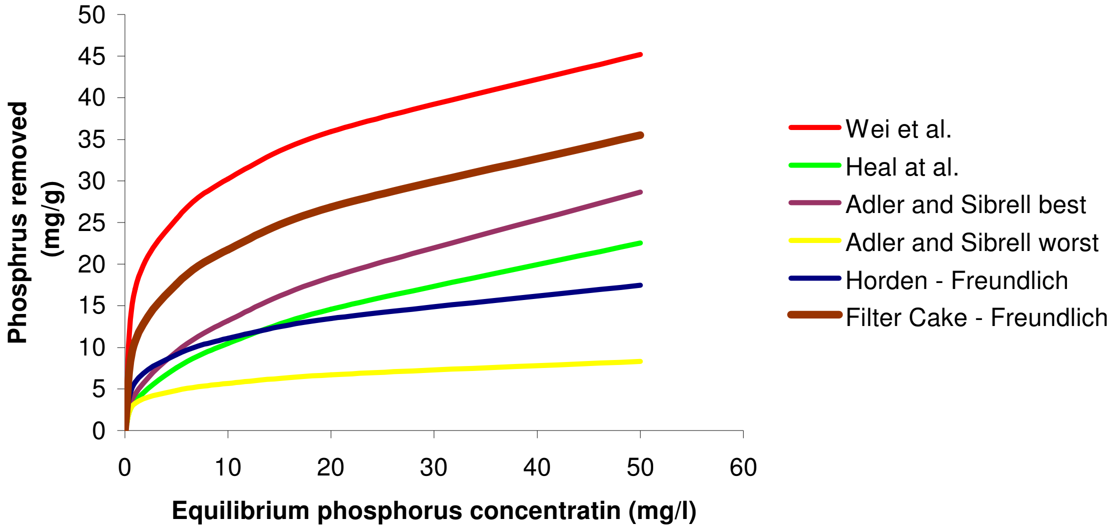


Figure 6.24 Comparison of the Freundlich isotherm for the filter cake solids from a water treatment works to that of the solids from Horden and select materials from the literature review.

In terms of removal per gram of dry solid the filter cake from the water treatment plant is performing well, significantly better than the sludge from the Horden minewater treatment plant. The filter cake solids are performing better than all but one of the materials from the literature presented here.

This section has presented the adsorption data for the water treatment filter cake solids and has shown this material to be a more effective phosphorus adsorbent than the solids from Horden. This is however only when results are normalised to dry solids as the filter cake has a very high moisture content of 80%. The Freundlich and Langmuir isotherms were calculated and, as with the solids from Horden, the Freundlich isotherm was found to be the more representative of the data.

6.4 Adsorption performance of commercial phosphorus adsorbent, Rowaphos

This section details the results from batch adsorption tests on the commercial phosphorus adsorbent Rowaphos. Rowaphos is marketed at use in aquariums but has also been used in large scale applications, see Chapter 5 for further details. The adsorptive performance of this material is presented from which the theoretical isotherms have been calculated and whereafter the results are compared to the materials from the previous two sections and materials from the literature review.

6.4.1 Phosphorus adsorption by the commercial adsorbent, Rowaphos

The results are presented in the same format as the previous two sections thus starting with the raw results from batch adsorption tests. Initial concentrations, as before, ranged from 28-550mg/l. the volume of the batch tests was 40ml and 0.5g of Rowaphos was used in its as received state (30% moisture content), this is a solids concentration of 3.75g/l. Rowaphos is stated as losing some capacity if it is not used dried (Jekel and Genz). Tests ran for 16 hours at room temperature and were carried out in triplicate. The results are shown in Figure 6.25 with the initial concentrations on the x-axis, and the equilibrium concentrations on the y-axis. Error bars represent ± 1 standard deviation.

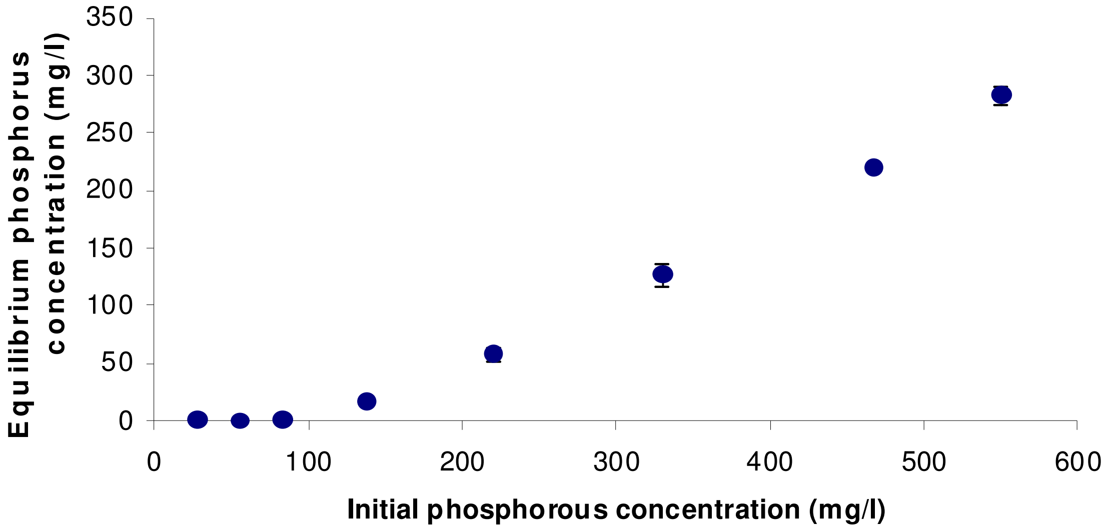


Figure 6.25 Results for batch adsorption tests on the commercial phosphorus adsorbent, Rowaphos

Figure 6.25 shows that for initial concentrations up to 80mg/l Rowaphos removed these to below 1mg/l. The highest initial concentration of 550mg/l was reduced to 280mg/l, this is a similar performance to that of the solids from Horden. Again a more direct comparison is enabled by the plotting of the adsorption isotherm, this involves plotting the phosphorus loadings achieved per dry mass (mg/g) against the relevant equilibrium concentration that these were obtained at.

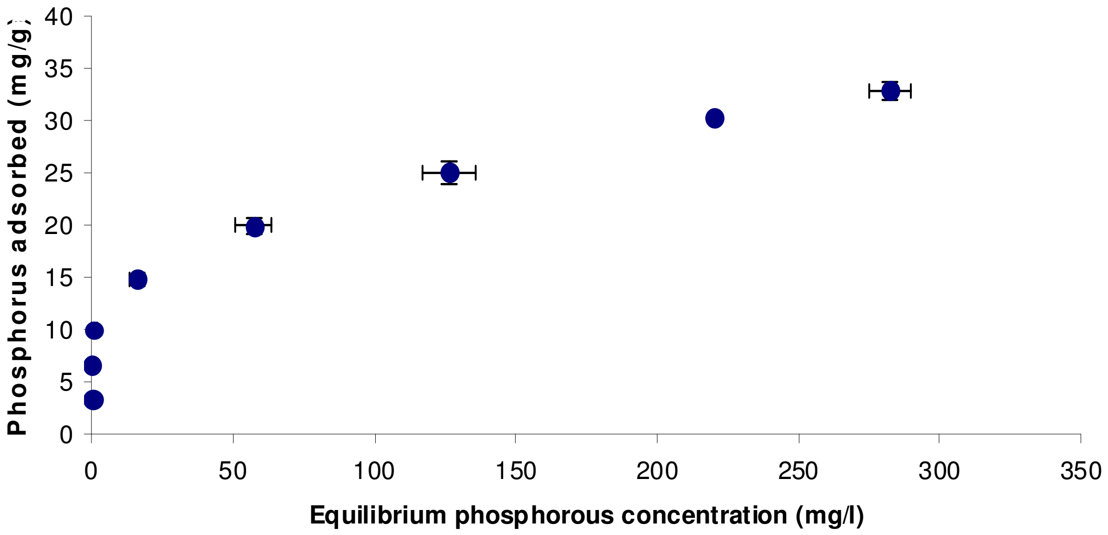


Fig 6.26 Adsorption data for the commercial phosphorus adsorbent, Rowaphos

The phosphorus loading achieved ranges from 3.34-32.89mg/g across the equilibrium concentration range of 0.31-282.33mg/l. These values are close to those of the Horden solids which achieved a maximum loading of 28mg/g at 215mg/l. This shows that the solids from Horden, currently an expensive waste problem is capable of phosphorus removal comparable to that of a commercial adsorbent, a full comparison is shown in Figure 6.33. The variation of initial pH with initial concentration is identical to that shown in Figure 6.5 and is therefore not replotted here. The variation of final pH with initial pH is shown in Figure 6.27

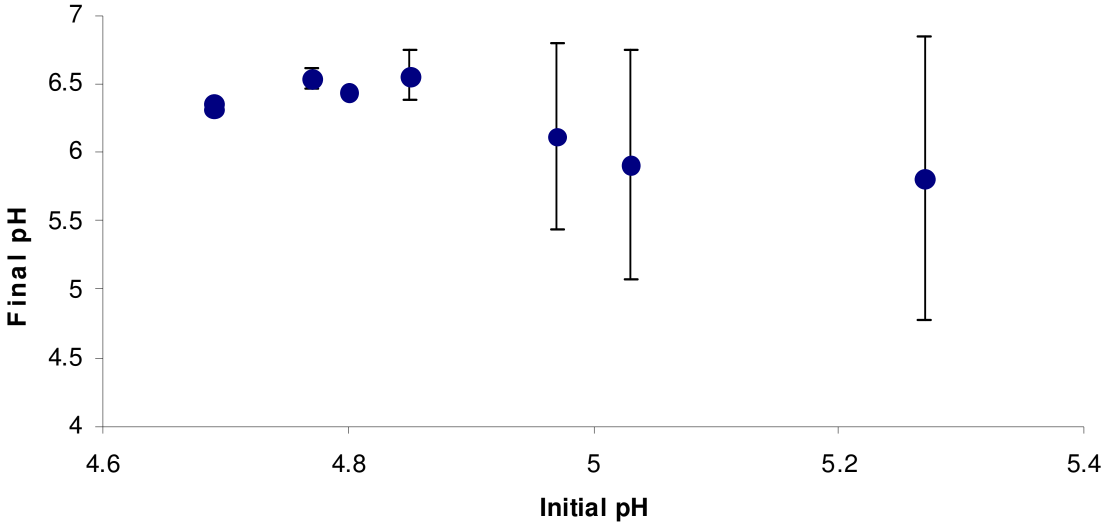


Figure 6.27 Initial and final pHs for adsorption tests on commercial phosphorus adsorbent, Rowaphos.

The final pH values in Figure 6.27 range from 5.81 to 6.31 and this low range could assist with the adsorption of anions. The final pH can be seen to vary little with initial pH, Rowaphos is pure iron oxide and so perhaps this explains the difference in the pH pattern between Figure 6.27 and the solids from Horden and the filter cake both of which contained calcium. Figure 6.28 plots the variation of phosphorus removed with final pH.

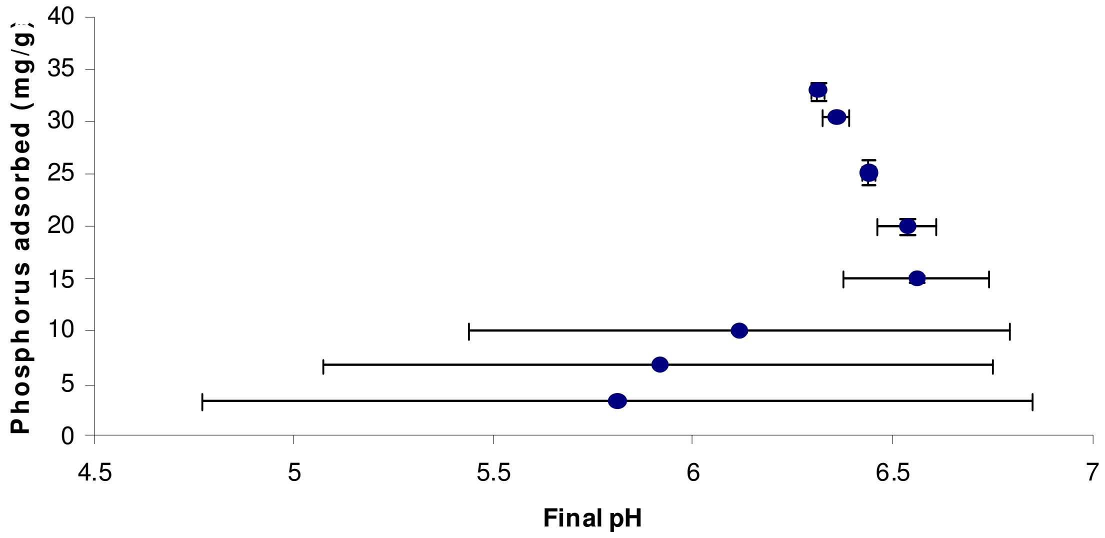


Figure 6.28 variation of phosphorus removed with final pH

As expected from the consistency in final pH from Figure 6.27 there is no real relationship between phosphorus removal and final pH with a large range of loadings achieved across a small range of final pHs. The three data points at the lower phosphorus loadings can be seen to have relatively large standard deviations.

6.4.2 Calculation of theoretical isotherms

The linear form of the Freundlich isotherm has been plotted by taking logarithms of both the phosphorus loading (mg/g) and the equilibrium concentration (mg/l).

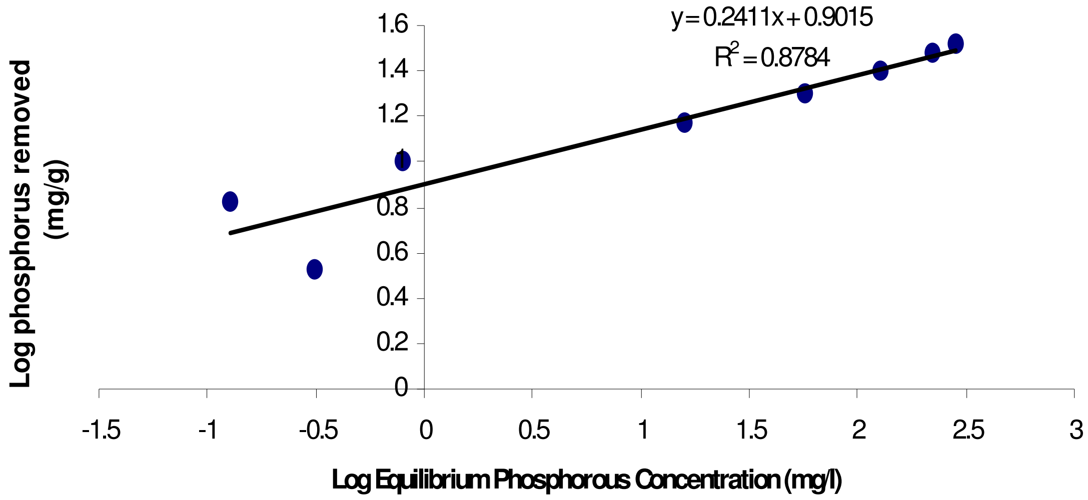


Figure 6.29 Linear plot for the Freundlich isotherm for the commercial phosphorus adsorbent, Rowaphos.

Figure 6.29 results in the equation

$$\frac{x}{m} = 7.97C^{0.2411} \qquad \text{Equation 6.9}$$

for the Freundlich isotherm with an R^2 value of 0.8784 showing good correlation.

The linear form of the Langmuir isotherm has been plotted in Figure 6.30, this is achieved through the inversion of the phosphorus loading and the equilibrium concentration.

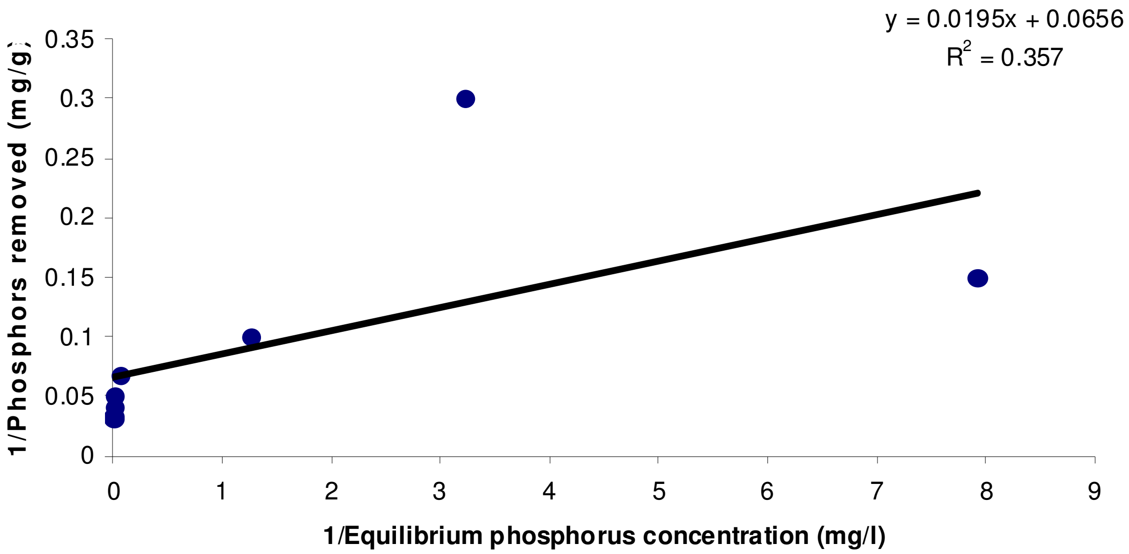


Figure 6.30 Linear plot for the Langmuir isotherm for the commercial phosphorus adsorbent, Rowaphos.

Figure 6.30 provides equation 6.10 for the Langmuir equation

$$\frac{x}{m} = \frac{3.36 * C * 15.24}{1 + (3.36 * C)} \qquad \text{Equation 6.10}$$

for the Langmuir isotherm. The line of best fit has a coefficient of determination of 0.357 which is low and therefore again it is expected that the Freundlich isotherm will provide a more accurate model. The data has been replotted as points alongside the isotherms represented by lines in Figure 6.31.

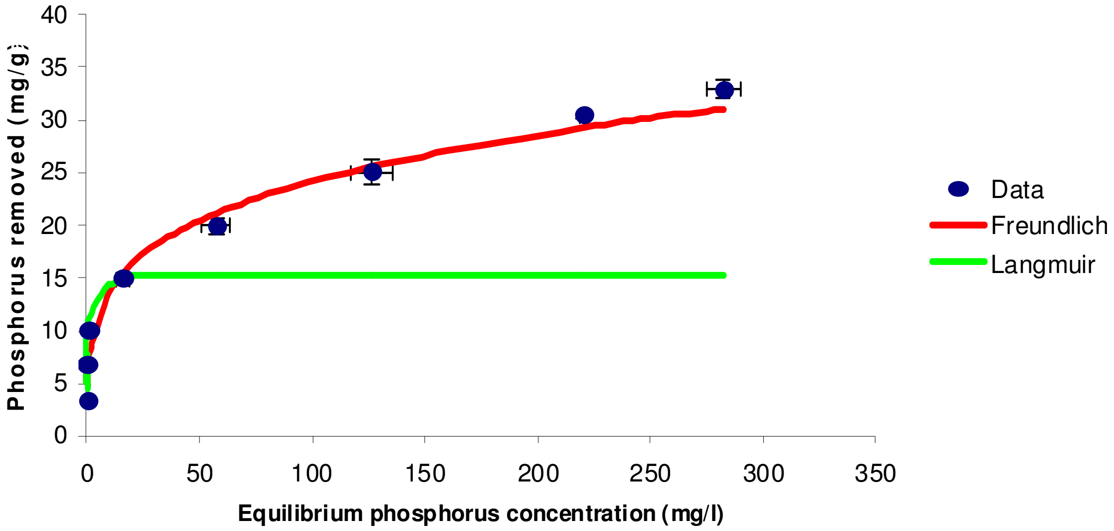


Figure 6.31 Freundlich and Langmuir isotherms alongside the adsorption data for the commercial phosphorus adsorbent Rowaphos

Again the Freundlich isotherm is providing a much better fit to the data than the Langmuir. Chi squared values of 3 for the Freundlich and 47 for the Langmuir were found, showing the Freundlich again to have the better fit.

As in previous sections, the data and Freundlich isotherm have been reproduced focused on the lower equilibrium concentrations in Figure 6.32.

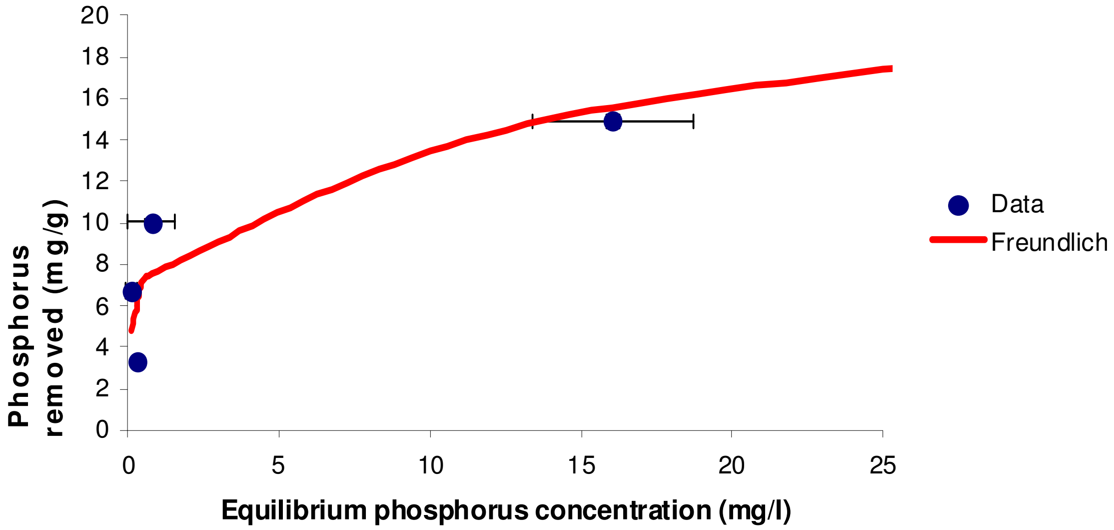


Figure 6.32 Freundlich isotherm and adsorption data for the commercial phosphorus adsorbent, Rowaphos, Focusing on the lower equilibrium concentrations.

In the range of equilibrium concentrations of 0-20mg/l Rowaphos removes 5-16mg/g, this compares to 4-13mg/g and 5-16mg/g for the solids from Horden and the water treatment plant filter cake respectively.

There have been independent reviews of Rowaphos' performance. Jekel and Genz looked at phosphorus removal by Rowaphos from both tap water and sea water. With tap water as a solvent, Jekel and Genz found Rowaphos to achieve a maximum of 17.3mg/g, this was found at an equilibrium concentration of 1mg/l. For an equilibrium concentration of 1mg/l the Freundlich isotherm from Figure 6.31 gives a phosphorus loading of 8mg/g around half that found by Jekel and Genz. Jekel and Genz ground the Rowaphos to sub 63 microns and this is likely to be largely responsible for the difference in phosphorus loadings found due to the resultant increase in surface area.

6.4.3 Comparison of adsorption performance to materials from the literature

The Freundlich isotherm for Rowaphos is compared to those of the other materials studied and materials from the literature review in Figure 6.33

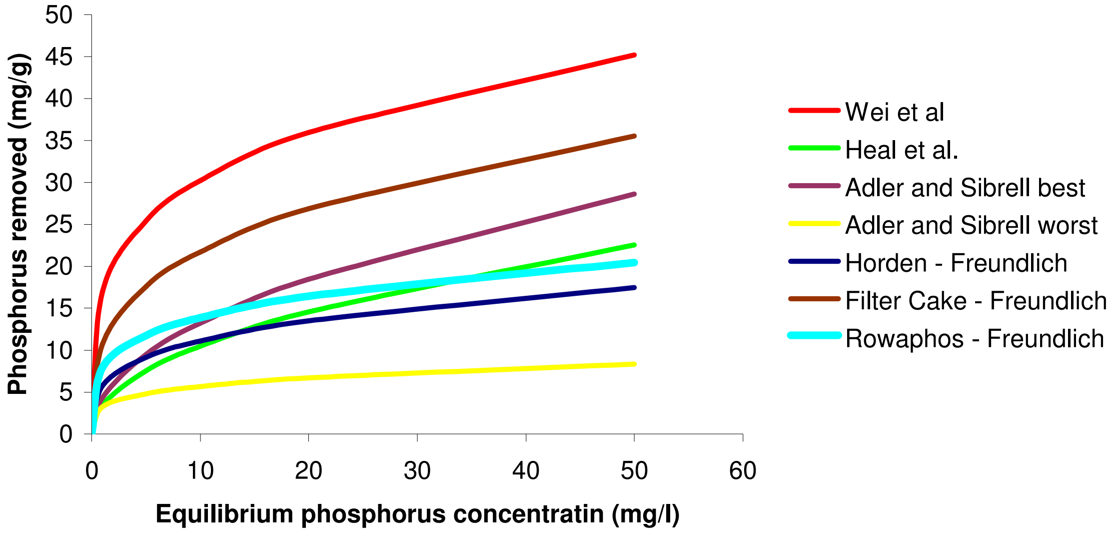


Figure 6.33 Comparison of Rowaphos Freundlich isotherm to that of other materials and those from the literature review.

The isotherms used as comparisons in Figure 6.33 are taken from Heal *et al.* (2004), Wei *et al.* (2008) and Adler and Sibrell (2003). Figure 6.32 shows that Rowaphos is performing only slightly better than the solids from Horden. This suggests that in terms of removal performance the solids from Horden could have potential as commercial phosphorus adsorbent, as could the filter cake solids which perform very strongly on a dry weight basis.

This section has followed the pattern of the previous two, presenting adsorption data and calculating the Freundlich and Langmuir isotherms for this data. As this material is a commercial product it offers a useful benchmark for the potential of commercial applications. Comparisons have shown that the solids from Horden perform to a similar standard and the filter cake solids outperform this commercial adsorbent on a dry weight basis.

6.5 Batch phosphorus adsorption tests on treated AMD solids from Dawdon mine water treatment plant

A second source of treated AMD solids was obtained from the minewater treatment plant at Dawdon as described in Chapter 5. The results from batch adsorption tests are presented, followed by the calculation of theoretical isotherms and the comparison of these results to the materials from the current study and select materials from the literature review.

6.5.1 Phosphorus adsorption by AMD solids from Dawdon mine water treatment plant

The performance of these solids was presumed to be similar to that of the Horden solids, therefore initial phosphorus concentrations of 50-150mg/l were chosen so to leave low equilibrium concentrations, these being of the most relevance to removal at WWTWs. As with the tests on Horden solids 0.5g of dried solids was used with a batch volume of 40ml, a solids concentration of 12.5g/l. The tests were run for 16 hours overnight at ambient room temperature. Firstly the equilibrium concentrations are plotted against the initial concentrations in Figure 6.34 Error bars represent ± 1 standard deviation.

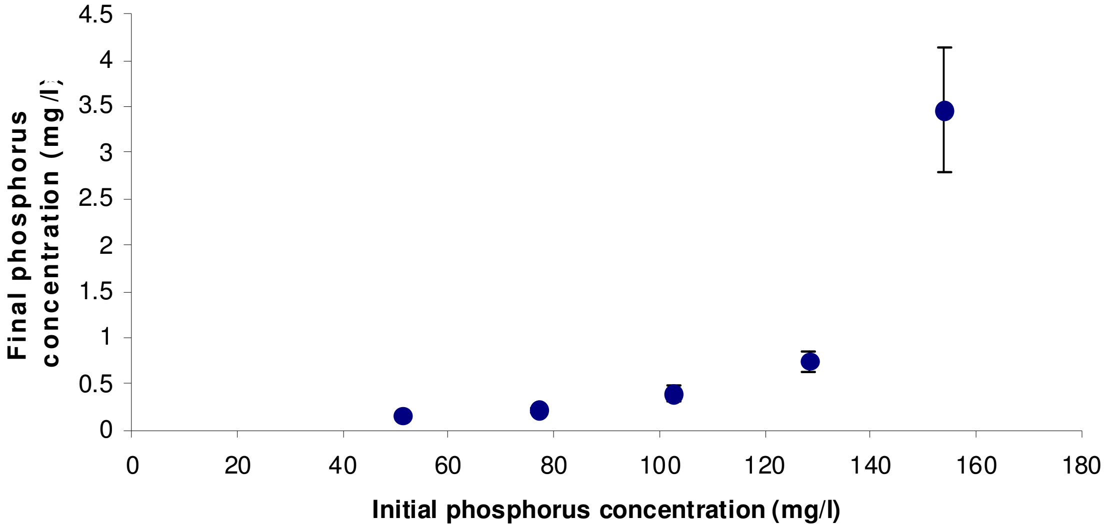


Figure 6.34 Raw results for the batch adsorption tests on the solids from Dawdon minewater treatment plant.

The test with the lowest initial concentration of 50mg/l was reduced to 0.16mg/l, the highest initial concentration of 150mg/l was reduced to 3.5mg/l, therefore the solids from Dawdon showed consistently high levels of removal for the initial concentrations studied. These results are presented in the adsorption isotherm form in Figure 6.35.

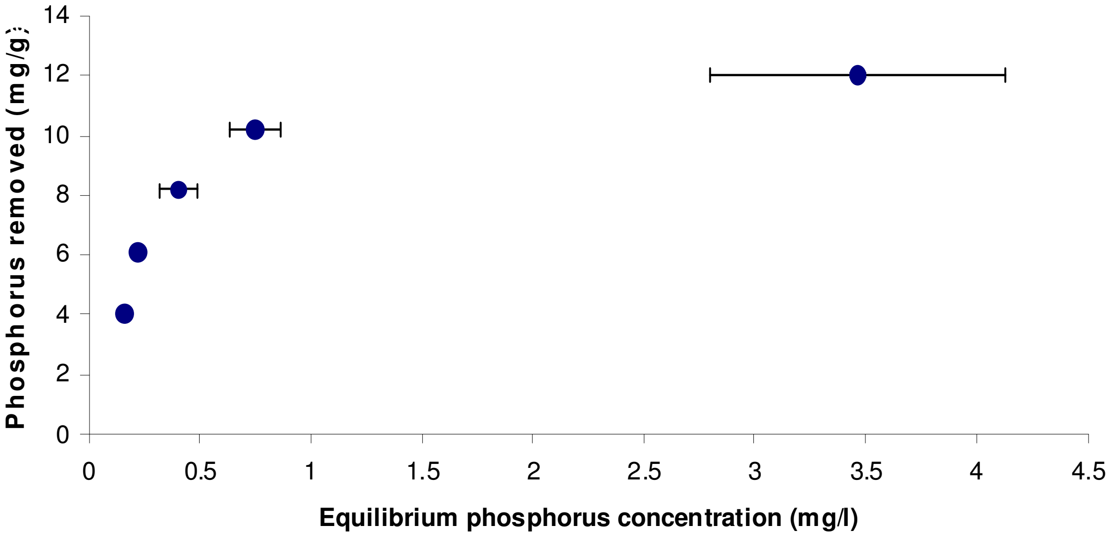


Figure 6.35 Adsorption data for the solids from the Dawdon minewater treatment plant.

Figure 6.35 shows that at the low equilibrium concentration range of 0-3.5mg/l the solids from Dawdon are removing 4.1-12.0mg/g. In the same range Horden solids removed up to 10mg/g showing that these materials are performing to a similar level. A full comparison is shown in Figure 6.40.

6.5.2 Calculation of theoretical isotherms

The linear forms of the Freundlich and Langmuir isotherms have been plotted to allow the determination of the coefficients and thus the adsorption isotherm equations.

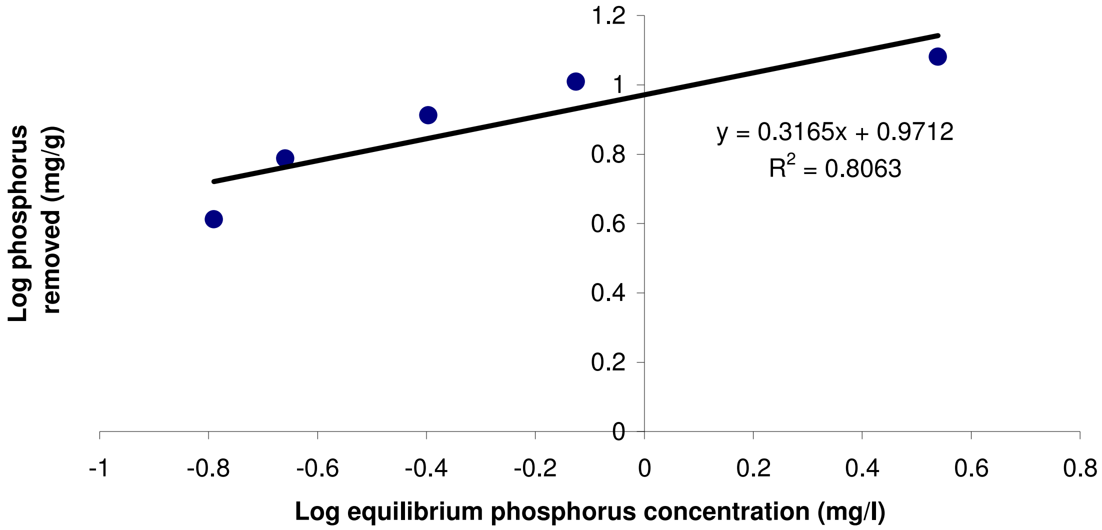


Figure 6.36 Linear form of the Freundlich isotherm for the solids from the Dawdon minewater treatment plant.

Figure 6.36 results in the Freundlich equation

$$\frac{x}{m} = 9.358C^{0.3165} \qquad \text{Equation 6.11}$$

With a coefficient of determination of 0.80, showing a reasonable correlation but the lowest value thus far for the Freundlich isotherm. The coefficients for the Langmuir isotherm are determined from the plot shown in Figure 6.37.

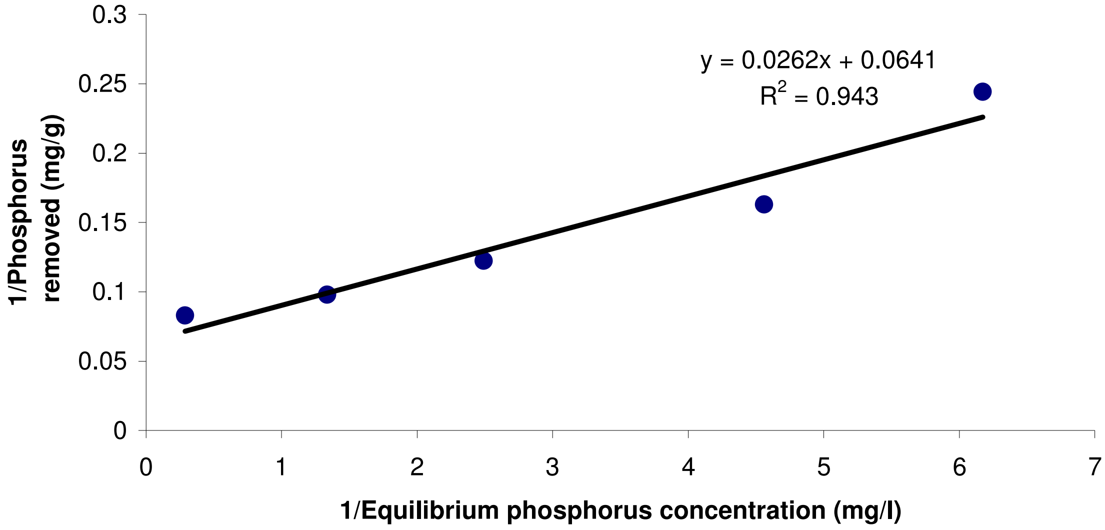


Figure 6.37 Linear form of the Langmuir isotherm for the solids from the Dawdon minewater treatment plant.

Figure 6.37 results in Equation 6.12 for the Langmuir isotherm equation

$$\frac{x}{m} = \frac{2.45 * C * 13.28}{1 + (2.45 * C)} \qquad \text{Equation 6.12}$$

Both the isotherms are presented as lines, alongside the data, presented as points in Figure 6.38.

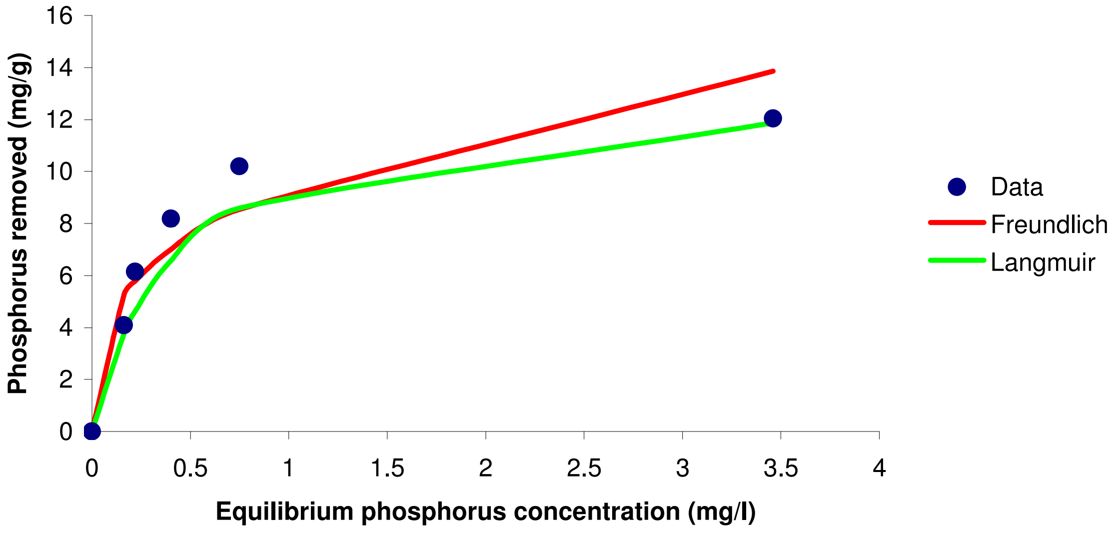


Figure 6.38 Freundlich and Langmuir isotherms alongside the adsorption data for the solids from the Dawdon minewater treatment plant

The Freundlich and Langmuir isotherms have chi squared values of 1.04 and 1.21 respectively. These are close values but suggest the Freundlich to fit the data better. The linear form of the Freundlich isotherm was found to have a lower coefficient of determination than the Langmuir. For this small range of data then both isotherms fit the data to a similar degree. The isotherms can be extended beyond the range where actual data is known for, this extrapolation is not ideal in terms of confidence in the pattern the data will take past the known range but will allow comparison to the other materials over a wider range of concentrations. It will also be possible to see whether the Langmuir isotherm will take the same shape as for the previous materials and reach a plateau.

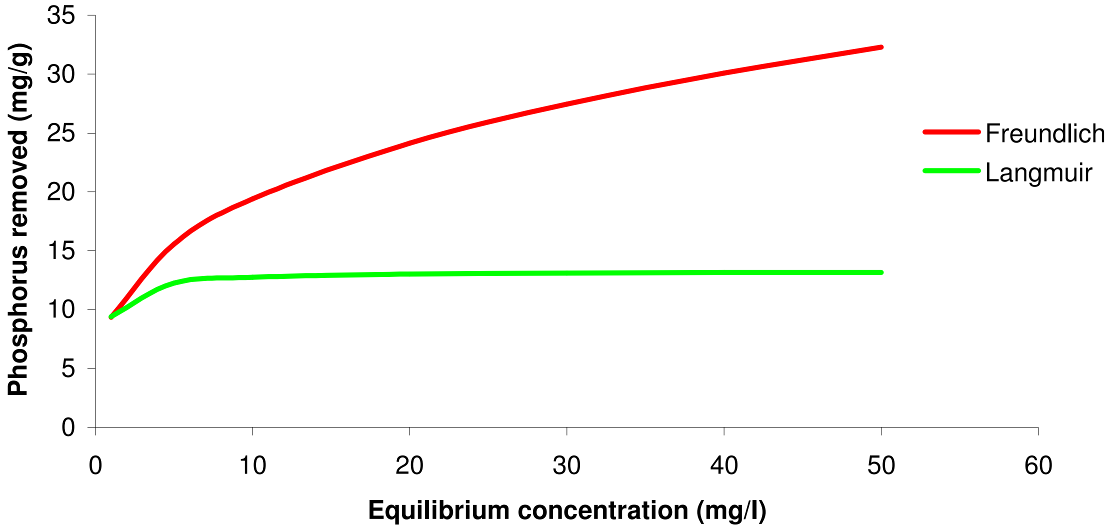


Figure 6.39 The Freundlich and Langmuir isotherms for the solids from Dawdon. The isotherms have been extended beyond the measured limits.

Figure 6.39 shows that when extended the Langmuir, as with the previous materials studied, reaches a plateau. The Freundlich isotherm has provided the better fit for all the previous materials and was found to have a lower chi squared value than the Langmuir. Therefore the Freundlich isotherm will be used to represent the data for the solids from Dawdon.

6.5.3 Comparison of adsorption performance to materials from the literature

The Freundlich isotherm for the solidsfromDawdon will now be compared to those for the other materials studied and to other materials from the literature review. The isotherms used as comparisons are taken from Heal *et al.* (2004), Wei *et al.* (2008) and Adler and Sibrell (2003).

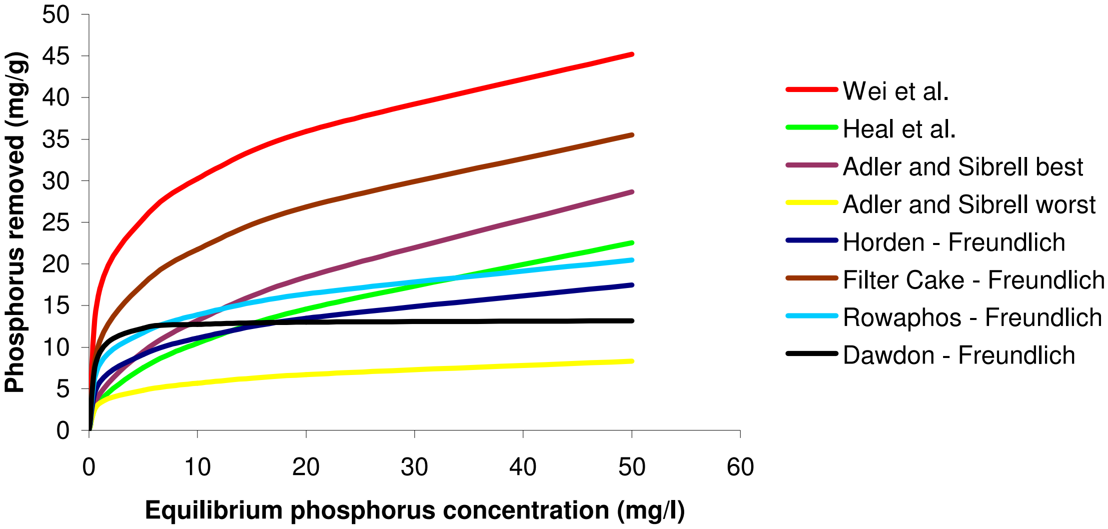


Figure 6.40 Comparison of the Freundlich isotherm for the solids from the Dawdon mine water treatment plant to those of the other materials tested and select materials from the literature review

Figure 6.40 shows that the solids from Dawdon minewater treatment plant are performing similarly to the solids from Horden, again showing a reasonable level of performance in comparison to the other materials.

This section has presented adsorption data and the theoretical adsorption isotherms for a second source of AMD solids, from the mine water treatment plant at Dawdon. It was again shown that the Freundlich isotherm showed a better fit than the Langmuir. This material performs similarly to the solids from Horden mine water treatment plant and the commercial adsorbent, Rowaphos, especially at the lower equilibrium concentrations.

6.6 Chapter 6 conclusions

This section summarises the results presented for the four raw materials studied and give an assessment of their suitability for use at WWTWs.

6.6.1 Comparison of adsorption performances

The Freundlich isotherms for the four materials have been presented alongside the isotherms for select similar materials from the literature in Figure 6.39, a fuller discussion of this comparison is provided here. The variation in performance can be seen by comparing the removal at 10mg/l, a typical WWTWs influent concentration. The highest performing material studied by Wei *et al.* (2008) is capable of 30.2mg/g at this, the lowest performing as studied by Sibrell *et al.* (2009) just 5.6mg/g, this is quite a range in performance and shows that not all solids from minewater treatment plants will have suitable capacities for phosphorus removal at WWTWs. Many sources of AMD may also be contaminated with undesirable elements, such as that from Parys Mountain discussed in Chapter 5. Therefore the potential of each AMD source would have to be individually assessed.

The Freundlich isotherm was found to have a superior fit to the data for the four materials studied for this thesis. The material studied by Wei *et al.* (2008) was found to be well fitted by the Freundlich isotherm as were the six materials studied by Sibrell *et al.* (2009). Heal *et al.* (2004) found the Langmuir to offer the better fit to their data.

The results from the literature are removed from Figure 6.40 to allow a clearer comparison of the materials studied in the present work in Figure 6.41.

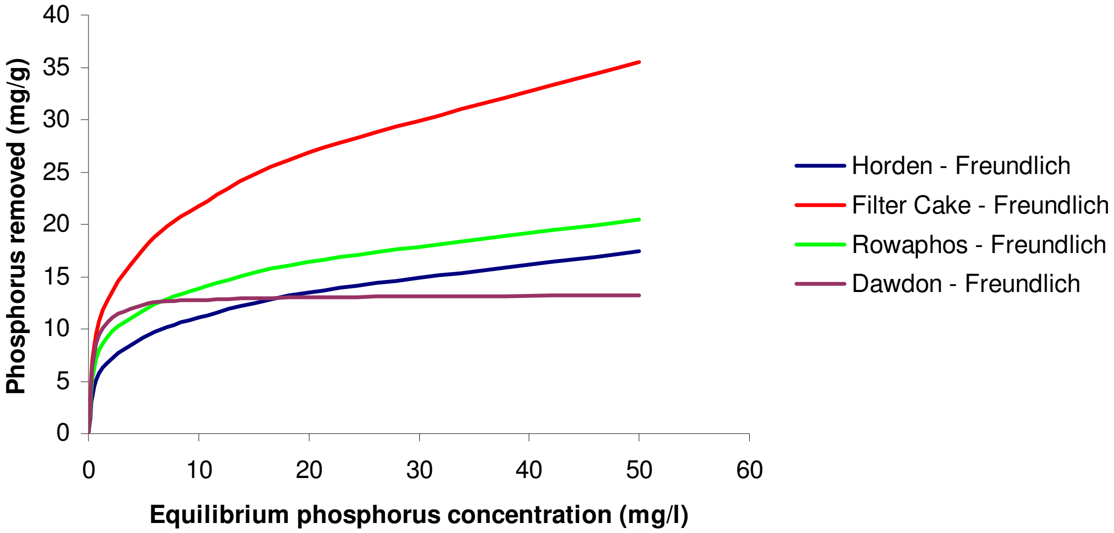


Figure 6.41 Comparison of the Freundlich isotherms for the four materials studied

Figure 6.41 shows that the two sources of AMD solids and the commercial adsorbent Rowaphos are performing to a similar standard. The solids from Dawdon perform relatively well at low equilibrium concentrations, but the isotherm predicts that it soon reaches its maximum loading, this is extrapolation however and may not completely accurately represent the materials performance at higher equilibrium concentrations. The filter cake from the water treatment works is outperforming all three by some measure, and this becomes more pronounced as the equilibrium concentration increases. The absolute data at specific equilibrium concentrations and the Freundlich equations for all four materials is shown in Table 6.1 to allow quick comparison.

Table 6.1 Comparison of Freundlich isotherms and specific data for the four materials studied

Material	Freundlich Isotherm	Removal at 1mg/l (mg/g)	Removal at 10mg/l (mg/g)	Max removal found (mg/g)	Conc for max removal (mg/l)
Horden	$\frac{x}{m} = 5.81C^{0.2813}$	5.8	11.1	27.9	214
Filter cake	$\frac{x}{m} = 10.75C^{0.3056}$	10.8	21.7	65.3	373
Rowaphos	$\frac{x}{m} = 7.97C^{0.2411}$	8.0	13.9	32.9	282
Dawdon	$\frac{x}{m} = 9.36C^{0.3165}$	9.4	12.8*	12.0	3.5

*this value is from the extension of the Freundlich isotherm beyond the measured data range.

The classic adsorption isotherm is presented on a dry weight basis, however these materials are not naturally dry and so the Freundlich isotherms will be transformed by the moisture content of the material to offer "real life" removal rates. The solids from Dawdon were received in a dry state and so for this exercise it will be assumed that they have the same moisture content as the solids from Horden.

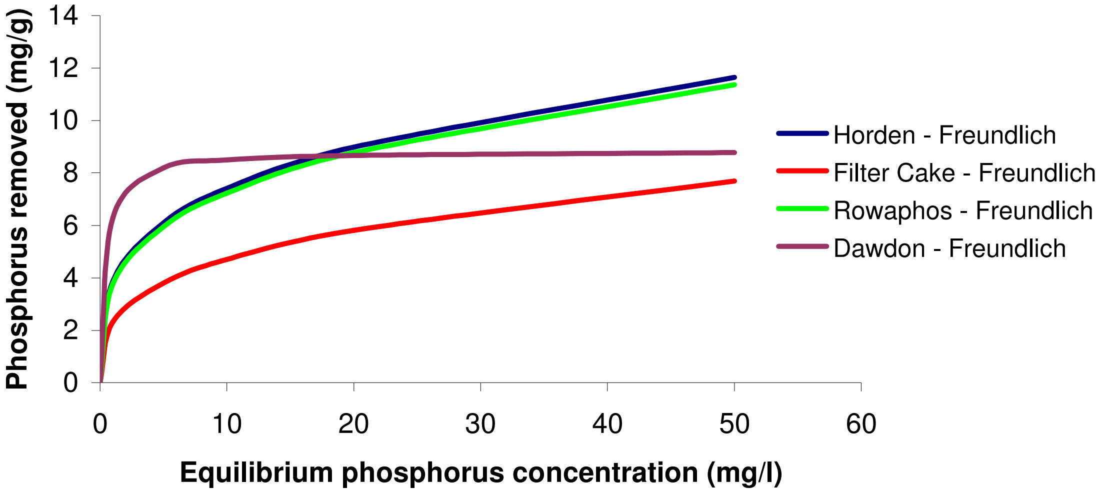


Figure 6.42 Comparison of the Freundlich isotherms for the four materials studied. Results are presented as per as per wet weight.

Figure 6.42 shows that on a wet solids basis the high performance of the filter cake drops from being the highest performing to the lowest. The Freundlich isotherm for the solids from Dawdon shows high performance at the low equilibrium concentrations, but this reaches a plateau and is taking over by the solids from Horden and Rowaphos, both of which are performing nearly identically. This again shows the solids from Horden performing close to the commercial product.

6.6.2 Factors affecting adsorption

pH, Iron content and surface area data are known for the solids from Horden, the water treatment filter cake and for Rowaphos, these factors will affect adsorption and can be compared to the maximum phosphorus loadings achieved to identify any patterns. Only three points are available for any data range and so strong conclusions will not be able to be made, yet the effect of these factors upon removal is worthy of consideration. The variation of the experimentally determined maximum phosphorus loadings with the average pH at equilibrium is plotted in Figure 6.43

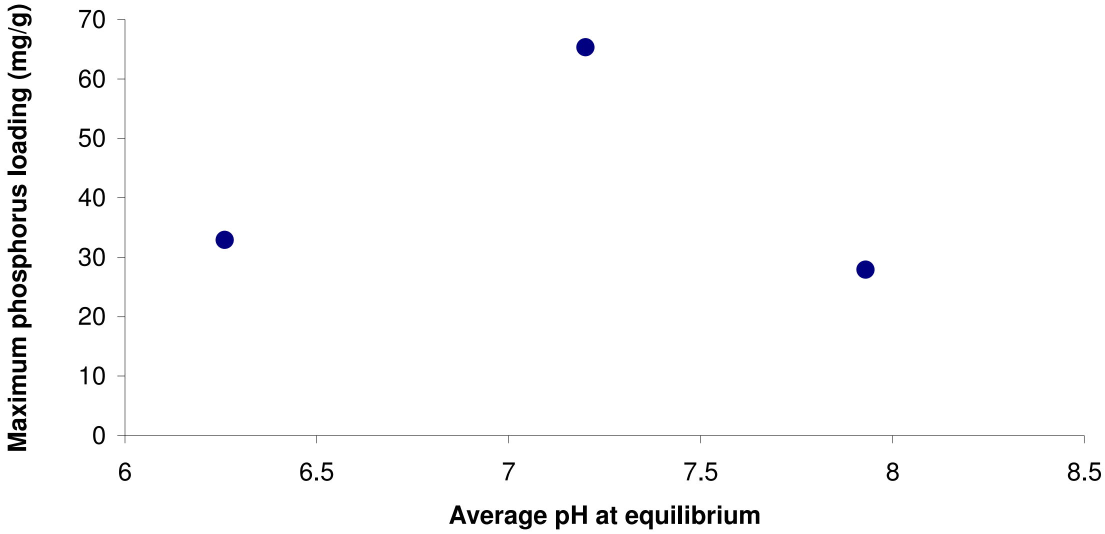


Figure 6.43 Variation of maximum phosphorus loading with average pH at equilibrium

There is no clear correlation between final pH and phosphorus loading for the three data points plotted in Figure 6.43. The average pH at equilibrium for the three materials is approximately neutral ranging from 6.3 to 7.9

Figure 6.44 plots the maximum phosphorus loading against the iron content of the materials.

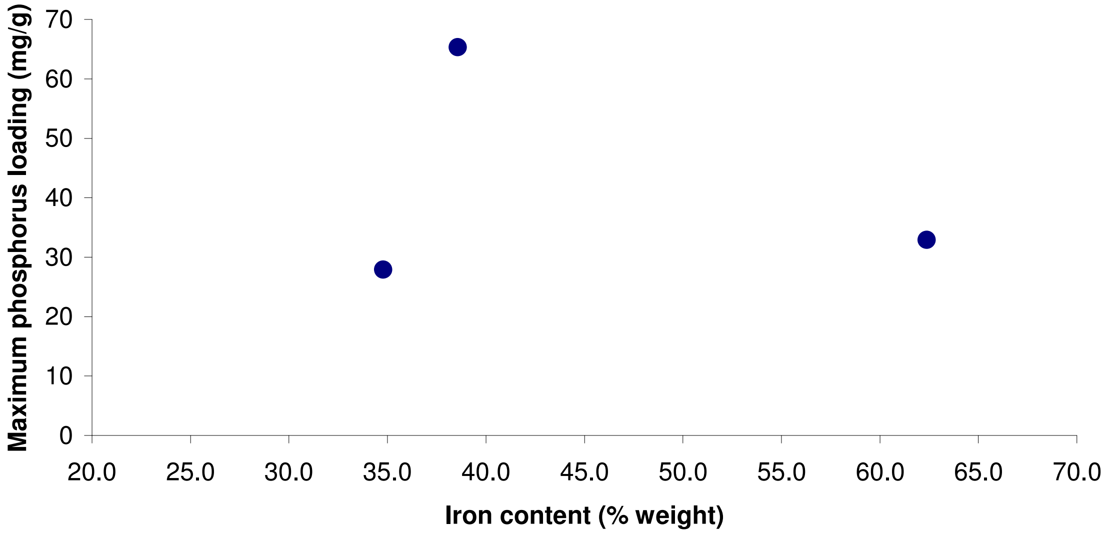


Figure 6.44 Variation of maximum phosphorus loading with iron content.

As with final pH, there is no correlation between iron content and maximum phosphorus loading in Figure 6.44, however again the data ranges are limited. Figure 6.45 plots the maximum experimentally determined phosphorus loading against the surface areas from Table 5.1.

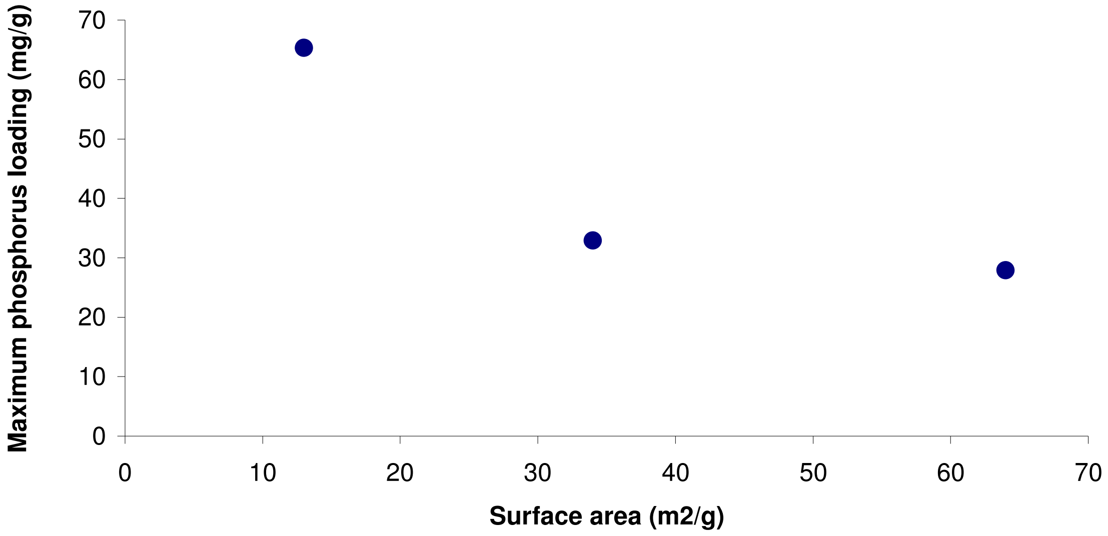


Figure 6.45 Variation of maximum phosphorus loading with surface areas

Figure 6.45 shows that there is a negative correlation between surface area and phosphorus loading, this is converse to logic as higher surface areas will provide more sites for adsorption. Figures 6.43, 6.44 and 6.45 show that the factors controlling adsorption are complex and are likely to be controlled by a combination of pH, chemical composition, surface area, morphology and crystalline structure (Colombo *et al.* 1994).

6.6.3 Estimations of tonnage required to remove phosphorus at WWTWs

Using the adsorption isotherms calculated it is possible to carry out a crude calculation to estimate the quantities of these materials required to remove phosphorus at a wastewater treatment plant. Data from the WWTWs at Moreton will be used to represent a typical smallish works. The data for this works is presented in Table 6.2.

Table 6.2 Data for the Moreton WWTWs (Coulton 2009)

DWF (m3/day)	Population equivalent	Indicative Total phosphorus load (kg/day)	Average influent P concentration (mg/l)
1086	4157	10.4	9.6

To calculate the tonnage required in Table 6.3 the removal rate (mg/g) for the materials at an equilibrium concentration of 1mg/l was used. This is generally considered a likely effluent limit imposed for many WWTWs. Using this figure will give a conservative estimation of the weight of material required.

Table 6.3 Tonnage required to remove phosphorus at Moreton WWTW

Material	Phosphorus loading at 1mg/l (mg/g)	Solid required to remove 1 litre down to 1mg/l (g)	Tonnes required per day (dry basis)	Tonnes required per day (wet basis)
Horden	5.8	1.48	1.61	2.4
Filter cake	10.7	0.80	0.87	4.1
Rowaphos	8.0	1.08	1.17	1.8
Dawdon	9.4	0.91	0.99	1.5

Table 6.3 shows that reasonably large weights of these materials would be required to remove phosphorus at a relatively small WWTWs. The principal material studied in this thesis, the solids from Horden are not ideal for use at WWTWs as they form a very dense and easily eroded cake. The next chapter of this thesis pelletises this material with cement to produce a more robust material with more favourable engineering properties.

6.7 Chapter Summary

This chapter was split into five sections and adsorption data was provided for four iron hydroxide based materials. A summary of each of these sections is provided below.

6.7.1 Summary of section 6.1

This section detailed the initial kinetic tests on the treated AMD solids from Horden. These tests were performed to gain an initial appreciation of the removals these solids were capable of and the time frame of removal. Both tests had a volume of 800ml and an initial concentration of 11mg/l. The test with a solids concentration of 1.25g/l resulted in a final concentration of 1.62mg/l and a phosphorus loading of 6.4mg/g. The test with a solids concentration of 3.75mg/l finished with a concentration of 0.19mg/ and a loading of 2.6mg/g. In both cases the majority of removal occurred during the earliest stages, this was particularly apparent for the 3.25g/l test where the vast majority of removal occurred within the first 20 minutes. The results found by these tests were comparable to those from similar studies in the literature both in terms of the phosphorus loadings at the equilibrium concentrations and also in terms of the time frame of removal.

6.7.2 Summary of Section 6.2

Section 6.2 reported on two equilibrium batch experiments on the solids from Horden, one with a wide range of initial concentrations and another focused on the lower concentrations. All batch adsorption tests were performed in triplicate and the reported values were the averages of the three tests, this is true of the results for all four materials studied in this chapter. The results from both tests laid directly on top of each other allowing them to be combined into a single data set, this also confirmed the consistency of the laboratory techniques. The phosphorus loadings achieved ranged from 2.23mg/g at an equilibrium concentration of 0.26mg/l to 27.85mg/g at an equilibrium concentration of 214.45mg/l. The results allowed the calculation of the Langmuir and Freundlich isotherms, with the Freundlich showing a much better, and very good fit to the data. The isotherms allowed clear comparison to studies on similar materials from the literature and this comparison showed the solids from Horden to be a typical AMD based phosphorus adsorbent. The results for these batch tests found comparable loadings at the equilibrium concentrations found in Section 6.1 showing good consistency across the two separate sets of tests.

6.7.3 Summary of Section 6.3

Section 6.3 studied an iron based filter cake from a water treatment works. As far as the author is aware the studying of the phosphorus removal of an iron based filter cake has not been performed before. The methods used were identical to those for the solids from Horden, the weight of solids was maintained but as these solids were used wet, the solids concentration was much lower than the tests on the Horden solids. This is an inconsistency but due to the nature of adsorption and the adsorption isotherm this discrepancy does not affect the comparability of the results in the adsorption isotherm form. On a dry solids basis the iron based filter cake performed strongly removing from 10mg/g at 0.88mg/l up to 65mg/g at 370mg/l. Again the Freundlich isotherm was found to have a superior fit to the data. Comparisons with the phosphorus adsorbing capacity of other waste materials showed this iron based filter cake to have a good adsorption capacity.

6.7.4 Summary of Section 6.4

Section 6.4 studied the commercial phosphorus sorbent, Rowaphos. This material was studied to offer a commercial comparison to the waste materials studied. The same methodology was again used. The phosphorus loadings achieved ranged from 3.34mg/g at 0.31mg/l to 32.89mg/g at 282.33mg/l. The Freundlich isotherm for Rowaphos was very close to that of Horden suggesting the potential of the Horden solids as commercial phosphorus sorbent. This material was also studied by Jekel and Genz who found loadings of up to double those found in the current study. This difference was attributed to Jekel and Genz having crushed the Rowaphos they used to sub 63µm thus increasing the number of available adsorption sites.

6.7.5 Summary of Section 6.5

Section 6.5 studied a second source of AMD solids this time from the Dawdon minewater treatment plant. This material became available later on in the study and was relatively briefly investigated. The tests on these solids were carried out with lower initial phosphorus concentrations and equilibrium concentrations of 0.16-3.5mg/l were obtained across which the solids from Dawdon removed 4.1-12.0mg/g. Due to the limited range of equilibrium concentrations found in these tests when comparing Dawdon to other materials the theoretical isotherm was extended beyond the tested limits and there is therefore a large degree of uncertainty with this extrapolation.

7 Phosphorus removal by pellets in batch tests: results and discussion

This chapter presents the results of batch phosphorus removal tests on pellets. The majority of this chapter reports on pellets that were produced from the addition of cement to the sludge from the Horden mine water treatment plant. The solids were pelletised to eliminate the potential engineering issues with the raw sludge from Horden and were therefore designed to be easy to handle and use whilst retaining/enhancing the phosphorus removal potential. The full description of the production of these pellets is presented in Chapter 5. This chapter is split into four sections as detailed below.

Section 7.1 shows the improvement of phosphorus removal with a reduction in pellet size, this led to the focus on sub 125 micron pellets.

Section 7.2 reports the results of kinetic tests on these sub 125 micron pellets. Tests lasting both 1 hour and 16 hours are reported on. The solutions for the 16 hour test were analysed for both phosphorus and calcium so as to investigate the relationship between these and the potential presence of a calcium phosphate precipitation mechanism.

Section 7.3 reports on tests which lasted up to three weeks. It is shown that these longer test lengths provide a good improvement in phosphorus removal. The increased removal of phosphorus was found to be linked to a decrease in both pH and calcium and this is indicative of removal through calcium phosphate precipitation. The dominance of the calcium phosphate precipitation removal mechanism is confirmed through analysis of the surface chemistry of used pellets with strong evidence of hydroxyapatite (HAP) as the end product.

Section 7.4 details the results of tests carried out on pellets without any solids from Horden. Pellets were produced with the solids from Horden directly replaced with crushed sand and pellets were also produced from a sample of concrete waste. A consistent relationship between calcium and phosphorus for both these pellets and those of Section 7.3 is shown again with strong evidence of this being HAP.

7.1 Batch tests lasting 16 hours

This section reports the phosphorus removal capability of pellets in batch tests lasting 16 hours. Section 7.1.1 presents the results for tests carried out to gain an initial appreciation of the phosphorus removal ability of 1-2mm and 2-4mm pellets. The effect of pellet size on phosphorus removal is further explored in Section 7.1.2 where the results of tests on pellets sized between 0.212mm and 2mm are tested. Section 7.1.3 provides comprehensive data sets for pellets sized 45-125μm.

7.1.1 Initial appreciation of pellet performance

(Dobbie *et al.* 2005) used 6.4-9.5mm pellets produced from AMD solids and cement. In his US patent Sibrell used 20-100 mesh sized pellets which is equivalent to 0.152-0.85mm. For the present study two initial pellet sizes were decided on, 1-2mm and 2.8-4mm. Tests were carried out in 100ml of solution with initial phosphorus concentrations ranging from 60-480mg/l. Half a gram of pellets was used in each test (5g/l solids concentration) and the tests lasted 16 hours. The final phosphorus concentrations these tests resulted in are plotted against the corresponding initial concentrations in Figure 7.1.

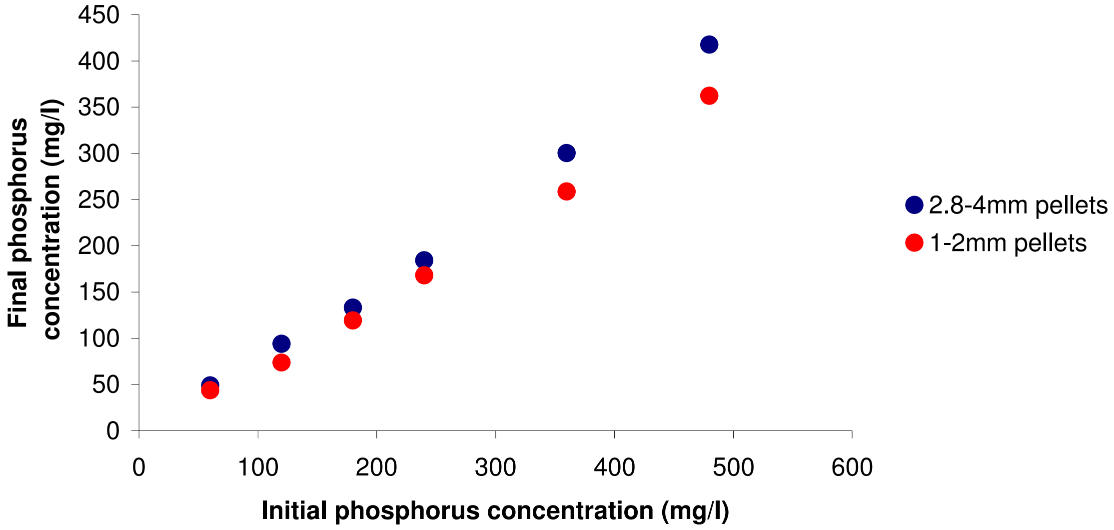


Figure 7.1 Results for the batch tests on 1-2mm and 2.8-4mm pellets

The smaller 1-2mm pellets can be seen to remove more phosphorus than the larger 2.8-4mm pellets. The 2.8-4mm pellets removed the initial concentrations of 60-480mg/l to 48.6-417.7mg/l. The 1-2mm pellets resulted in final concentrations of 43.4-362.2mg/l. The 1-2mm pellets are smaller and therefore will likely have a larger specific surface area which will assist removal in providing more adsorption sites or in terms of a calcium precipitation mechanism, higher release of calcium into solution through improved contact with water. The difference in performance between the two pellet sizes becomes clearer in Figure 7.2 where the phosphorus removed in terms of milligrams of phosphorus removed per gram of total pellet is plotted against the final phosphorus concentrations
(mg/l).

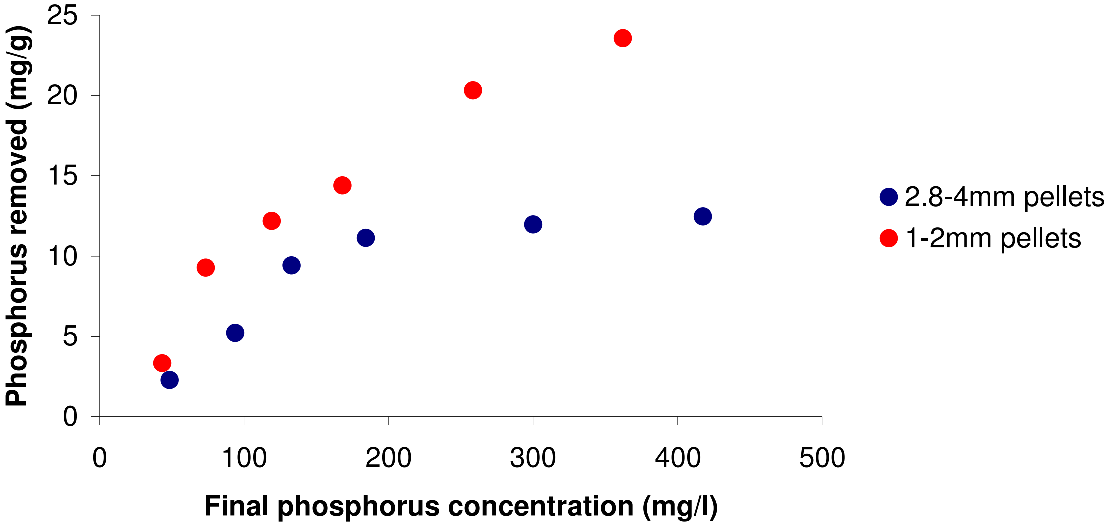


Figure 7.2 Phosphorus removal data for batch tests on 1-2mm and 2.8-4mm pellets.

Figure 7.2 clearly shows the difference in performance between the two pellet sizes. The 2.8-4mm pellet data reached a plateau at a removal of 12.5mg/g, at a final concentration of 184 mg/l these pellets are removing 11.1mg/g and when the final concentration rises to 417mg/l, the removal only rises to 12.5mg/g. This contrasts with the results for the 1-2mm pellets where no such plateau is evident. For the final concentrations studied in this test the 1-2mm pellets are removing up to 23.6mg/g at a final concentration of 362mg/l. This is nearly double the value that the 2.8-4mm pellets removed and with no plateau apparent these pellets will be capable of higher phosphorus loadings with higher initial concentrations. Figure 7.2 therefore shows a relationship between higher phosphorus removal and a reduction in pellet size. Adsorption isotherms are not calculated for the results in this chapter due to their lack of applicability due to the dominance of calcium phosphate precipitation which is fully explored throughout this chapter.

The phosphorus loadings for these pellets are compared to the Freundlich isotherm for the solids from Horden in Figure 7.3. The Freundlich isotherm is taken from Equation 6.3. The pellet results are reported as milligrams of phosphorus removed per gram of total pellet and the Freundlich isotherm for the Horden solids is per gram of dry solids. The data for the pellets are presented as data points and the Freundlich isotherm for the solids from Horden as a line.

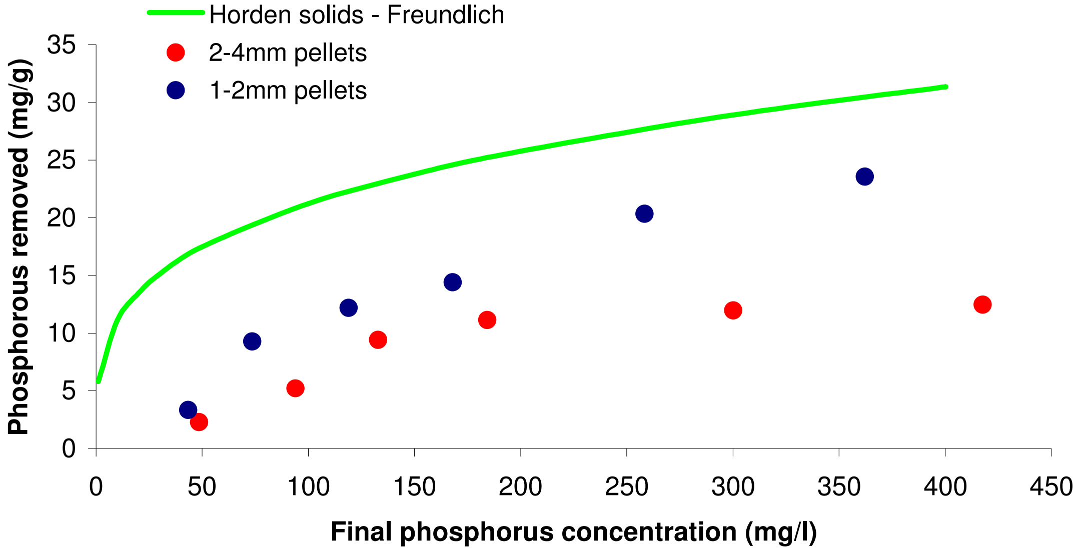


Figure 7.3 Comparison of the results for the 2.8-4mm and 1-2mm pellets and the Freundlich isotherm for Horden solids.

For the 2-4mm pellets the lowest final phosphorus concentration found was 48.6mg/l at which 2.28mg/g had been removed. The highest final concentration was 417.7mg/l with a loading of 12.47mg/g, for these two final concentrations the Freundlich isotherm gives loadings of 17.23mg/g and 31.73mg/g respectively. For the 1-2mm pellets the lowest final concentration found was

43.40mg/l at which the loading was 3.32mg/g and the highest final concentration was 362.2mg/l with a loading of 23.56mg/g, for these two final concentrations the Freundlich isotherm gives loadings of 16.78mg/g and 30.48mg/g. Figure 7.3 clearly shows that pellets of these sizes are relatively poor removers of phosphorus compared to the unpelletised Horden solids.

The pH of the solutions was measured before the pellets were added to the solutions and also once the tests had completed and had been filtered. Figure 7.4 shows the variation of initial pH with initial phosphorus concentration.

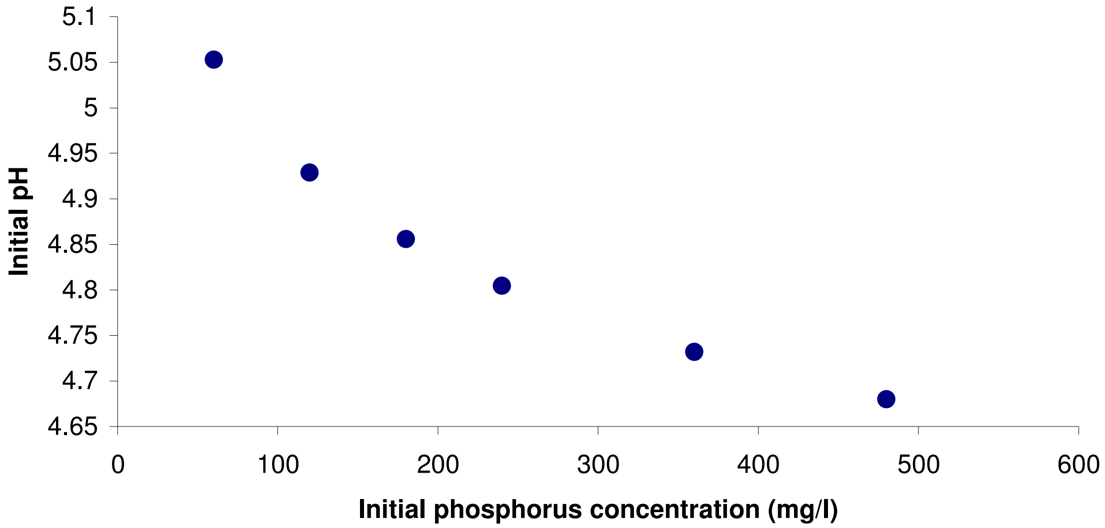


Figure 7.4 The variation of initial pH with initial phosphorus concentration for 1-2mm and 2-4mm pellets.

The initial pH values ranged from 4.68 to 5.05. An increase in phosphorus concentration resulted in a decrease in the initial pH of the solution due to the acidic nature of the KH_2PO_4 used to create the stock solution. The final pHs are plotted against the initial pH values in Figure 7.5. These final pHs were measured once the test was completed and the solution had been filtered.

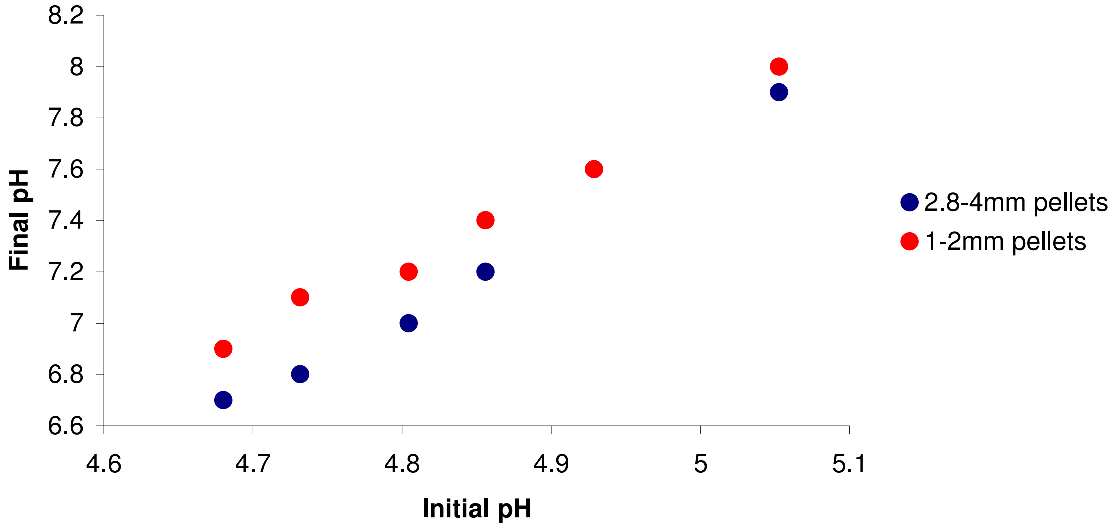


Figure 7.5 Variation of final pH with initial pH for batch phosphorus removal tests on pellets

Figure 7.5 shows that for the 1-2mm pellets the final pH ranged from 6.9-8.0 and the final pH for the 2.8-4mm pellets ranged from 6.7-7.9, the smaller pellets resulting in a consistently higher final pH than the poorer performing 2.8-4mm pellets. This suggests a link between a higher range of final pHs and improved removal. Papers such as Johansson and Gustafsson (2000) suggest that high pHs are required for efficient calcium phosphate precipitation. This relationship between size and final pH is expected as the smaller pellets will have a larger surface area and therefore leach calcium ions and hydroxide ions from the cement more readily than the larger pellets. These final pH values are comparable to those found for the tests on the solids from Horden which ranged from 7.5-8.5 (see Section 6.2). Therefore the addition of cement is not having a large effect on the final pH for pellets of this size, although the increase in solution volume from 40ml to 800ml will have an effect. All final pHs are below 9 which is the lower limit for calcium phosphate precipitation stated by Johansson and Gustafsson (2000). This could explain the poorer performance of these pellets compared to the dried solids from Horden. The pH has not been raised high enough to efficiently precipitate any calcium in solution with the phosphorus and the number of adsorption sites present will have been reduced due to the reduction in surface area. The variation of phosphorus removal with final pH is shown in Figure 7.6.

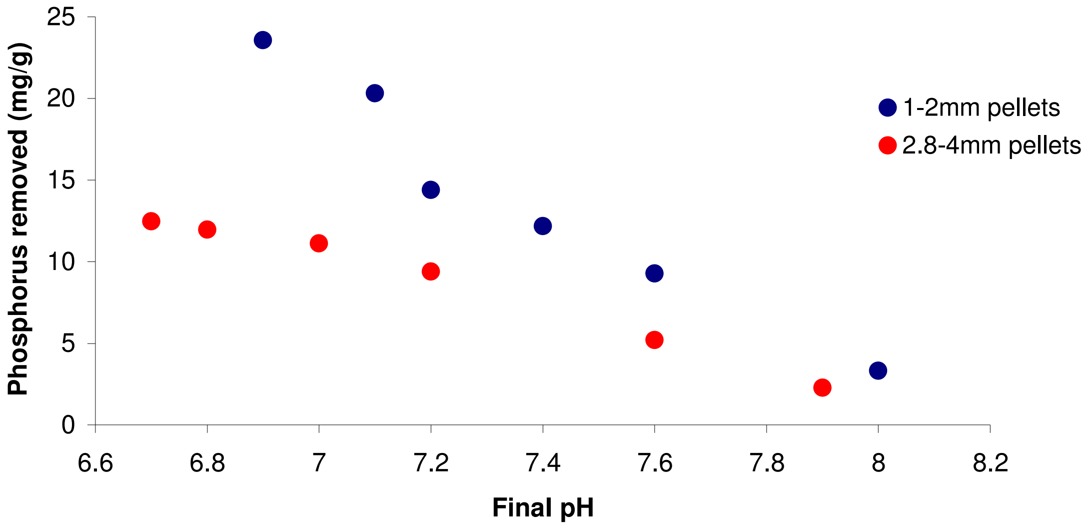


Figure 7.6 Variation of phosphorus removed with the final pH for batch phosphorus removal tests on pellets.

Figure 7.6 shows that higher removal of phosphorus is correlated with a reduction the final pH, these results fit in with those of Lu *et al.* (2009) who studied phosphorus removal by fly ash. Lu *et al.* (2009) found that the pH of their experiments was decreased with the addition of phosphorus and this combined with the drop in calcium concentration led them to conclude that calcium phosphate precipitation was the major removal mechanism. The results in Figure 7.6 are following the same pattern as far as pH is concerned. The correlation with initial pH means that this could also be having an effect and so no rash conclusions can be drawn at this point. Figure 7.6 shows that higher removal is linked to a higher range of pHs and that, within this range higher removal is correlated with a reduction in pH.

Initial tests on pellets produced from the addition of cement to the solids from Horden mine water treatment plant have shown that pellets in the size of 1-2 and 2.8-4mm have a lower phosphorus capacity than the dry solids from Horden. The reduction in size from 2.8-4mm to 1-2mm pellets has resulted in an increase in performance. The relationship between pellet size and removal capacity is further explored in Section 7.1.2.

7.1.2 Influence of pellet size on removal

Section 7.1.1 showed improved phosphorus removal when the pellet size was reduced from 2-4mm to 1-2mm. This section presents the results from further tests investigating the relationship between pellet size and performance. Tests were carried out on a wide range of pellet sizes (1.18-2mm, 0.86-1mm, 0.212-0.300mm, 0.125-0.212mm). The initial phosphorus concentrations for all tests ranged from 14-111mg/l, 0.1g of pellets were used for each test with a volume of 40ml (2.5g/l solids concentration) full experimental details are provided in Chapter 5. Firstly the final phosphorus concentrations are plotted against the relevant initial concentrations in Figure 7.7.

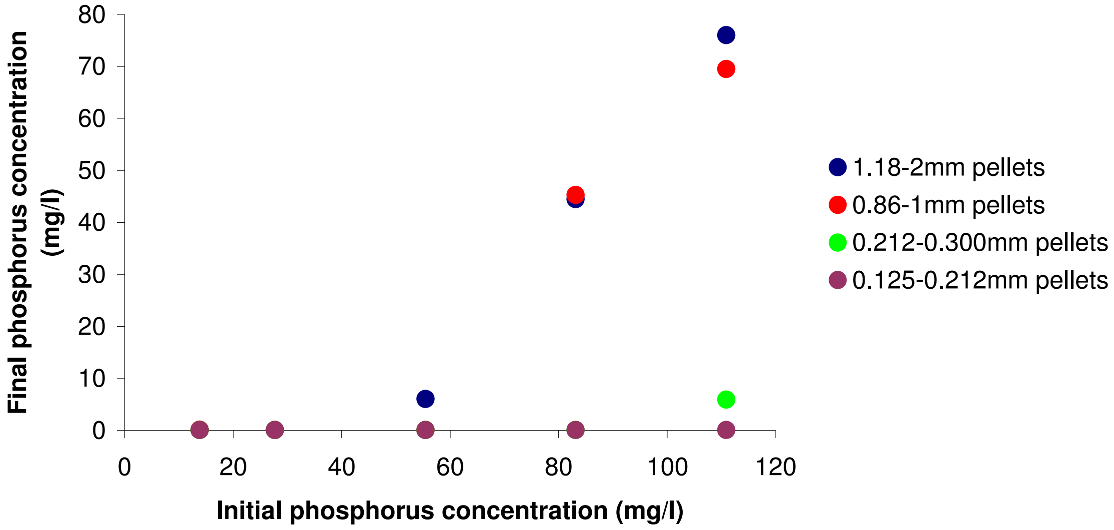


Figure 7.7 Results for the batch tests on pellets from 0.212-2mm

Many of the final phosphorus concentrations in Figure 7.7 are below the limit that the ICP was calibrated for (0.1mg/l). This includes all the data for the 0.125-0.212mm pellets, all but one point for the 0.212-0.300mm pellets and much of the data for the two other pellet sizes. For the 0.85-1mm and 1.18-2mm pellets, Figure 7.7 shows them to be performing to a similar standard. For the highest initial concentration (111mg/l) the 1.18-2mm pellets left a residual concentration of 76mg/l, the 0.85-1mm pellets 70mg/l and the 212-300mm just 6mg/l. The improvement in performance by reducing the pellet size from 0.85-1mm to 0.212-0.300mm is seen to be large. There is therefore, as found in with Section

7.1.1, a clear benefit achieved from a reduction in pellet size. The results are now converted to the adsorption isotherm form with the phosphorus removed (mg/g) plotted against the final phosphorus concentration (mg/l) in Figure 7.8. The tests that reduce the phosphorus concentration below the ICP calibration limit cannot be presented here.

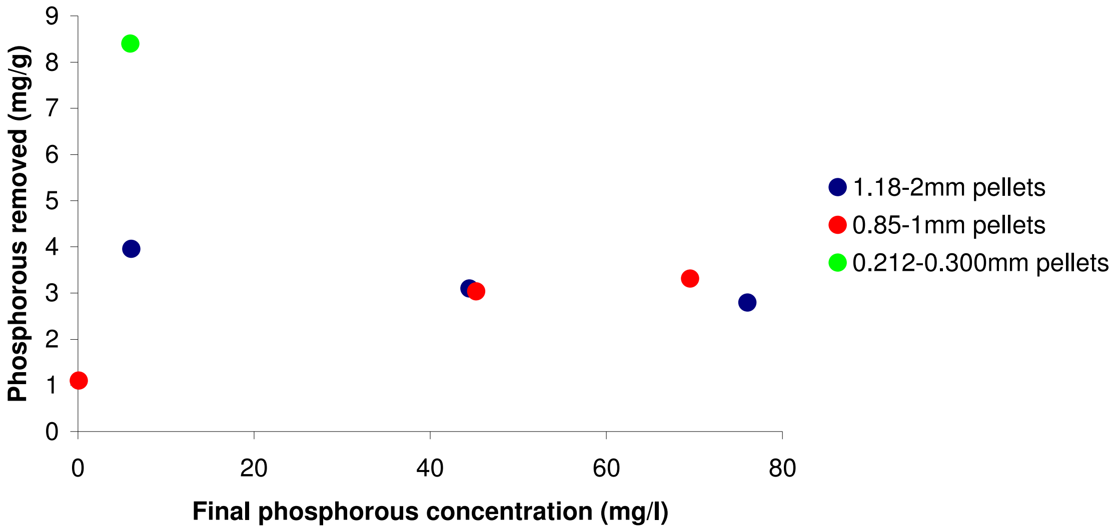


Figure 7.8 Phosphorus loading achieved by pellets ranging from 0.212-2mm.

Figure 7.8 shows that the larger two pellet sizes are performing relatively poorly. The 1.18-2mm pellets removed 3.1mg/g at both 45 and 76mg/l final concentrations. This compares to the 1-2mm pellets from Section 7.1.1 which removed 3.3mg/g at a final concentration of 43.4mg/l, showing a consistency in results. The 0.85-1mm pellets removed up to 4mg/g at a final concentration of 6mg/l. The 0.212-0.300mm pellets are performing better, removing 8.4mg/g at the final concentration of 6mg/l.

The phosphorus removal by these pellets is plotted alongside the Freundlich isotherm for the Horden solids from Section 6.2.3 in Figure 7.9 to allow a direct comparison of performance. It must be noted that the pellet data is presented as milligrams of phosphorus removed per gram of total pellet and the Freundlich isotherm is per gram of dry solids from Horden.

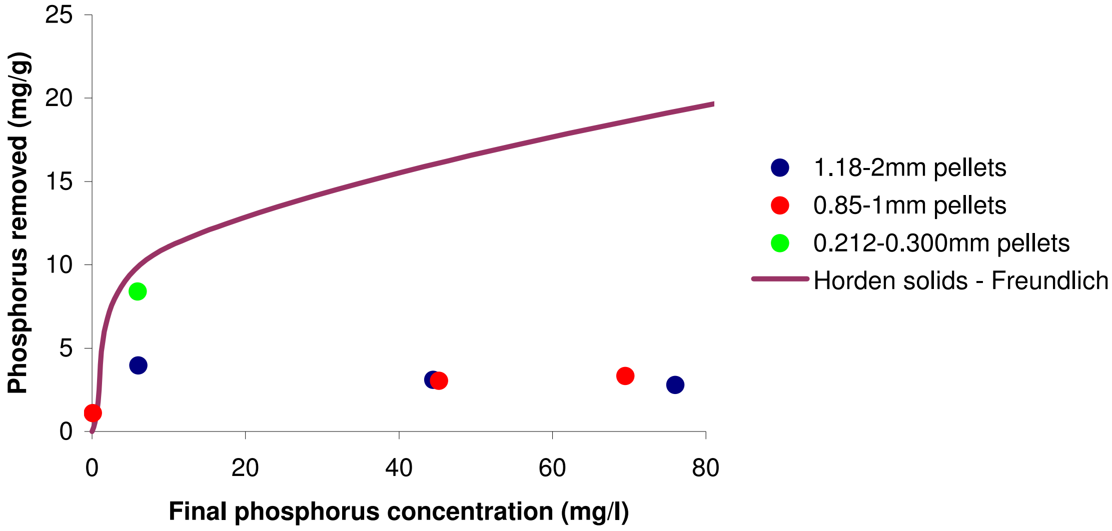


Figure 7.9 Comparison of the results for the pellets and the Freundlich isotherm for the solids from Horden.

Figure 7.9 again shows the relatively poor performance of the larger pellets. It also shows that the 0.212-0.300mm pellets are performing to a standard close to that of the unpelletised solids from Horden. These pellets removed 8.4mg/g at an equilibrium concentration of 6.0mg/l at this final concentration the Freundlich isotherm gives a loading of 9.6mg/g. The 0.125-0.212 pellets removed more phosphorus than the 0.212-0.300mm pellets and would therefore likely be capable of removing more phosphorus than the solids from Horden.

Figure 7.9 presented the pellet results as phosphorus removed per weight of total pellets. These results are replotted in Figure 7.10 with the phosphorus removed expressed as per weight of Horden solids, these make up 48% by weight of the pellets. This is equivalent to assuming that the Horden solids are the only active ingredient and adsorption is the sole removal mechanism.

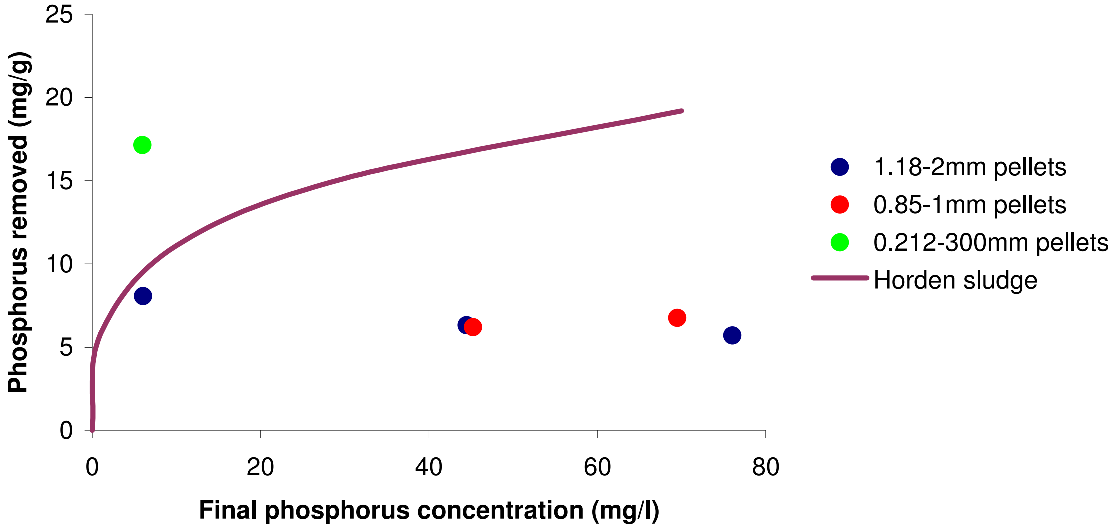


Figure 7.10 Comparison of the results for pellets and the Freundlich isotherm for the solids from Horden. All results normalised to removal per weight of solids from Horden.

The 0.212-0.300mm pellets are outperforming the solids from Horden a loading of 17.14mg/g is found at the final concentration of 5.98mg/l, the value from the Freundlich isotherm at this point is 9.6mg/g. This increase in performance is counterintuitive if adsorption was the main mechanism, as these pellets will have a much smaller surface area than the fine solids from Horden. The resultant high pHs which are shown in Figure 7.13 would also inhibit adsorption of the anionic phosphate ions as higher pHs could lead to the pellet surfaces becoming negatively charged which would repel the negatively charged phosphate ions. Figure 7.10 therefore suggests that another removal mechanism is present and from the literature review it seems likely that this is some of calcium phosphate precipitation due to the use of cement as a binder, this idea is fully explored throughout this chapter.

Figure 7.11 compares the results from this section, those of Section 7.1.1 and the Freundlich isotherm for the solids from Horden from Section 6.2.3. Pellet results are expressed as phosphorus removal per weight of total pellet and the Freundlich as per weight of dry Horden solids.

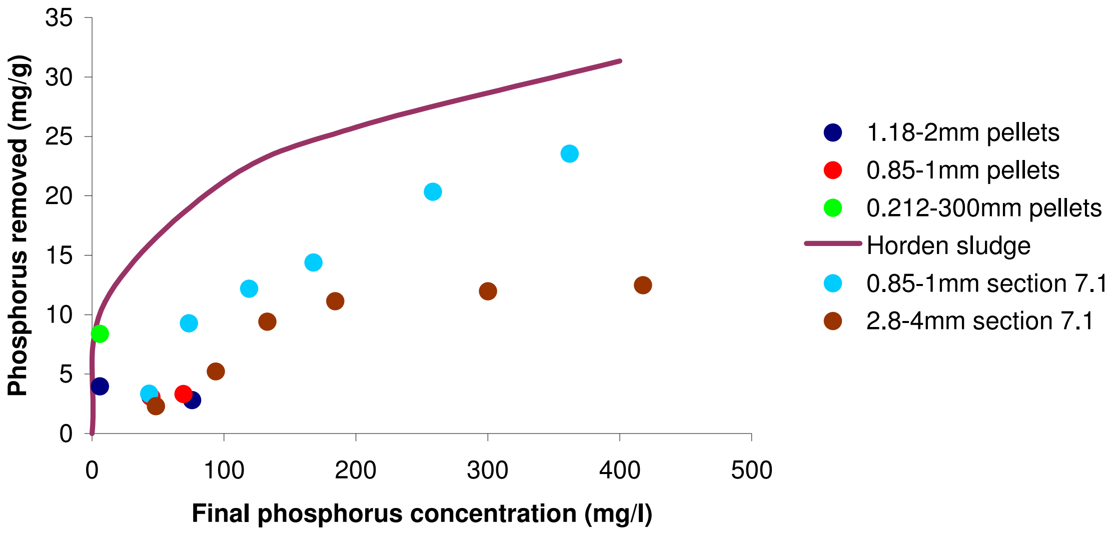


Figure 7.11 Comparison of all pellet results from Sections 7.1.2 and 7.1.1and the Freundlich isotherm for the solids from Horden

Figure 7.11 shows the improvement in phosphorus removal with reduction in pellet size. The results for the 0.85mm pellets from this section (bright red data points) can be compared to those from Section 7.1 (dark green data points). The test reported in this section found 0.85-1mm pellets removed 3.0mg/g at a final concentration of 45.2mg/l. This is nearly identical to the 3.3mg/g at 43.4mg/l found in Section 7.1. However Section 7.1 found that 0.85-1mm pellets removed 9.3mg/g at a final concentration of 73.6mg/l which compares to the 3.3mg/g at 69.5mg/l found in this section. There is therefore disparity between these two tests. The two tests were carried with different solution volumes and different initial concentrations and on separate batches of pellets so some variation is to be expected. Results are still plotted in the adsorption isotherm form, but if precipitation is the major removal mechanism, the phosphorus loading achievable will be less a function of the final concentration but more the initial concentration and the mass of pellets used.

The variation of initial pH with initial phosphorus concentration for the tests reported in this Section is shown in Figure 7.12.

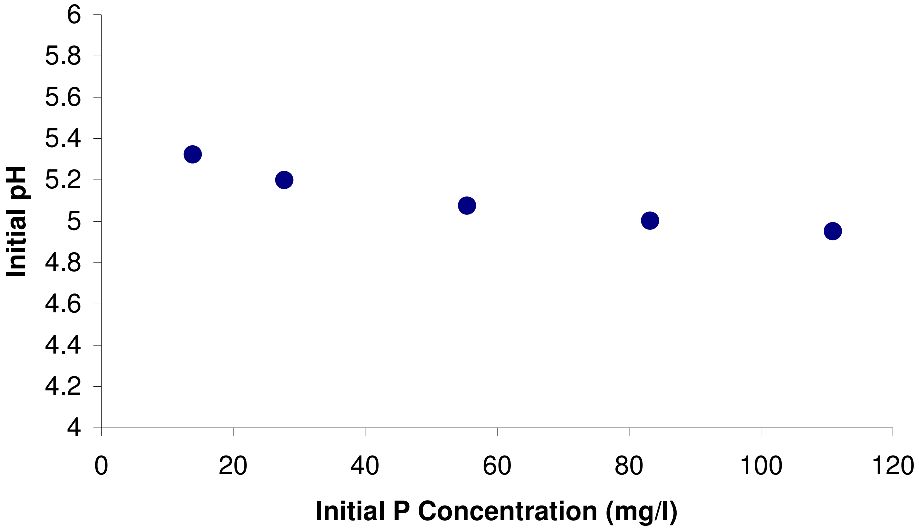


Figure 7.12 Variation of initial pH with initial phosphorus concentration for all pellet sizes

Figure 7.12 shows that the initial pHs ranged from 5.32 to 4.95. There is a slight negative correlation between the initial concentration and initial pH due to the increased addition of the acidic KH_2PO_4 salt. Figure 7.13 presents the final pHs plotted against the initial pHs.

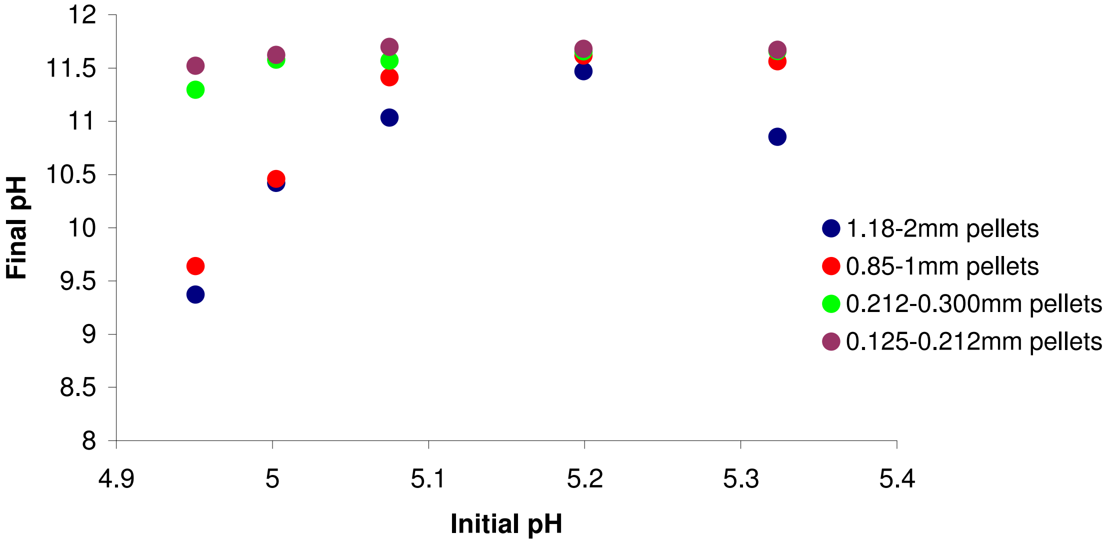


Figure 7.13 Variation of final pH for batch phosphorus removal tests on pellets

The final pHs are very high for these tests. The 0.125-0.212mm and 0.212-0.300mm pellets perform closely with pHs ranging from 11.52-11.67 and 11.30-

11.67 respectively. The two larger pellet sizes are also performing closely. The 1.18-2mm pellets have a final pH range of 9.37-11.47 and the 0.85-1mm pellets 9.64-11.50. The pH ranges and how they are affected by pellet size are more easily compared in Table 7.1.

Table 7.1 Comparison of final pH ranges for all pellet sizes studied thus far

Pellet size (mm)	Final pH range
2.8-4mm (Section 7.1.1)	6.7-7.9
1-2mm (Section 7.1.1)	6.9-8
1.18-2 (Section 7.1.2)	9.4-11.5
0.85-1 (Section 7.1.2)	9.6-11.6
0.212-0.300 (Section 7.1.2)	11.3-11.6
0.125-0.212 (Section 7.1.2)	11.5-11.7

Table 7.1 shows that there is a step change in final pH between the results from this section and those from Section 7.1.1, this is likely due to the reduction in batch volume size from 100ml to 40ml and all final pHs from this section are now very high. These high pHs could inhibit anionic adsorption due to the pellet surfaces becoming negatively charged as essentially all final pHs from these tests are above the upper limit of 6.3-9.5 suggested by Cornell and Schwertmann 2003 for the point of zero charge of iron oxides. All final pHs are also above the suggested limit by Johansson and Gustafsson (2000) of a pH value of 9 for efficient calcium phosphate precipitation and therefore a change in the dominant removal mechanism is likely. There is a clear increase in final pH as the pellet size decreases, as expected with the higher surface area of smaller pellets facilitating easier release of hydroxide ions.

The relationship between the final pH and the phosphorus removed (mg/g) in these tests is explored in Figure 7.14.

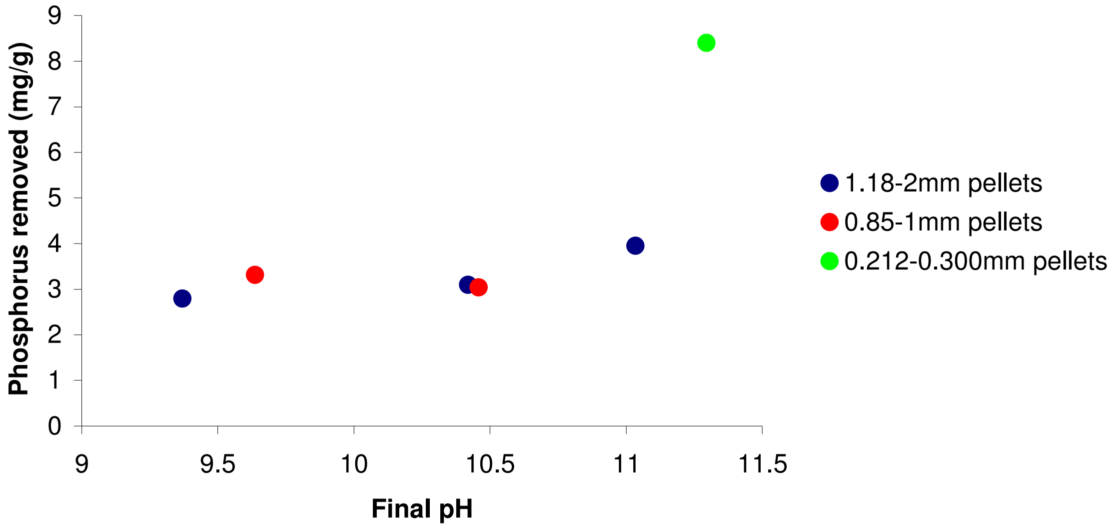


Figure 7.14 Variation of phosphorus removed with final pH.

The 1.18-2mm pellets and the 0.85-1mm pellets are resulting in similar phosphorus loadings at similar final pHs. The limited data ranges mean that no strong conclusions regarding patterns can be made. The higher removal by the 0.212-0.300mm pellets was found at a higher final pH (8.40mg/g at a pH of 11.30).

This section has provided phosphorus removal data for pellets in the size range of 0.212-2mm. It was shown that there is a clear link between reducing pellet size and increasing phosphorus removal, this reduction in pellet size has also resulted in higher final pHs. By presenting data on a phosphorus removed per weight of solids from Horden basis, it has been shown that removal exceeds that by the unpelletised Horden solids and therefore a removal mechanism in addition to or replacement of adsorption has been introduced, likely to be calcium phosphate precipitation.

7.1.3 Phosphorus removal by sub 125 micron pellets

This section details the batch phosphorus removal tests carried out on 45-63μm and 63-125μm pellets. Due to the production method of pellets, detailed in Chapter 5, these were the smallest pellet sizes it was thought reasonable to produce. The results for tests that were conducted with a wide range of initial concentrations are presented as are those for tests which focused on lower initial, and therefore final, phosphorus concentrations.

7.1.3.1 Tests with a wide range of initial concentrations

This section presents the results of tests carried out with a wide range of initial phosphorus concentrations (70-170mg/) on 45-63µm and 63-125µm pellets. These tests were carried out with 40ml solutions containing 0.1g of pellets (2.5g/l solids concentration). The initial and final phosphorus concentrations for these tests are shown in Figure 7.15.

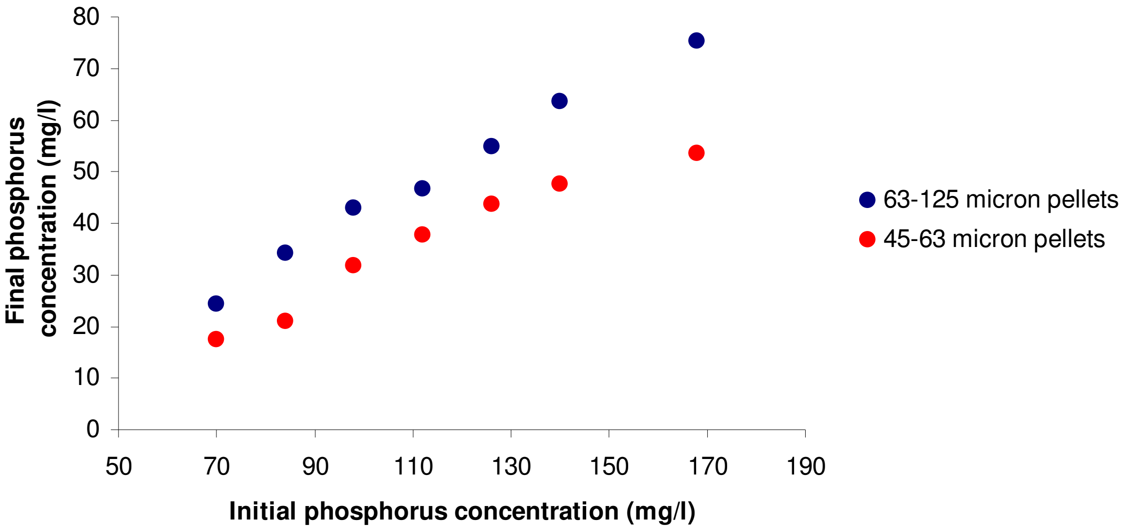


Figure 7.15 Results for phosphorus removal tests on 45-63 and 63-125 micron pellets.

The smaller pellets (45-63µm) as expected are removing phosphorus to a lower concentration than the larger (63-125µm) pellets. The 45-63µm pellets reduced the initial concentration range of 70-168mg/l to 24.29-75.43mg/l. The 63-125µm reduced the initial concentrations to 17.43-53.64mg/l. These results are presented as phosphorus removal per gram of pellet against the relevant final phosphorus concentration in Figure 7.16.

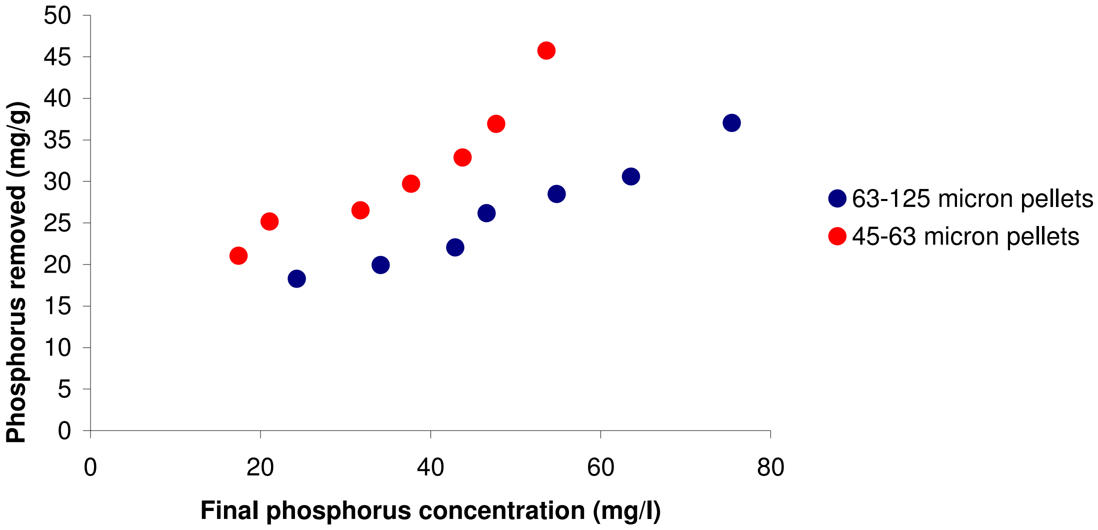


Figure 7.16 Phosphorus loading results for 45-63µm and 63-125µm pellets.

Figure 7.16 shows the higher phosphorus loadings achieved by pellets of the smaller size range. The 45-63µm pellets are removing 21-45mg/g over a final concentration range of 17-54mg/l, this compares to 18-37mg/g over the range of 24-75mg/l for the 63-125µm pellets. From Section 6.2 the Freundlich isotherm shows dry solids from Horden on their own remove 13-20mg/g in these ranges, a full comparison is made in Figure 7.21. Pellets under 125µm therefore have a higher ability to remove phosphorous than the solids from Horden. The performance of these sub 125µm pellets at lower initial and final concentrations is fully explored in Section 7.1.3.2

7.1.3.2 Tests focusing on low concentrations

Tests were carried out on the sub 125 micron pellets focusing on low final concentrations. Seven tests were carried out on the 63-125µm pellets with initial concentrations ranging from 14-98mg/l. Only four tests were carried out on the 45-63µm pellets due to limited material, these had initial concentrations ranging from 28-70mg/l. Again 0.1g of pellets was used with a solution volume of 40ml and all tests in this section were carried out in triplicate. Figure 7.17 plots the final concentrations against the relevant initial concentrations. Data points are the mean value and error bars ± one standard deviation.

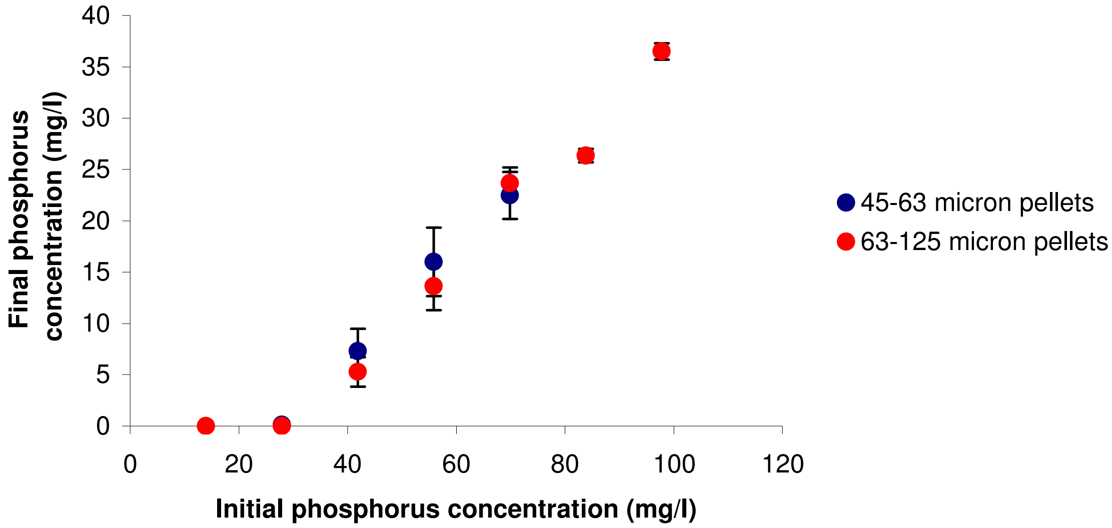


Figure 7.17 Phosphorus removal by 45-63 and 63-125 micron pellets focused on low concentrations

For the low concentration ranges studied in these tests the two pellet sizes removed phosphorus to a similar standard. The 45-63µm pellets reduced the initial concentrations of 28-70mg/l to final concentrations of 0.1-22.5mg/l. The 63-125µm pellets reduced the two lowest initial concentrations (14 and 28mg/l) below the detection limit of the ICP-OES and will not be included in further analyses. The initial concentration of 41.9mg/l was reduced to 5.3mg/l, and the highest initial concentration of 98mg/l was reduced to 38.5mg/l by the 63-125µm pellets. The phosphorus removed per gram of pellet is plotted against the final phosphorus concentration in Figure 7.18.

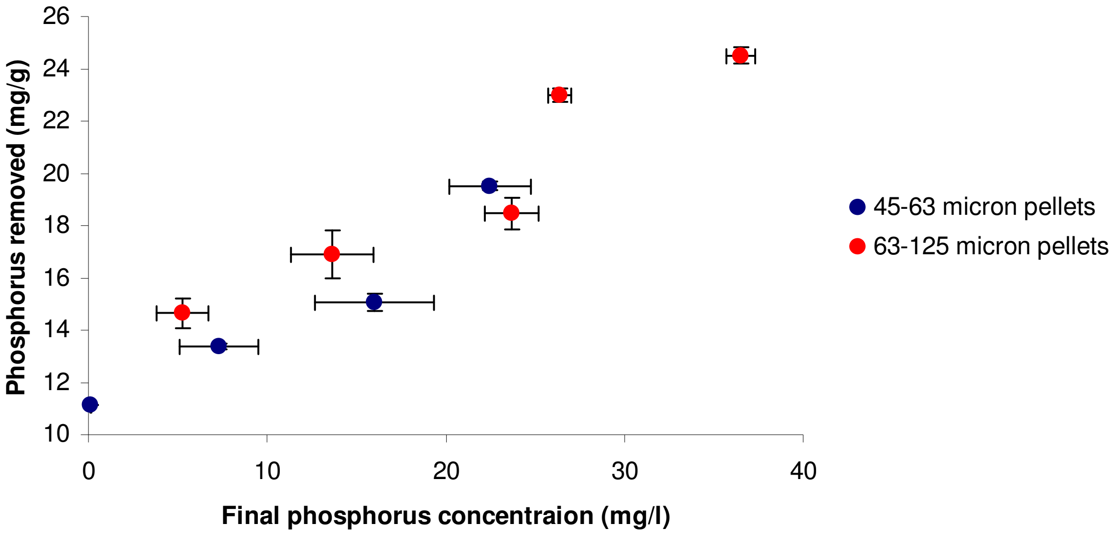


Figure 7.18 Phosphorus loading for the low concentration test on 45-63µm and 63-125µm pellets.

At these lower final phosphorus concentrations the two pellet sizes are performing to a similar standard with similar phosphorus loadings achieved. The 45-63µm pellets removed between 11.1 and 19.5mg/g across the range of final concentrations of 0.1-22.4mg/l. The 63-125µm pellets removed 5.2-36.5mg/g across 14.7-24.5mg/l. The results from Figure 7.18 are added to Figure 7.16 to produce a complete phosphorus removal data range for the 45-63 and 63-125µm pellets in Figure 7.19.

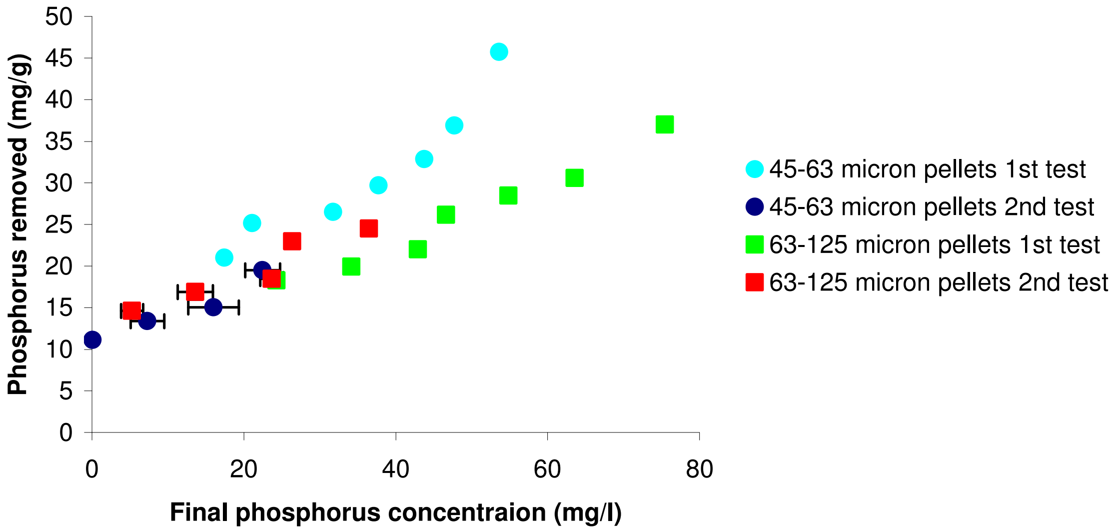


Figure 7.19 Complete data set for 45-63µm and 63-125 micron pellets

Figure 7.19 shows that the two separate tests for both pellet sizes fit well together with slight variation between the two sets of data. The results from Section 7.1.3.1 found a phosphorus loading of 18.2mg/g at a final concentration of 24.3mg/l for the 63-125µm pellets. The results from the current section found a loading of 18.67mg/g at a final concentration of 23.7mg/l these two data points are very similar. For the 45-63µm pellets Section 7.1.3.1 found a phosphorus loading of 21.1mg/g at a final concentration of 25.2mg/l. The results from the current section show a loading of 19.6mg/g at a final concentration of 22.46mg/l. Again these results are close, the slight discrepancy between the two sets of tests seems reasonable for two separate tests with different initial concentrations and two separate batches of pellets. For clarity the two data sets for each pellet size are combined into one in Figure 7.20.

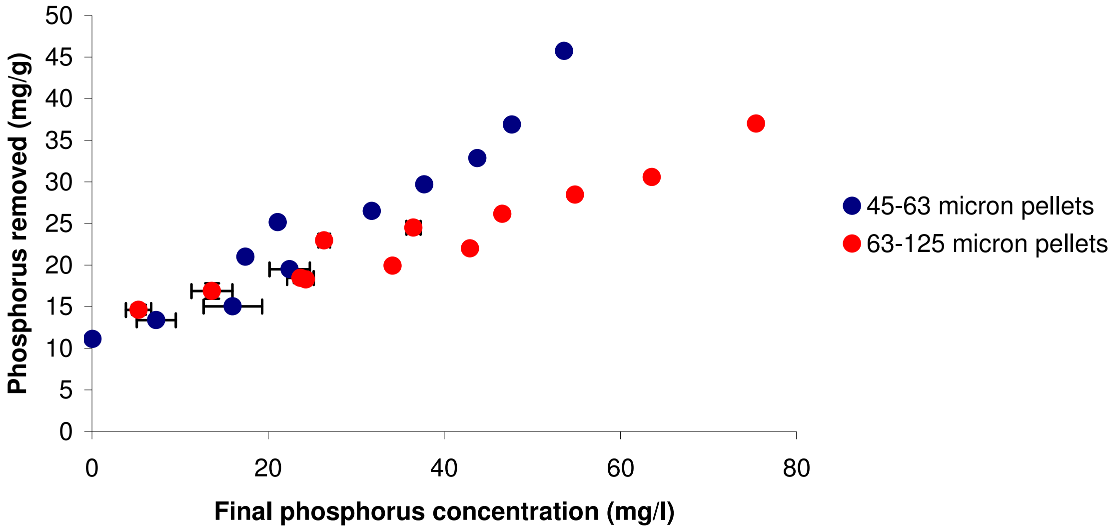


Figure 7.20 Complete phosphorus removal data for both tests on 45-63µm and 63-125µm pellets.

The 45-63µm pellets are removing between 11 and 46 mg/g at a final concentration range of 0.1-54mg/l. The 63-125µm pellets removed 15-37mg/g across the range of 5-75mg/l final concentrations. These data sets are compared to the Freundlich isotherm for the solids from Horden in Figure 7.21. The pellet results are presented as phosphorus removed per gram of pellet and the Freundlich isotherm is presented per weight of dry solids from Horden.

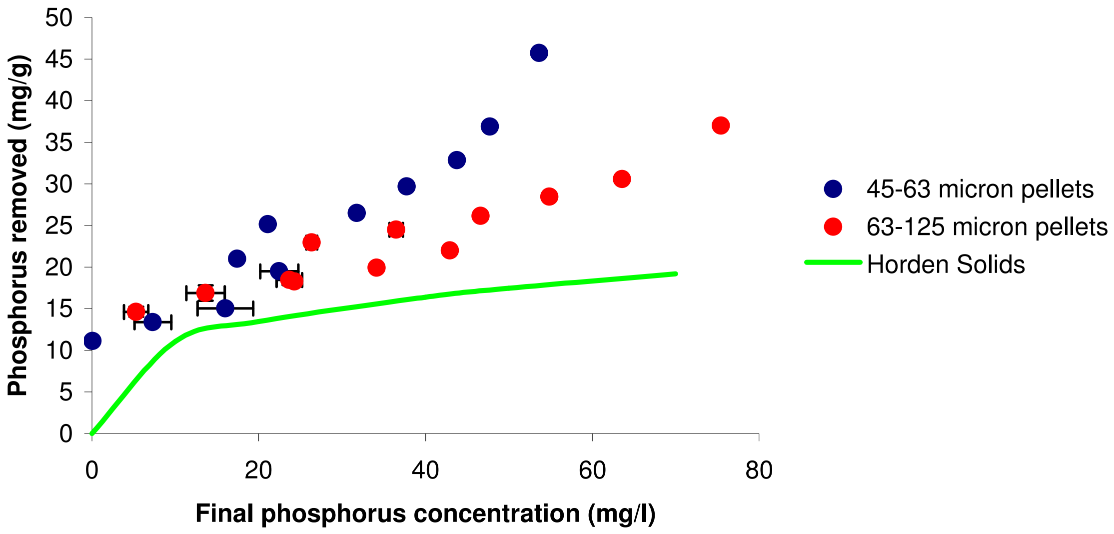


Figure 7.21 Comparison of phosphorus removal data of pellets and Horden solids.

Figure 7.21 shows these sub 125 micron pellets to be performing better than the unpelletised solids from Horden particularly for the higher final concentrations. The 45-63µm pellets removed between 11 and 46 mg/g for final concentrations in the range of 0.1-54mg/l. The Freundlich isotherm gives loadings of 3.0 to 17.8mg/g for this range of equilibrium concentrations. The 63-125µm pellets achieved loadings between 15 and 37mg/g across the final concentration range of 5-75mg/l, over this range the Freundlich isotherm provides loadings of 9.1 to 19.6mg/g. These increases in phosphorus loading show the presence of another removal mechanism in replacement of adsorption, especially considering the undesirable pH values in respect to anionic adsorption found for these tests and the large reduction in surface area.

Figure 7.21 shows that pellets are capable of removing more phosphorus than the solids from Horden. This difference in performance is further highlighted in Figure 7.22 where pellet results are plotted on a per weight of solids from Horden basis. This is therefore assuming that the Horden solids are the only active ingredient. The solids from Horden represent 48% by weight of the pellet this therefore results in close to a doubling of the phosphorus loading value.

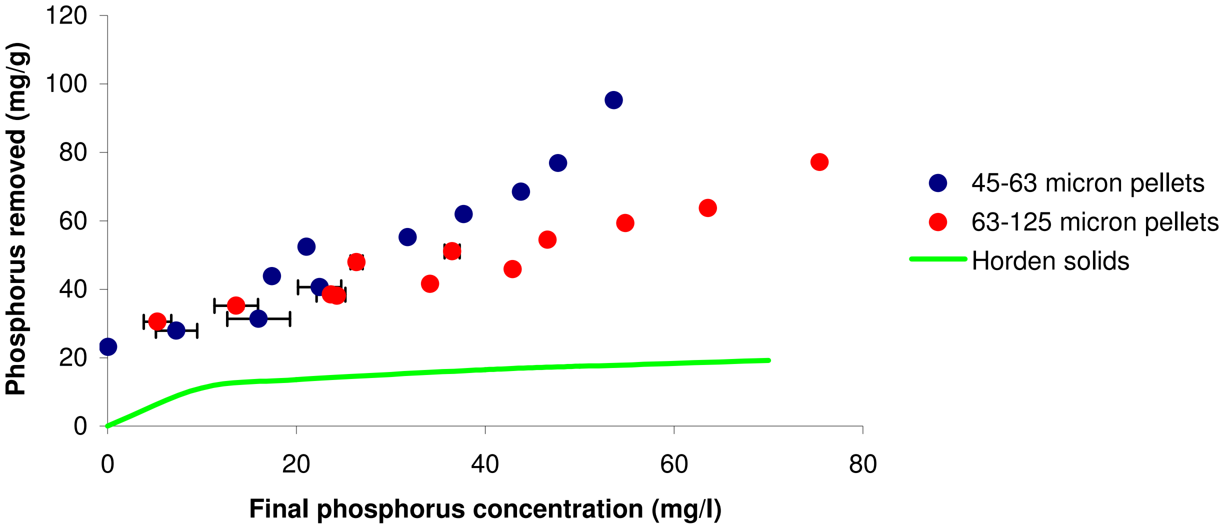


Figure 7.22 Phosphorus removal data for 45-63 and 63-125 micron pellets normalised to removal per weight of solids from Horden.

Figure 7.22 further highlights the disparity between the pellet results and the results expected purely by adsorption onto the solids from Horden. The 45-63µm pellets have phosphorus loadings of between 23.2 to 95.3mg/g over the 0.1-53.6mg/l range of final concentrations. The Freundlich isotherm provides loadings of 3.0 to 17.8mg/g in the same range. The 63-125µm pellets removed between 30.5 and 77.1mg/g at final concentrations between 5.3 and 75.4mg/l. The Freundlich isotherm gives loadings of between 9.1 to 19.6mg/g for this final concentration range. Figure 7.22 shows that the phosphorus removal cannot be explained purely by adsorption onto the Horden solids and the discrepancy in performance is significant, this is thought to be a result of the introduction of a calcium phosphate precipitation mechanism.

The initial pH of these tests was measured before the addition of the pellets and the final pH measured once the solution had been filtered. The variation of initial pH with initial phosphorus concentration is shown in Figure 7.23.

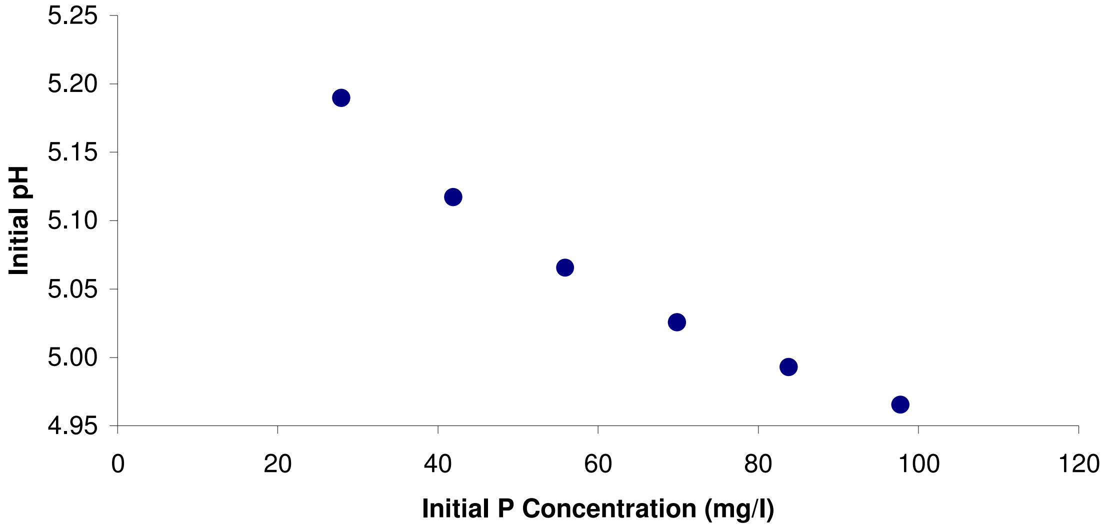


Figure 7.23 Variation of initial pH with initial concentration

Figure 7.23 shows the initial pHs ranged from 5.19 to 4.97. The decrease of initial pH with the increase in initial phosphorus concentration is due the higher addition of KH_2PO_4. The final pHs, measured once the solutions had been filtered are plotted against the initial pHs in Figure 7.24.

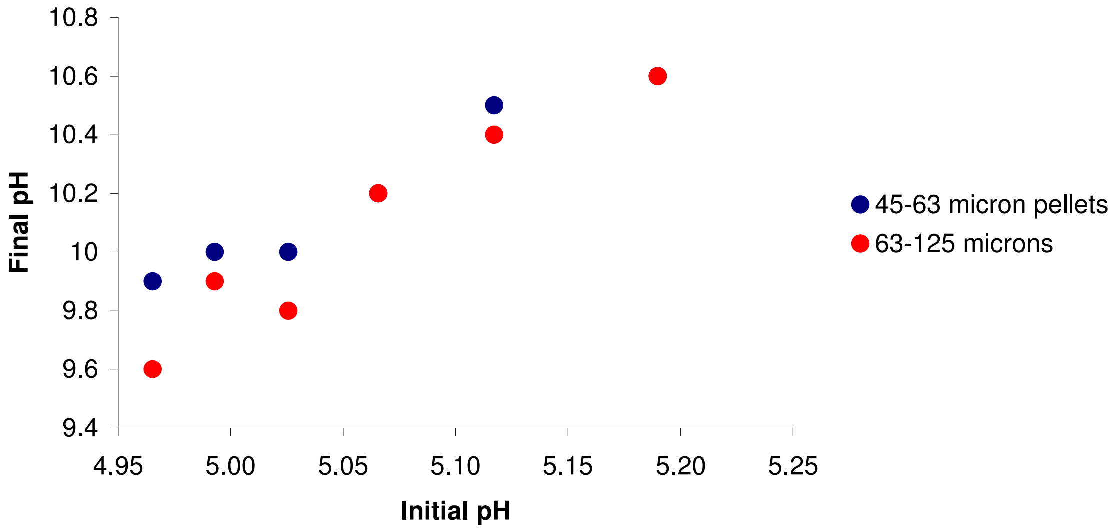


Figure 7.24 Variation of final pH with initial pH for 45-63µm and 63-125µm pellets

The 45-63µm pellets are resulting in pH values in the range of 9.9-10.6 and the 63-125µm pellets 9.6-10.6. As with phosphorus removal these two pellet sizes are also showing similar behaviour in respect to pH. These final pH results are above both the suggested range for the point of zero charge for iron oxides Cornell and Schwertmann (2003) and above a pH of 9 suggested by Johansson and Gustafsson (2000) as ideal for calcium phosphate precipitation, suggesting that conditions would favour calcium phosphate precipitation rather than adsorption. The correlation of phosphorus removal with final pH is explored in Figure 7.25.

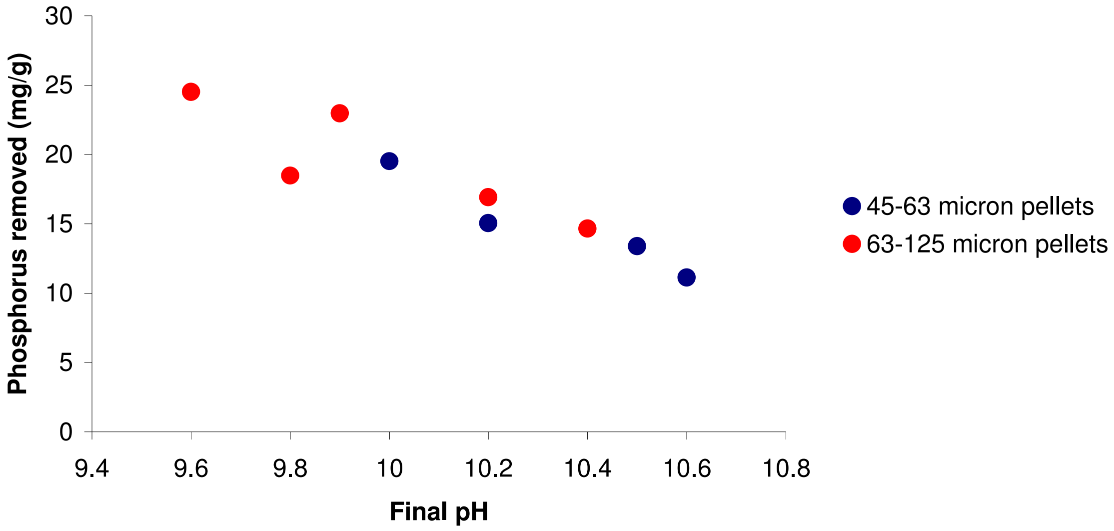


Figure 7.25 Variation of phosphorus removed (mg/g) with final pH for 45-63µm and 63-125µm pellets

Figure 7.25 shows the pattern of increasing phosphorus removal with decreasing final pH. This pattern is the same found by Lu *et al.* (2009) and Johansson and Gustafsson (2000) who suggested this pattern fits in with that expected for calcium phosphate precipitation. Many papers reviewed in Chapter 3 suggest hydroxyapatite (HAP) as a likely end product of calcium phosphate precipitation. The equations shown in Section 7.2.2 show this precipitate consumes hydroxide ions and so explains this relationship of higher removals at a higher range of pHs and within these ranges consumption of pH and phosphorus is linked.

This section has presented the results for 16 hour batch tests on 45-63µm and 63-125µm pellets. It has been shown that by reducing the pellet size down to this range removal is improved and exceeds the removal found by the unpelletised solids from Horden. This higher removal is occurring for a material with a smaller surface area and at pHs likely to be above the point of zero charge for the Horden solids. Both these factors mean that calcium phosphate precipitation may be the dominant removal mechanism rather than adsorption.

7.2 Kinetics of phosphorus removal by pellets

This section presents the results of tests carried out to determine the kinetics of phosphorus removal by pellets. This section reports on two tests, a test carried out to determine the progression of phosphorus removal up to an hour and another to determine the progression of removal up to 16 hours. The filtered solutions from the test lasting 16 hours were analysed for both calcium and phosphorus so as to investigate the relationship between them and provide evidence for the presence of a calcium phosphate precipitation mechanism.

7.2.1 Contact times up to one hour

This section details the progression of phosphorus removal by pellets up to an exposure time of one hour. The tests were conducted using the flocculator shown in Figure 5.6, the test volume was 800ml and the initial phosphorus concentration 11mg/l. Two tests were carried out on 45-63µm pellets with 0.3g and 0.4g of pellets (0.375 and 0.5g/l pellet concentration). One test was performed on 63-125µm pellets with 0.3g (0.375g/l pellet concentration). A small sample of 20-30ml was taken at the appropriate time and filtered. Small samples were taken to avoid overly reducing the total solution volume which would thus increase the pellet concentration. The variation of phosphorus concentration with time is plotted in Figure 7.26.

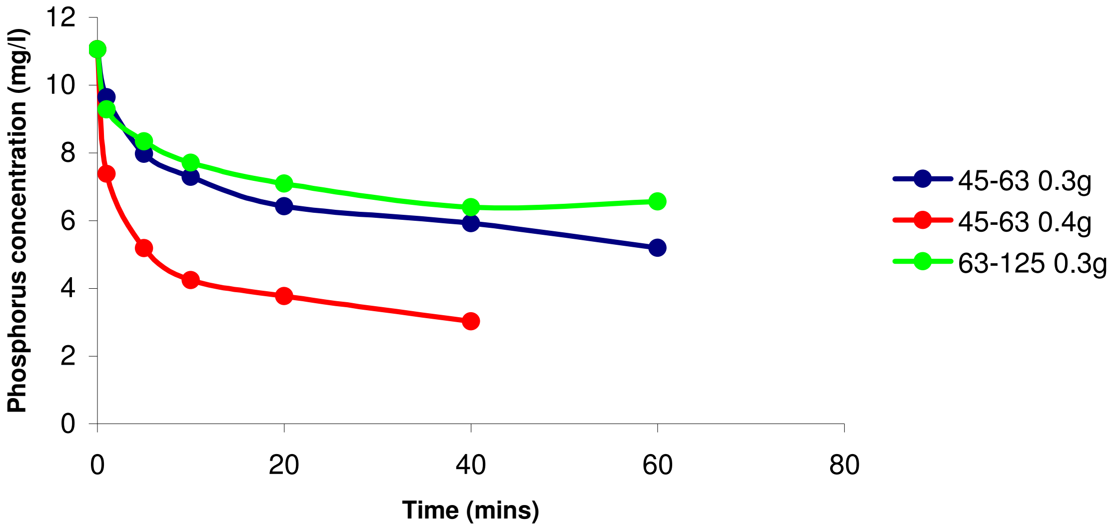


Figure 7.26 Phosphorus removal kinetics up to an hour for 45-63µm and 63-125µm pellets.

The results for all tests show a high initial rate of phosphorus removal for all tests whereafter the rate of removal declines. As with the results in Section 7.1.3 there is a slight benefit found through the reduction in pellet size. The large improvement in performance through raising the pellet mass used from 0.3g to 0.4g can be seen. After 60 minutes the 63-125µm pellets removed 4.5mg/l of phosphorus this is a phosphorous loading of 12mg/g at a final concentration of 6.6mg/l. The 16 hour batch test results reported in Section 7.1.3 found a loading of 14.6mg/g at a final concentration of 5.3mg/l. The results in this section therefore suggest that the majority of removal that occurs within 16 hours is happening within the first hour. Of the 4.5mg/l the 63-125µm pellets removed after one hour, 75% was removed within the first 10 minutes and no removal was reported between 40 and 60 minutes. The concentration after 60 minutes for the test on the 63-125µm pellets was in fact higher than that after 40 minutes (6.562mg/l vs 6.344mg/l), this difference is concentration is minimal, and the concentrations can be considered as equal.

The test on 0.3g of the 45-63µm pellets found a total change in phosphorus concentration of 5.9mg/l. This is equivalent to 15.6mg/g at a final concentration of 5.2mg/l. The results from Section 7.1.3 found a loading of 13.4mg/g at a final concentration of 7.3mg/l, these one hour kinetic results are again not dissimilar from the 16 hour batch results. 64% of the total phosphorus removal occurred within the first 10 minutes compared to 12% in the last 20 minutes again showing the importance of the early stages.

The test on 0.4g of 45-63µm pellets after 60 minutes removed 8mg/l phosphorus equivalent to 16.0mg/g at a final concentration of 3.0mg/l thus removing more per gram than the 0.3g tests but still performing to a standard comparable to the batch tests. A value for removal after 60 minutes for this test is not reported due to the loss of the sample. Of the 8mg/l removed after 40 minutes, 42% was within the first 10 minutes and 9% within the last 20 again showing a reducing rate of removal. All three tests show that the early stages are the most important and that there is only a small difference between results for the 1 hour tests and those lasting 16 hours. The gradients of the three tests are shown in Table 7.2 to highlight the drop in removal rate with time.

Table 7.2 Gradient analysis of Figure 7.26

Time (mins)	45-63µm 0.3g (mg/l/min)	45-63µm 0.4g (mg/l/min)	63-125µm 0.3g (mg/l/min)
1	1.42	3.68	1.78
5	0.42	0.55	0.23
10	0.14	0.19	0.13
20	0.09	0.05	0.06
40	0.03	0.04	0.03
60	0.04	-	-0.01

Table 7.2 shows the dramatic reduction in the rates of change as the test length increases up to the relatively short exposure time of an hour. The final pH of these tests was monitored, the pH being measured once the solution had been filtered after the appropriate time, this is plotted against the elapsed time in Figure 7.27.

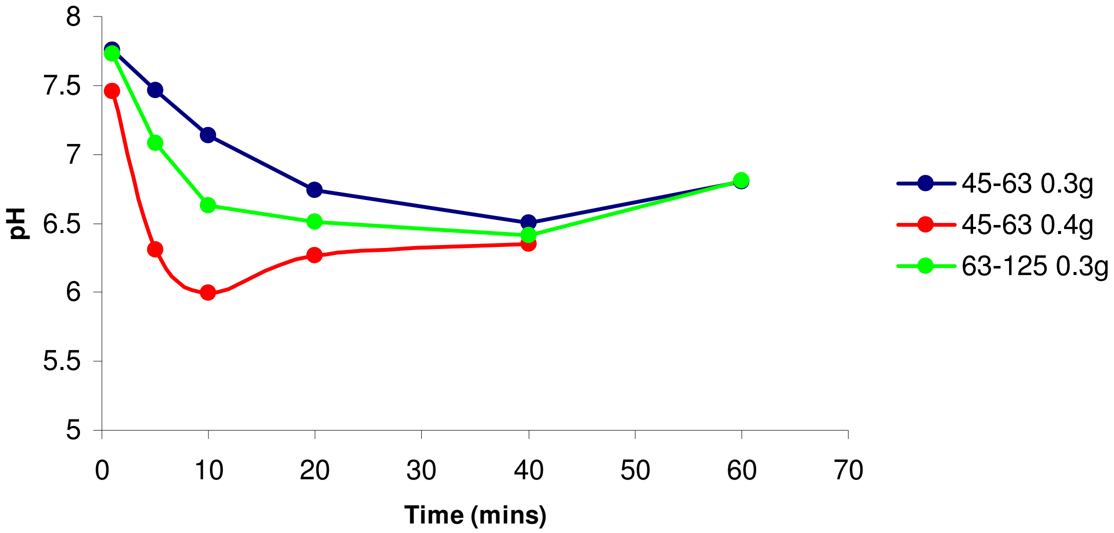


Figure 7.27 Variation of pH with time for kinetic tests lasting an hour on 45-63μm and 63-125μm pellets.

Figure 7.27 shows that all three tests follow the same pattern with an initial dip in pH whereafter the pH stabilises, and for the two 60 minute samples begins to rise slightly. For both tests with 0.3g of solids after 1 minute a pH of 7.7 was found, this then dips over 1-20 minutes and the raises again slightly to a final pH of 6.8 after 60 minutes. The 0.4g test has a more dramatic dip in pH over the 1-20 minute period but after 40 minutes had the same pH (6.4) as the two 0.3g tests. These pH values compare to the range of 9.6-10.6 for the tests lasting 16 hours in Section 7.1.3. These tests used a much larger batch volume (800ml compared to 40ml) this will have an effect on the range of pHs. For the early stages of the test on 0.4g of 45-63μm pellets the pH was lower than that for 0.3g. This is unexpected as a high mass of pellets would have a higher mass of cement binder which therefore should release more hydroxide ions. The only period of time where there is an increase in pH is the 40-60 minutes, and this is a very slight increase. The range of pHs is lower than the pH value of 9 Johansson and Gustafsson (2000) suggests is required for efficient calcium phosphate precipitation however the phosphorus loadings achieved are at a comparable value to the 16 hours tests from Section 7.1.3 which finished at a much higher pH values.

This section has shown that the early stages of these batch tests are by far where the highest rates of removal are occurring. Again tests with 45-63µm and 63-125µm pellets are performing very closely, the smaller pellets performing slightly better. The rate of removal reduces as the time increases, and this is most dramatic at the early stages of the test whereafter the rate of removal is reduced to a very slow rate. These tests found similar results to those by Section 7.1 and show that the vast majority of removal that occurs after 16 hours has occurred within the first hour.

7.2.2 Contact times up to 16 hours

Batch kinetic tests lasting from 30 minutes to 16 hours were performed to chart the progression of phosphorus removal by 63-125µm pellets over this longer time frame. Six tests in triplicate with 40ml volume, an initial phosphorus concentration of 130mg/l and 0.1g of pellets were started at the same time. These conditions are the same as the tests whose results are presented in Section 7.3.3. Tests were stopped after 0.5,1, 3, 5, 8 and 16 hours. The filtered samples from this test were analysed for both phosphorus and calcium, this allows comparisons and correlations to be drawn between the two and the investigation of the presence of a calcium phosphate precipitation mechanism.

7.2.2.1 Phosphorus removal

The progression of phosphorus removal with time is plotted in Figure 7.28.

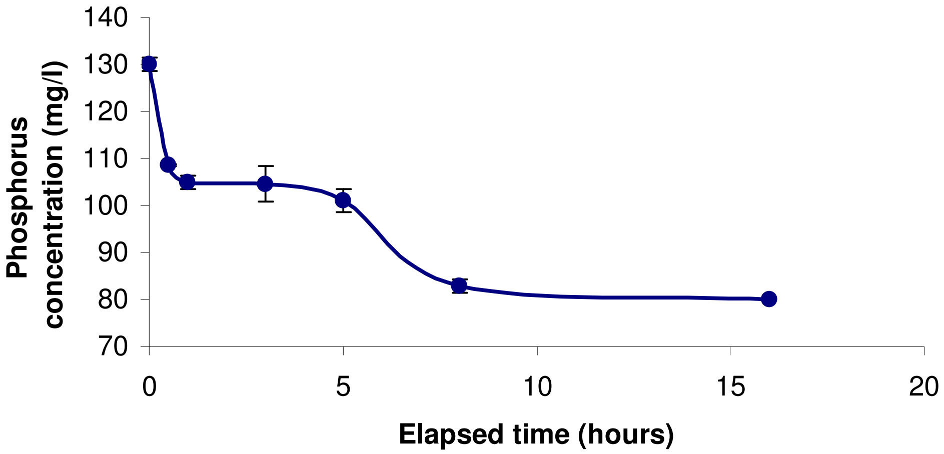


Figure 7.28 Variation of phosphorus concentration with time for kinetic tests on 63-125μm pellets lasting up to 16 hours.

There is a high rate of removal during the first 30 minutes, the rate then drops until after 5 hours where there is an increase in the rate of removal, there is then little removal between 8 and 16 hours. These results are supported by those in Section 7.2.1 where the majority of removal occurred at the early stages of the test. After 16 hours the pellets have reduced the initial concentration of 130mg/l to a final concentration of 80.0mg/l representing a phosphorous loading of 20mg/g. The nearest comparison to this test is from the tests lasting 24 hours from Section 7.3.3 where an initial concentration of 130mg/l was reduced to 47.7mg/l resulting in a loading of 34.2mg/g. There is quite a difference between these two sets of results even considering that the tests from Section 7.3.3 lasted eight hours longer. The progress of removal in Figure 7.28 can be more clearly seen by a plot of percentage of total removal against time in Figure 7.29.

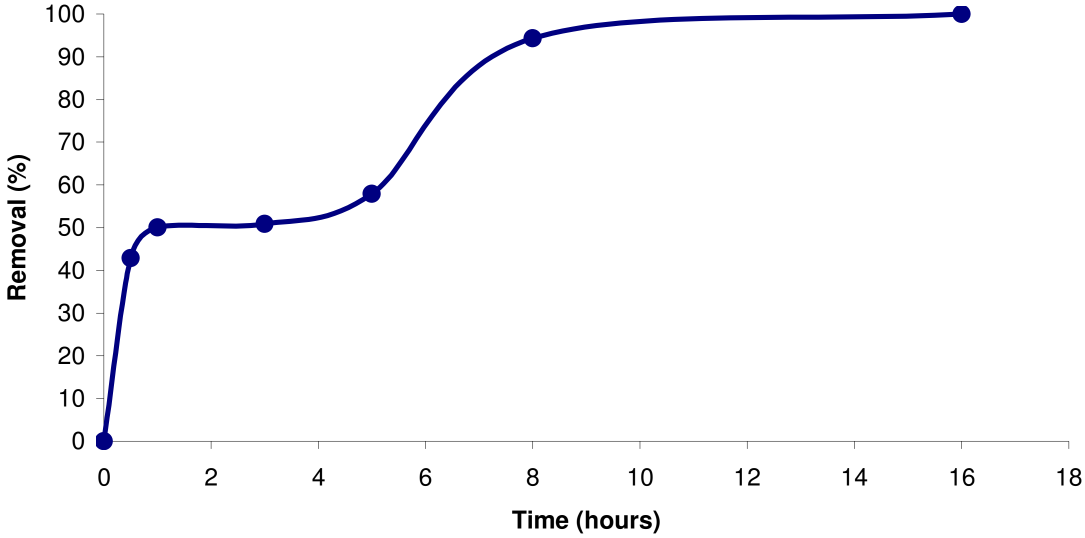


Figure 7.29 Progression of cumulative percentage phosphorus removal by 63-125µm pellets over 16 hours

The fastest rate of removal occurs at the initial stages. Within the first 30 minutes over 40% of the removal found after 16 hours has occurred. There appears to be two step changes in removal. The first occurs within this first 30 minutes then between 30 minutes and 5 hours there is a slow increase in removal from 40-60%. Between 5 and 8 hours the removal rises to 94% of that after 16 hours. The reasons behind this pattern of removal will be explored once the calcium concentrations have been reported in Section 7.2.2.2.

7.2.2.2 Calcium analysis

Papers such as Agyei *et al.* (2002) Berg *et al.* (2005) and Oguz *et al.* (2003) state that calcium phosphate can be an important phosphorus removal mechanism by cement based materials. Through the use of cement as a binder in the pellets for the current study the introduction of a calcium phosphate precipitation removal mechanism seems probable. Section 7.1.3 has shown that sub 125 micron pellets are capable of achieving higher phosphorus loadings than the unpelletised Horden solids. Mayes *et al.* (2009) used similar pellets to those studied in this thesis and reported elevated pHs and calcium levels due to the use of cement as a binder releasing calcium and hydroxide ions. Mayes *et al.* (2009) provide the following equation for the dissolution of portlandite/calcium hydroxide ($Ca(OH)_2$) from cement.

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad \text{Equation 7.1}$$

Equation 7.1 explains both the elevated calcium concentrations and pH levels found in tests on these pellets compared to those on the dry solids from Horden reported on in Chapter 6.

Many papers in the literature review suggest hydroxyapatite (HAP) as the likely end product of calcium phosphate precipitation (Johansson and Gustafsson 2000), (Kim *et al.* 2006), (Drizo *et al.* 2006). HAP takes the form $Ca_5(PO_4)_3(OH)$. The stages of removal from KH_2PO_4 and portlandite dissolution to HAP formation could take the general simplified form

$$KH_2PO_4 \rightarrow K^+ + 2(H^+) + PO_4^{3-} \qquad \text{Equation 7.2}$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad \text{Equation 7.3}$$

$$5(Ca^{2+}) + 3(PO_4^{3-}) + OH^- \rightarrow Ca_5(PO_4)_3(OH) \qquad \text{Equation 7.4}$$

These general equations explain the drop in initial pH with the increase in initial phosphorus concentration. The concurrent consumption of phosphorus, calcium and hydroxide ions for the formation of HAP can be clearly seen in Equation 7.4. Equations 7.2-7.4 show the basic stages in what is believed to be occurring. HAP is generally considered to have amorphous precursor phases which precipitate quickly and are followed by crystallisation (Kim *et al.* 2005), (Seckler *et al.* 1999) (Onumo and Ito 1998). This process may take the form of octacalcium phosphate (OCP), ($Ca_8H_2(PO_4)_6$) initially forming, this is unstable and transforms to amorphous calcium phosphate (ACP), ($Ca_3(PO_4)_2$) $x H_2O$). OCP has a calcium to phosphorus molar ratio of 1.33, ACP has a ratio of 1.5. These are calcium deficient in terms of HAP and a slow ripening process occurs to produce stoichiometric HAP (Liu *et al.* 2001).

Filtered solutions for the test presented in this section were analysed for both phosphorus and calcium. Figure 7.30 plots the progression of the calcium concentration through the 16 hour test.

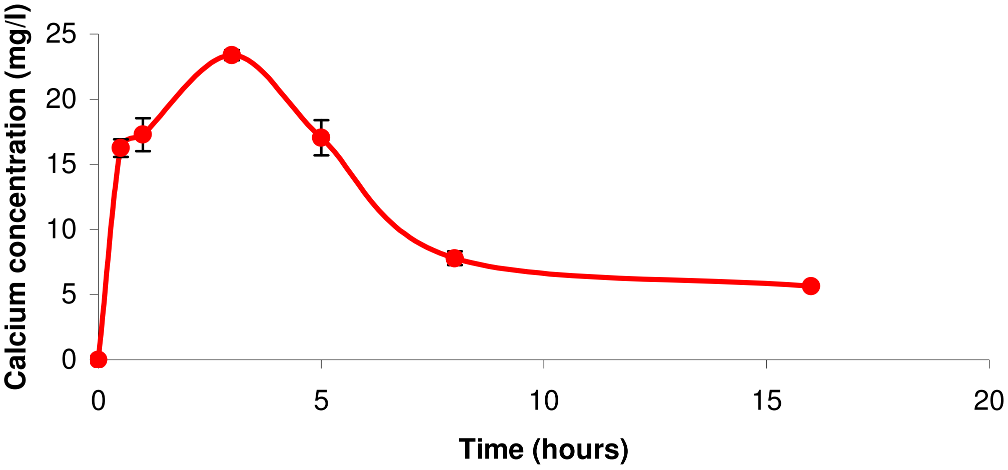


Figure 7.30 Variation of calcium concentration with time for kinetic tests on 63-125µm pellets lasting up to 16 hours.

Figure 7.30 shows that there is an initial relatively rapid increase in calcium concentration from 0-16mg/l within the first half hour and this continues to increase till a maximum concentration of 23mg/l after 3 hours. After this point the calcium concentration drops consistently until after 8 hours the concentration has dropped to 7.8mg/l. Between 8 and 16 hours the rate of decrease in calcium concentration slows down and the calcium concentration drops from 7.8mg/l to 5.6mg/l. After 24 hours the equivalent test from Section 7.3.3 had a calcium concentration of 0.370, thus the higher phosphorus removal for the test from Section 7.3.3 would appear to occur with further removal of calcium. The test in Section 7.3.3 where 0.1g of pellets was shaken in 40ml of deionised water for 24 hours found a release of 117mg/l calcium, far higher than the values reported here, showing concurrent consumption of calcium and phosphorus. The relationship between phosphorus and calcium concentrations is explored in Figure 7.31 where the progression of both their concentrations is shown.

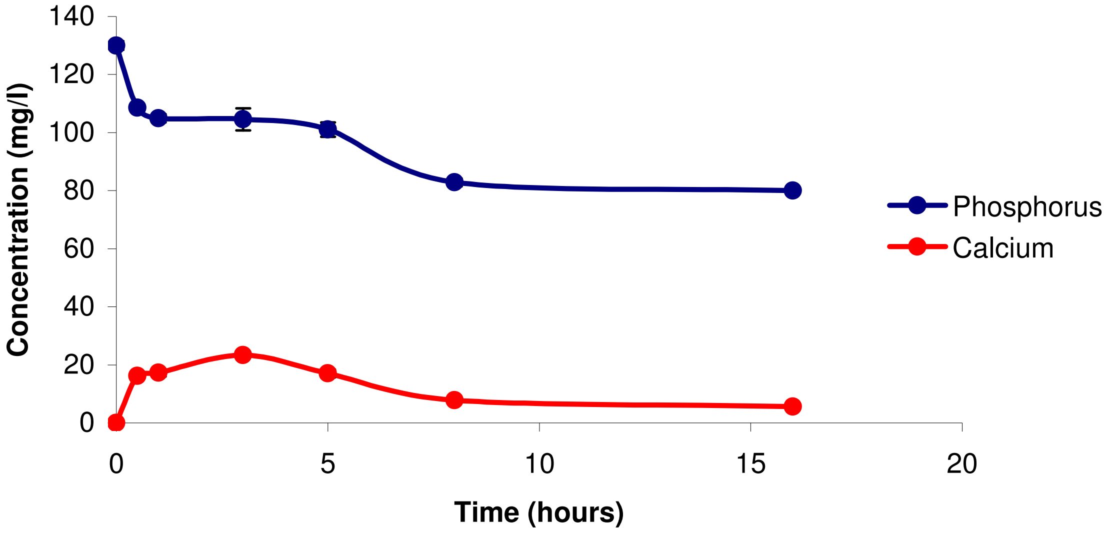


Figure 7.31 Variation of both phosphorus and calcium concentrations with time for kinetic tests on 63-125µm pellets lasting up to 16 hours.

Figure 7.31 shows that for the initial period of 0-1 hours calcium concentration is increasing as the phosphorus decreases, this is not expected with calcium phosphate precipitation as the two elements should combine and be taken out of solution. Figure 7.31 shows that the calcium is released very quickly for the first hour. During this first hour it could be that the calcium and phosphate are not combining fast enough to remove all of the calcium being released by the pellets and so the calcium concentration rises. After this initial hour the rate of calcium release may slow down and between 1 and 5 hours there is little change in either calcium or phosphorus concentration. Between 5 and 16 hours both the phosphorus and calcium concentrations show similar patterns of rates of change. The rate of change in both elements is slowing as time progresses. Higher phosphorous concentrations are correlated with higher calcium concentrations. Therefore it can be seen that reduction in the concentrations of the two elements coincides suggesting that they are combining and thus offering evidence towards the calcium phosphate precipitation theory. These findings fit in with those of Lu *et al.* (2009) and Johansson and Gustafsson (2000) who both suggest this concurrent reduction as evidence of calcium phosphate precipitation. The pH was monitored at all stages and is presented in Figure 7.32.

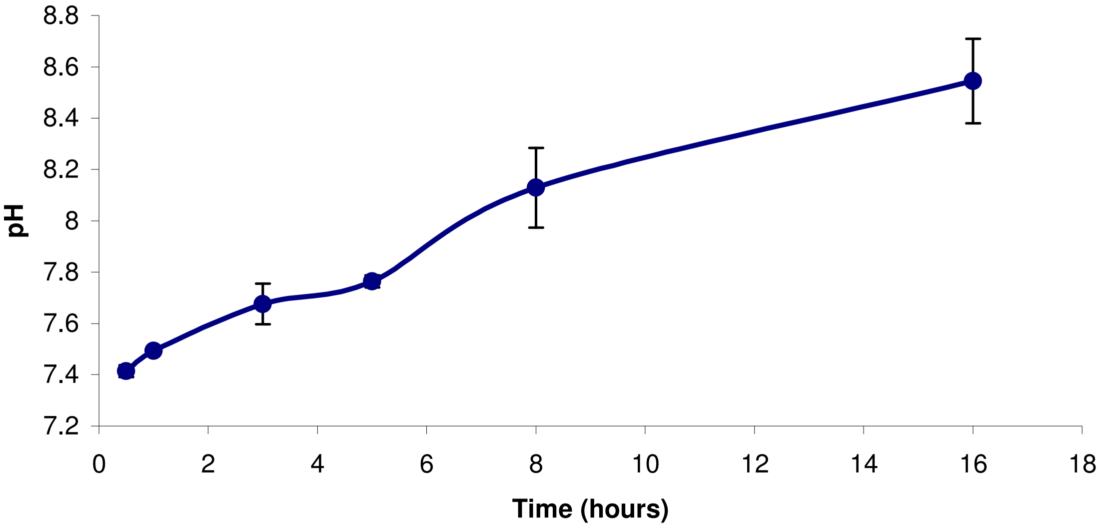


Figure 7.32 Progression of pH with time for kinetic tests on 63-125μm pellets lasting up to 16 hours.

Figure 7.32 shows that the pH for these tests rose consistently with time up to a final value of 8.6. This compares to the pH value of 10.20 for the 24 hour tests from Section 7.3.3 again a reasonably large discrepancy likely due to the further eight hours that test lasted for and also some variation between batches of pellets. The pH increases alongside phosphorus removal. If calcium phosphate precipitation is the major removal mechanism this would be expected to consume hydroxide ions and therefore lower pH. It seems likely that calcium phosphate precipitation is consuming hydroxide ions but rather than reducing the pH this is reducing the rate at which the pH is increasing. The tests presented in Section 7.3.3 shook 0.1g of 63-125μm pellets in 40ml of deionised water devoid of phosphorus for 24 hours, this resulted in a pH of 11.2. This is far above the maximum value of 8.5 found in the tests in this section. This further suggests that hydroxide ions are being consumed by calcium phosphate precipitation.

This section has charted the development of both the phosphorus and calcium concentrations up to 16 hours. It was found that the initial period is where the highest rate of phosphorus reduction occurred. The early stages also showed fast release of calcium from the pellets. After 3 hours the decrease of calcium and phosphorus occurs simultaneously and follows a similar pattern until 16 hours. This section therefore lends a further piece of evidence towards the theory of calcium phosphate precipitation as the major phosphorus removal mechanism of pellets.

7.3 Tests lasting from 1 day to 3 weeks

This section investigates the potential of long term phosphorus removal by pellets composed of Horden solids and cement. Tests lasting up to three weeks were carried out to investigate this as is reported in Section 7.3.1. Section 7.3.2 reports the progression of phosphorus removal up to a week, Section 7.3.3 also reports this and investigates the relationship between phosphorus and calcium in solution. Scanning Electron Microscope (SEM) micrographs are shown of the used pellets and their surface chemistry was analysed using Energy-Dispersive X-ray spectroscopy (EDX). Batch tests with a constant initial concentration of 11mg/l and varying pellet weights are shown in Section 7.3.4 and the relationship between calcium and phosphorus concentrations for these tests is also discussed.

7.3.1 Tests lasting up to three weeks

Three sets of tests with initial concentrations ranging from 90-150mg/l were carried out lasting 1, 2 and 3 weeks. The test volume was 40ml and 0.1g of pellets was used in each case (2.5g/l solids concentration). All tests were carried out in triplicate on 63-125µm pellets.

7.3.1.1 Phosphorus removal

The final phosphorus concentrations are plotted against the initial concentrations in Figure 7.33. Error bars represent ± 1 standard deviation, these error bars are often too small to be visible.

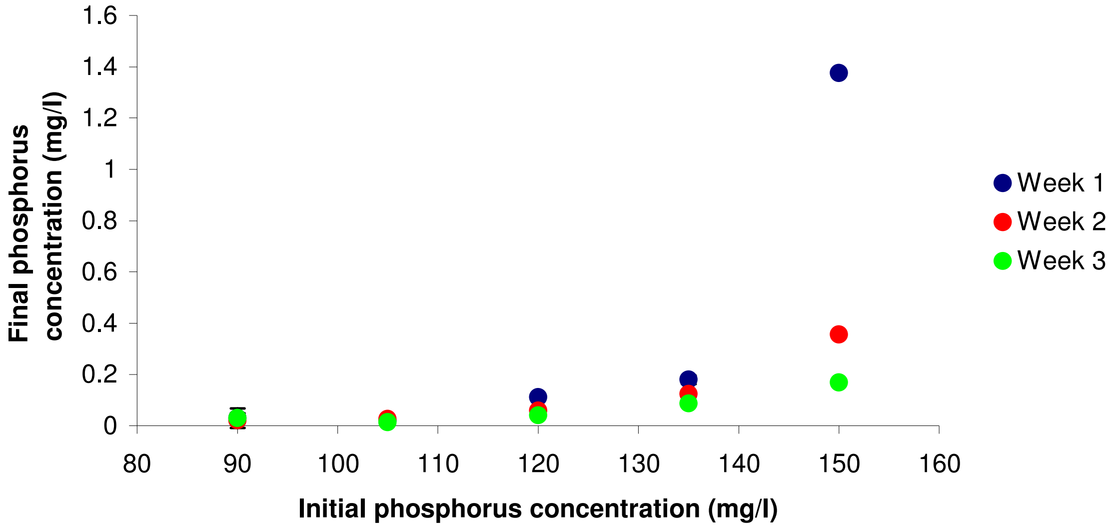


Figure 7.33 Results for phosphorus removal tests on 63-125μm pellets.

Figure 7.33 shows that all three tests have removed the phosphorus concentrations down to very low concentrations, over 99% removal was achieved in all cases and many tests had phosphorus concentrations reduced to below the 0.1mg/l detection limit that the ICP-OES was calibrated to. Figure 7.33 shows that there is long term removal with further removal occurring until the third week. Taking the test with the highest initial concentration (150mg/l), after 1 week this was reduced to 1.38mg/l, after 2 weeks 0.36mg/l and after 3 weeks 0.17mg/l showing consistent removal even at these low concentrations. Those results with final concentrations above 0.1mg/l are plotted as the phosphorus loading achieved (mg/g) against the relevant final phosphorus concentration (mg/l) in Figure 7.34.

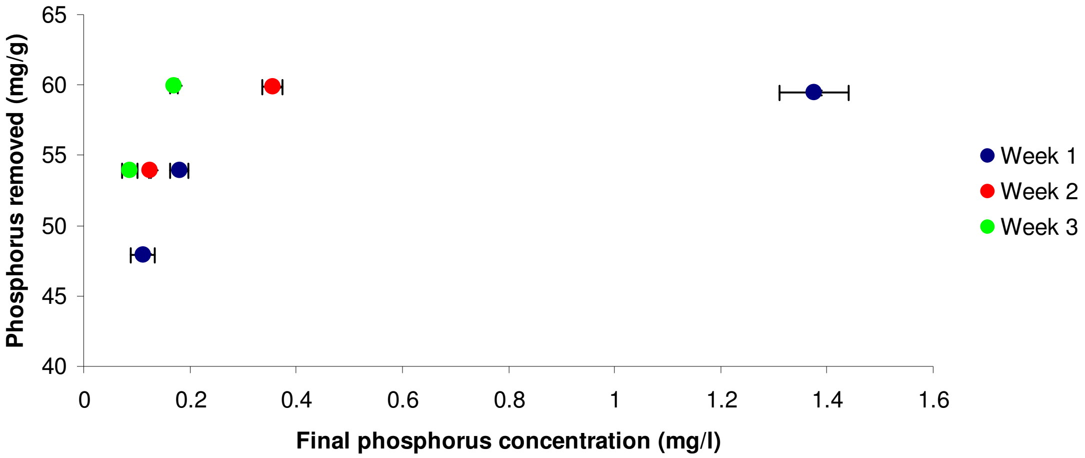


Figure 7.34 Phosphorus loading results for pellets in tests lasting up to 3 weeks.

These long exposure times have resulted in high phosphorus loading capacities for these pellets. The test with the highest initial concentration (150 mg/l) provided a loading of 59.4mg/g after 1 week, 59.9mg/g after 2 and again 59.9mg/g after 3 weeks. These high loadings were found at final concentrations of 1.4, 0.4 and 0.2mg/l respectively. These values compare to the loading of 14.6mg/g found at the final concentration of 5.28mg/l from Figure 7.20 for the tests lasting 16 hours. There are limited data points due to many tests having their concentrations reduced below the 0.1mg/l that the ICP-OES was calibrated to. Figure 7.35 shows the results from Figure 7.34 plotted alongside the results for 16 hour batch tests from Section 7.1.3 and the Freundlich isotherm for the Horden solids from Section 6.2.

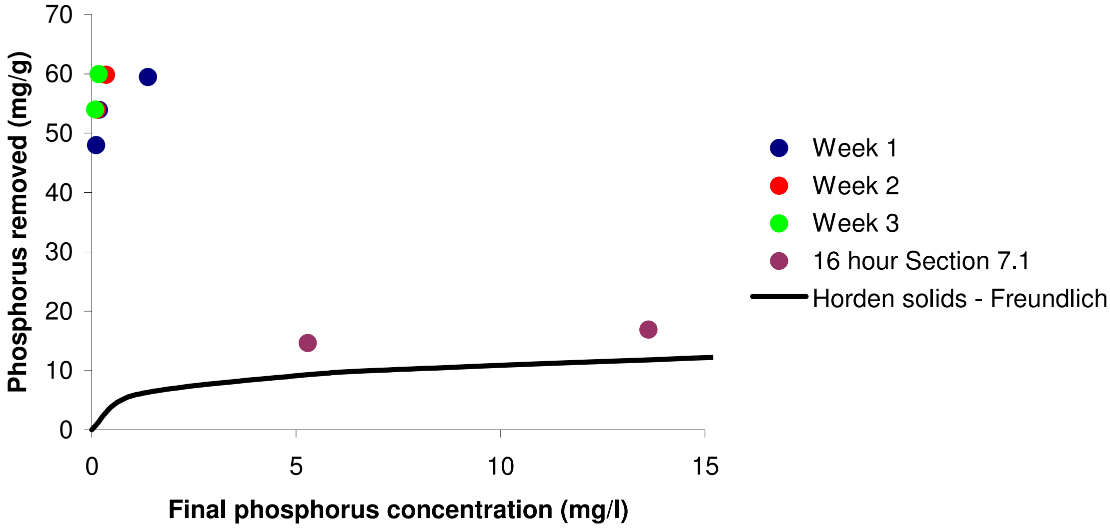


Figure 7.35 Comparisons of tests on pellets lasting 1,2 and 3 weeks to those lasting 16 hours and the Freundlich isotherm for the solids from Horden.

Figure 7.35 highlights the large increase in performance that these long term tests have resulted in, with large phosphorus removal capacities found at very low residual concentrations. The highest loading from this new set of tests is 59.9 mg/g, this loading is found at a final phosphorus concentration of 0.17mg/l and compares to the value of 3.5mg/g which the Freundlich isotherm for the solids from Horden provides for this final concentration. For the 16 hour long tests from Section 7.1 a loading of 14.6mg/g was found at a final concentration of 5.3mg/l. The difference in performance is clearly showing the presence of a removal mechanism other than adsorption, this is thought to be some form of calcium phosphate precipitation and these longer batch tests may be providing the necessary time for crystal growth and formation/ripening of HAP which the test lasting up to 16 hours were not providing. The kinetic tests reported on in Section 7.2 show that there is rapid precipitation of calcium phosphates, the results from this section show that there is also a slow mechanism which may be attributed to crystal growth or transformation of amorphous calcium phosphates to crystalline HAP (Liu *et al.* 2001).

The initial pH of these tests are plotted against the initial concentrations in Figure 7.36

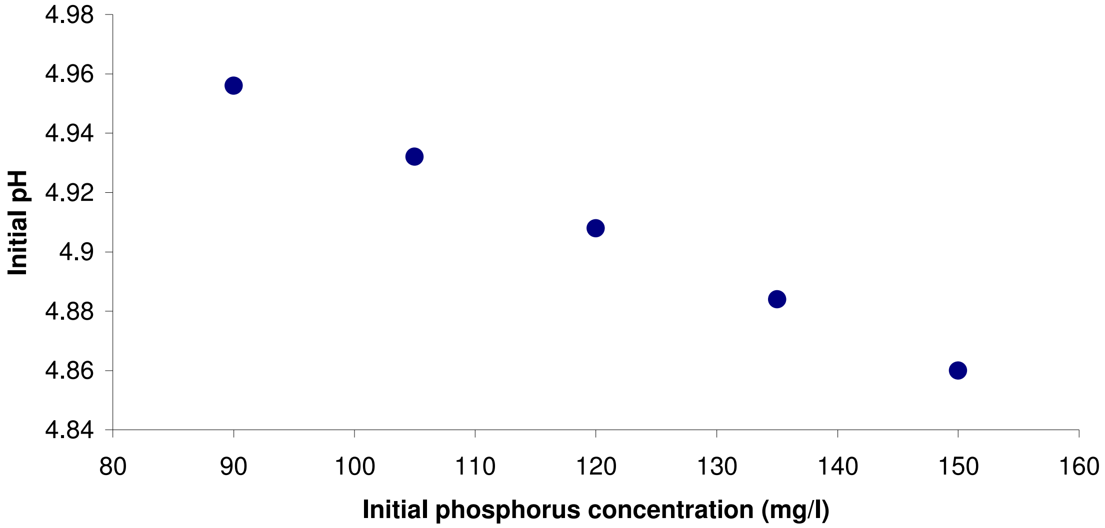


Figure 7.36 Variation of initial pH with initial concentration

Figure 7.36 shows the initial pHs range from 4.96 to 4.86, the initial pH being reduced with the increased addition of the acidic salt KH_2PO_4. Figure 7.37 plots the variation of the final pH with the initial pH.

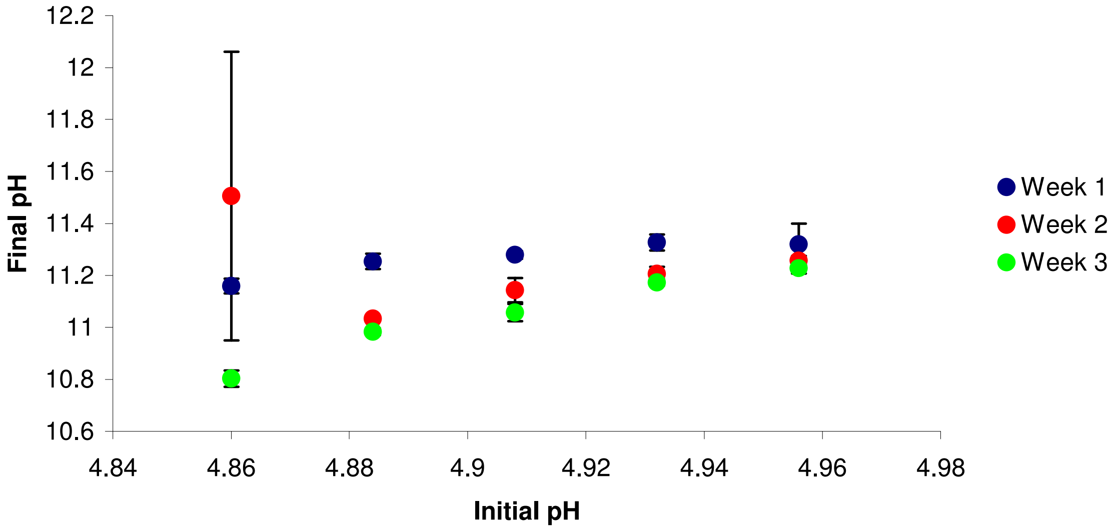


Figure 7.37 Initial and final pH values for the tests lasting 1,2 and 3 weeks

Figure 7.37 shows the high final pHs that these tests have resulted in. There is a general increase in final pH with an increase in initial pH and a decrease in final pH with an increase in test length. The data point for the lowest initial pH for the two week test is a clear outlier with a large standard deviation. The longer the test the more phosphorus was removed and Figure 7.37 shows that this is correlated with lower final pHs. This could be as a result of the hydroxide ions being consumed in the formation of calcium phosphates. The difference in final pH is more pronounced for the tests with higher initial concentrations that left a phosphorus residue. Those tests where the phosphorus concentration was effectively reduced to zero have similar pH behaviour. These results are higher than the range of 9.6-10.6 for the tests from Section 7.1.3 that lasted for 16 hours, the results for all test lengths in Figure 7.37 range from 10.8 to 11.5 showing a significant increase. These final pHs are comfortably above the pH of 9 Johansson and Gustafsson (2000) suggested is a minimum for efficient calcium phosphate precipitation. Figure 7.38 plots the phosphorus removed against these final pHs.

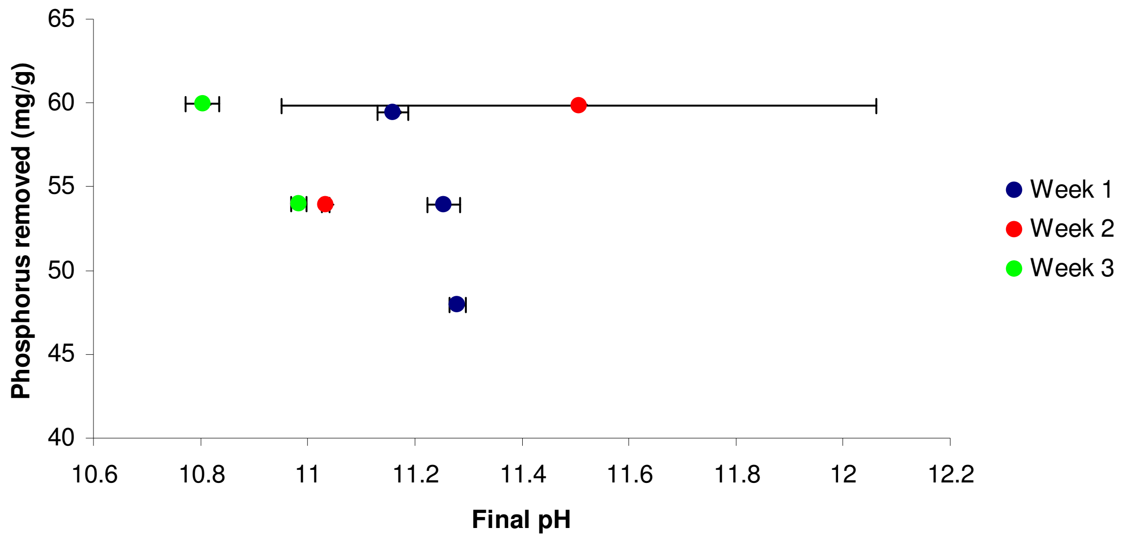


Figure 7.38 Variation of phosphorus removed with final pH.

Figure 7.38 shows how the phosphorus removed varies across the range of final pHs. For the 1 and 3 week results there is a general trend of higher phosphorus removals occurring at lower pHs. This is the expected pattern for calcium phosphate precipitation and is reported in many papers such as Johansson and Gustaffsson (2000) and Ugurlu and Salman (1998). The results for the test lasting two weeks do not follow this pattern due to the more variable data point at a final pH of 11.5. The data ranges in Figure 7.38 are limited and so the identification of patterns is also limited.

7.3.1.2 Contribution to removal by adsorption

The results in Figure 7.35 are recalculated in Figure 7.39 so that the y-axis represents the milligrams of phosphorus removed per gram of Horden solids (48% of the pellets).

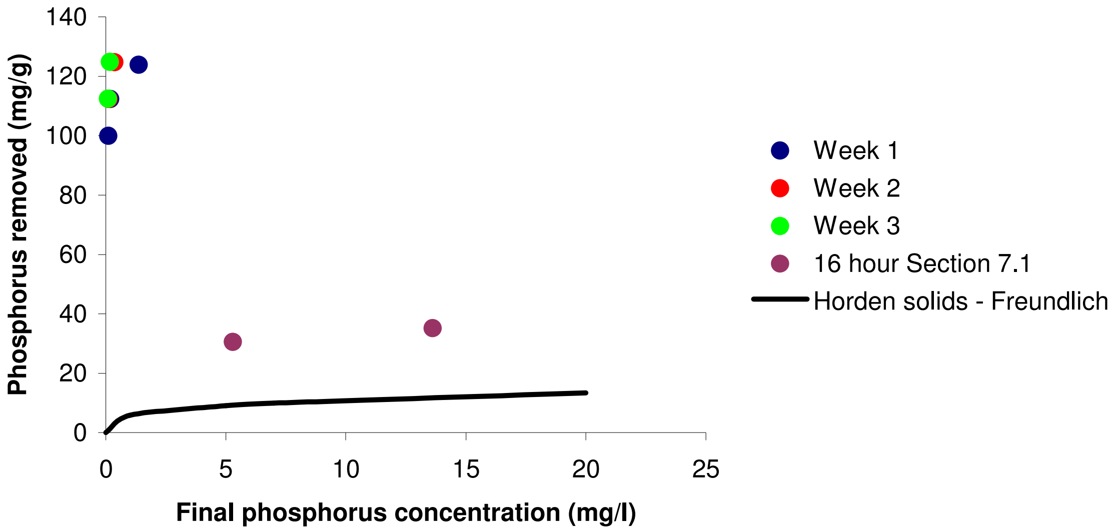


Figure 7.39 Comparison of the tests lasting 1, 2 and 3 weeks to those lasting 16 hours and the Freundlich isotherm for the solids from Horden.

Figure 7.39 further highlights the minimal contribution of adsorption to the total removal. The three week test is removing up to 124.9mg/g at a final concentration of 0.17mg/l. The Freundlich isotherm gives a loading of 3.5mg/g at this concentration a highly significant difference suggesting that the solids from Horden are in fact contributing little to removal.

The final phosphorus concentrations shown in Figure 7.34 were used to calculate the phosphorus loadings for the Freundlich isotherm from Section 6.2 at these concentrations. These loadings were then used to calculate the maximum percentage contribution of adsorption to the total removal by the pellets these are plotted against the phosphorus loadings achieved by the pellets in Figure 7.40.

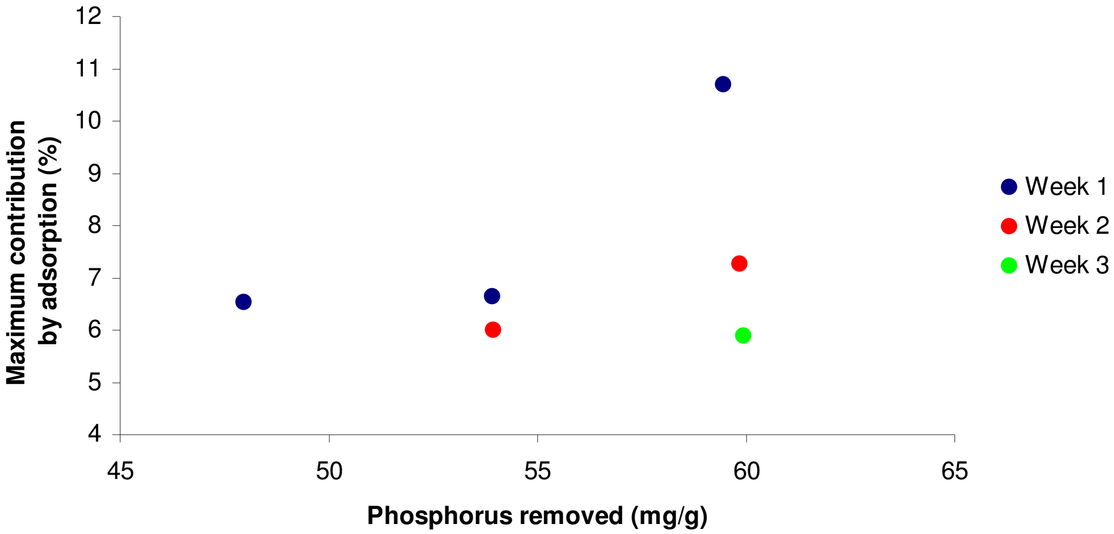


Figure 7.40 Maximum contributions to removal by adsorption towards total removal by the pellets

Figure 7.40 shows that adsorption as calculated from the Freundlich isotherm for the solids from Horden could be contributing as little as 6% to the total removal by pellets. These tests had high final pH values above the point of zero charge range of 6.3-9.5 suggested by Cornell and Schwatermann (2003). These high values will therefore inhibit anionic adsorption as discussed in Chapter 3. Pelletisation also reduced the specific surface area of the material, therefore reducing the number of adsorption sites. BET analysis showed the solids from Horden to have a specific surface area of 64 m^2/g, the 63-125μm pellets 2.9 m^2/g, a large reduction. These conditions mean that adsorption is likely to contributing a negligible amount to total removal.

This section has shown that large increases in performance can be achieved through longer exposure times potentially due to slow crystal growth. Phosphorus loadings up to four times that of the 16 hour tests on the pellets and seventeen times that of the tests on the solids from Horden were realised. The potential contribution by adsorption to these large performances has been shown to be minimal and due to the decrease in surface area and increase in pH past the point of zero charge even this minimal contribution may be an overestimation. Calcium phosphate precipitation therefore appears to be by far the dominant removal mechanism.

7.3.2 Tests lasting up to one week

Section 7.3.1 showed the large improvement in phosphorus removal as a result of extended test lengths, this section charts the progression of phosphorus removal up to an exposure time of a week. Although there is evidence that these tests are still removing phosphorus after two and three weeks these are long periods to carry out tests for and so tests lasting a week were used as a compromise. The phosphorus removal results for this test are shown and the rate of removal throughout the week long test is investigated.

7.3.2.1 Phosphorous removal

Three tests with initial concentrations ranging from 130-230mg/l were performed. One test was ran for 1 day (24 hours) the second test for 3 days (72 hours) and the third test for 7 days (168 hours). The test volume was 40ml and 0.1g of pellets was used (2.5g/l solids concentration). After the allotted time the tests were removed from the shaker table, filtered and analysed for phosphorus using ICP-OES. All tests were carried out in triplicate at room temperature. Figure 7.41 shows the raw results from these tests, with the final phosphorus concentrations plotted against the initial.

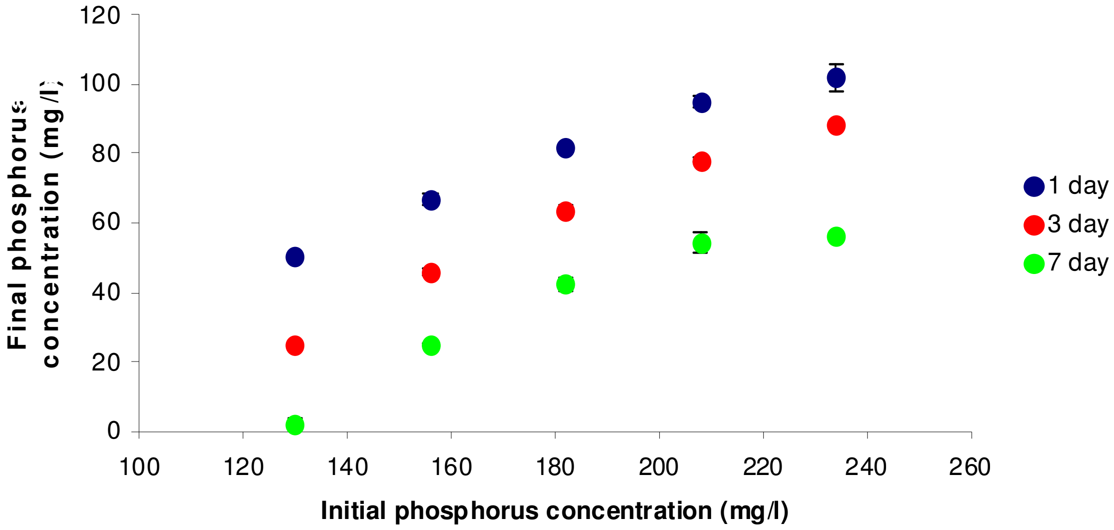


Figure 7.41 Results for phosphorus removal tests on 63-125µm pellets lasting up to one week.

The removal of phosphorus by these pellets is progressing throughout the seven days. Taking the test with the lowest initial concentration of 130mg/l as an example after 1 day this 130mg/l was reduced to 50.5mg/l, after 3 days, the phosphorus concentration was reduced to 24.9mg/l and after 7 days it had been reduced to 2.2mg/l. As with the kinetic results from Section 7.3 the highest rate of removal is found at the initial stage. There is little difference between the absolute change from 1-3 days and that of 3-7, although the latter is a longer time frame. Figure 7.42 shows the progression of the phosphorus concentration throughout the test length.

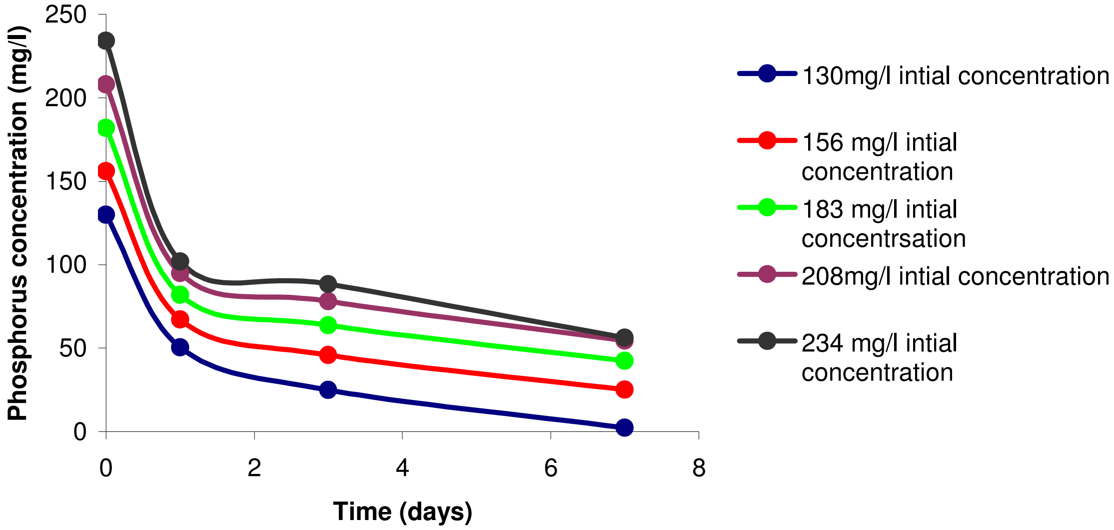


Figure 7.42 Variation of final phosphorus concentration with time for week long tests on 63-125µm pellets

The period with the largest amount of removal for all tests is the initial 0-1 day period after which there is a large reduction in the rate of removal. The tests in Section 7.2 also found the highest rates of removal at the early stages. Figure 7.42 appears to be showing the classic crystal growth form as shown in Figure 4.5. There will be an induction period during the 0-1 day period where nucleation but little removal occurs, results from Section 7.2.2 suggest this should be a short period. Also during the 0-1 day period the rapid precipitation/crystallisation occurs and then the 1-7 day period appears to be showing slow crystallisation. The gradients for the results in Figure 7.42 are analysed in Table 7.3, the gradient representing the rate of change of phosphorus concentration (mg/l/day).

Table 7.3 Gradient analysis for Figure 7.42

Initial Concentration (mg/l)	Gradient day 0-1 (mg/l/day)	Gradient day 1-3 (mg/l/day)	Gradient day 3-7 (mg/l/day)
130	79.5	12.8	5.7
156	89.0	10.6	5.2
182	100.0	9.2	5.3
208	113.1	8.4	5.9
234	131.9	6.8	8.1
Average	102.7	9.6	6.0
St Dev	20.6	2.3	1.2

The average removal rate can be seen to dramatically drop between the periods 0-1 days and 1-3 days, there is then a slight drop to the rate found for 3-7 day period. The data from Figure 7.42 is converted to phosphorus removed (mg/g) and is plotted against the relevant final phosphorus concentration (mg/l) in Figure 7.43.

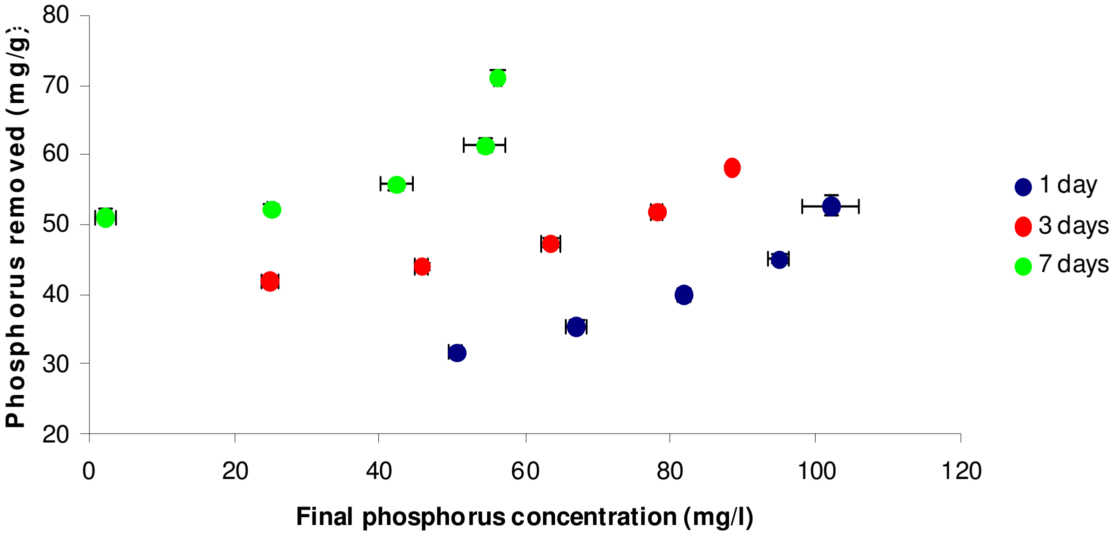


Figure 7.43 Phosphorus loading results for 63-125μm pellets for tests lasting 1,3 and 7 days.

Using the test with the lowest initial concentration (130mg/l) as an example, after 1 day 31.8mg/g has been removed by the pellets, this rises to 42mg/g after 3 days and 51.1mg/g after 7 days. This 51.1mg/g is at a final concentration of 2.2mg/l and compares to 48.0mg/g at 0.1mg/l found by the test lasting a week from Section 7.3.1 showing good repeatability. The highest phosphorus loading shown in Figure 7.43 is 71.1mg/g at a concentration of 56.2mg/l. Figure 7.44 plots the variation of initial pH with the initial phosphorus concentrations.

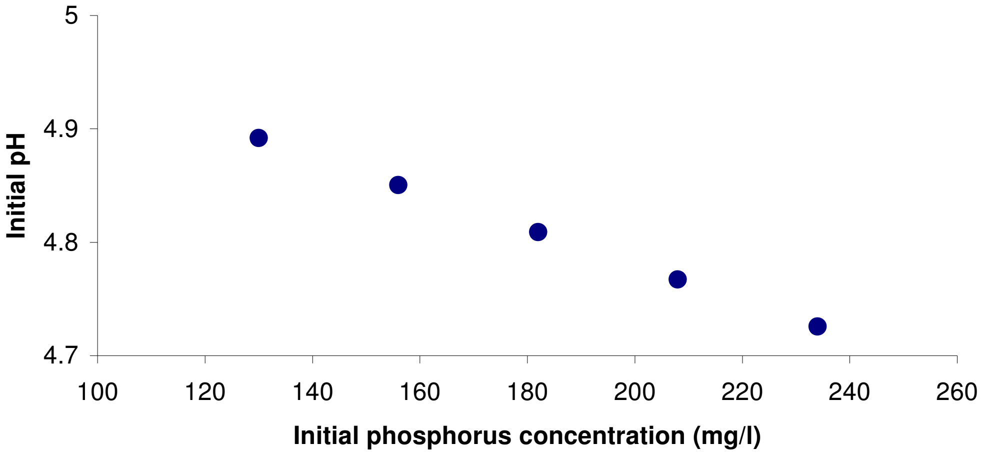


Figure 7.44 Variation of initial pH with initial phosphorus concentration

Figure 7.44 shows the initial pHs range from 4.89 to 4.73, the reduction of initial pH is due to higher addition of the acidic KH_2PO_4. Figure 7.45 plots the variation of final pH with initial pH.

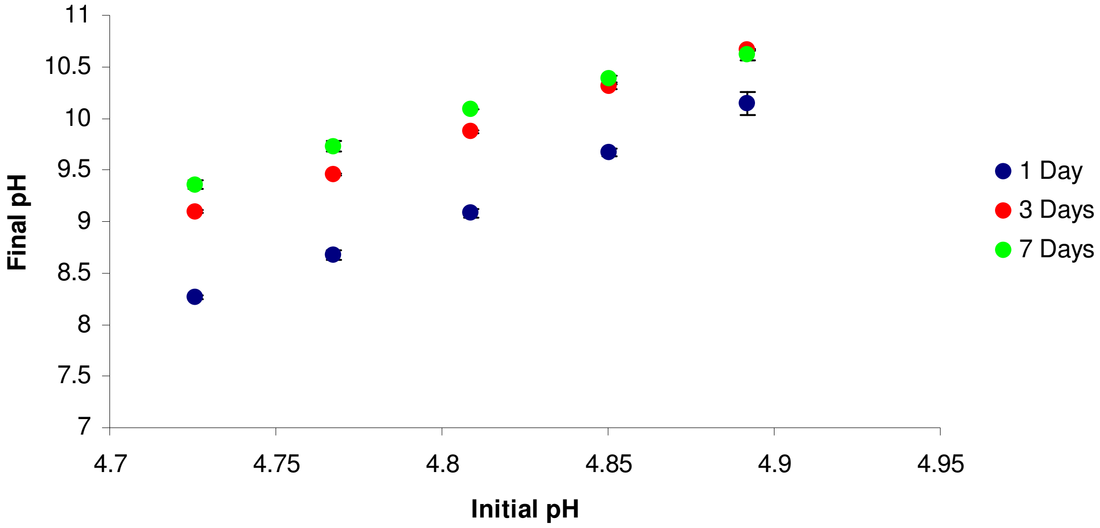


Figure 7.45 Variation of final pH with initial pH for 63-125µm pellets

Final pHs range from 9.4 to 10.6 for the 7 day test compared to 11.2-11.3 for the tests lasting a week in Section 7.3.1. This difference will likely be due to the differences in initial phosphorus concentrations, these high values could be problematic if this technology was implemented. Virotec found similar issues when pelletising their Bauxsol material with cement. The results for the 1 day test are showing slightly lower final pHs (8.3-10.1) than the 3 day (9.1-10.6) and 7 day tests (9.4-10.6). These pHs are again generally above 9, suggested by Johansson at Gustafsson (2000) as a minimum pH for efficient calcium phosphate precipitation. The phosphorus removed (mg/g) is plotted against the final pH in Figure 7.46

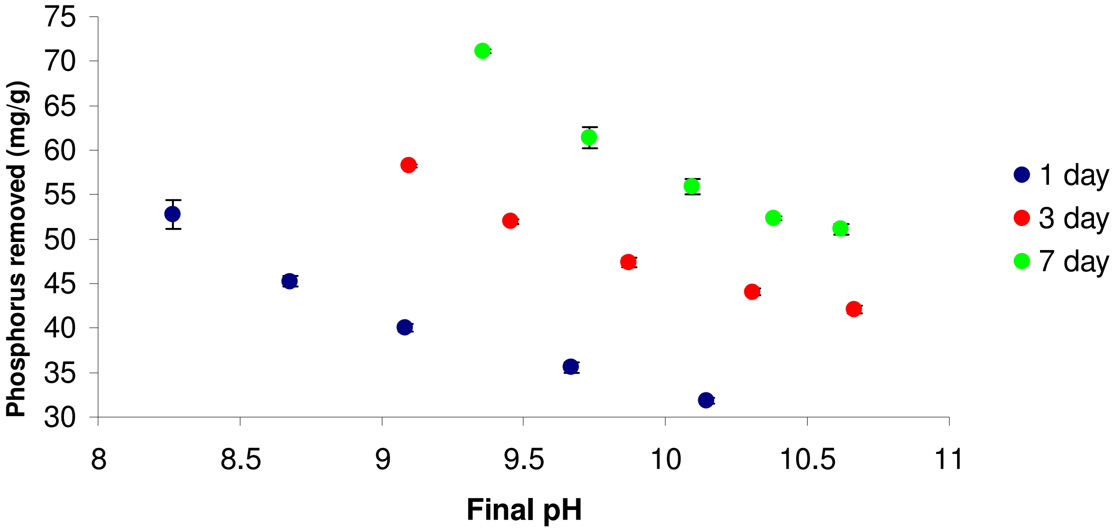


Figure 7.46 Variation of phosphorus loading with final pH for 63-125µm pellets

For each of the three tests the higher phosphorus loadings are represented by the lower pHs. For example, for the 7 day test, as the phosphorus loading rises from 51.1 to 71.1mg/g, the final pH drops from 10.6 to 9.4, the same pattern is evident for the other two tests. This is the same pattern found in Section 7.1.3 and by papers such as Johansson and Gustafson (2000) who found this pattern as indicative of calcium phosphate precipitation. The lower pHs could be reflecting the consumption of hydroxide ions as they form part of calcium phosphates. When comparing the three test lengths, there is an increase in pH range as the length of the test increases.

7.3.2.2 Contribution removal by adsorption

The loadings shown in Figure 7.43 are expressed in Figure 7.47 as removal in terms of milligrams per gram of Horden solid which forms 48% of the pellet.

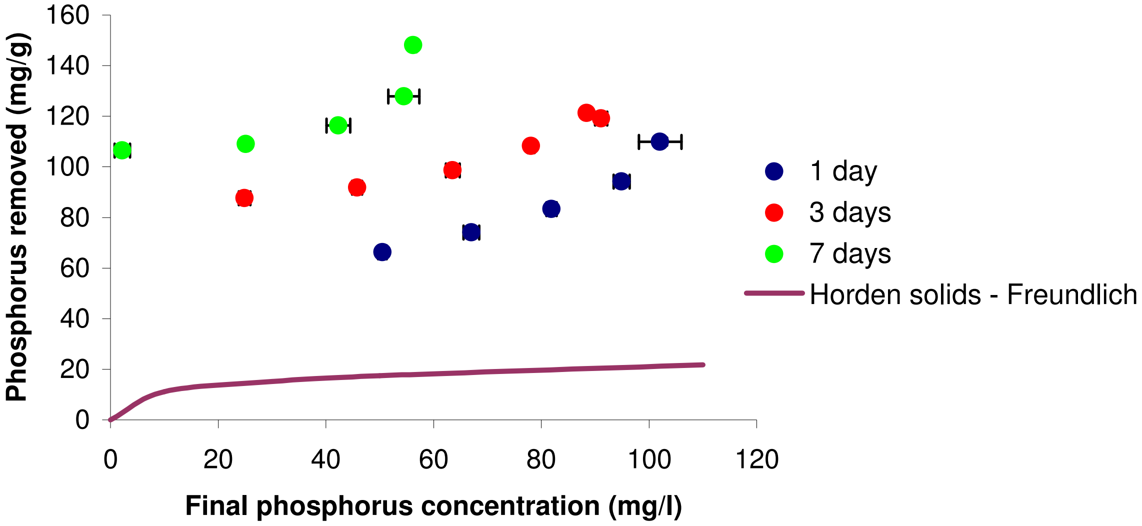


Figure 7.47 Comparison of phosphorus removal data for the tests on 63-125µm pellets and the Freundlich isotherm for the solids from Horden solids

Figure 7.47 shows that when compared on a per weight of solids from Horden basis the disparity between the pellet and Horden solids results is large. This again highlights that there must be another removal mechanism in addition to adsorption onto the solids from Horden. The test lasting 7 days which finished with a concentration of 2.2mg/l is removing the equivalent of 106.4 mg per gram of the solids from Horden, this compares to 7.3mg/g from the Freundlich isotherm.

The final concentrations from Figure 7.43 were used to calculate the phosphorus loadings that the Freundlich isotherm from Section 6.2 predicts adsorption could achieve. These loadings were then used to calculate the maximum percentage contribution by adsorption towards the loadings shown in Figure 7.43. This is plotted against the relevant residual phosphorus concentration in Figure 7.48.

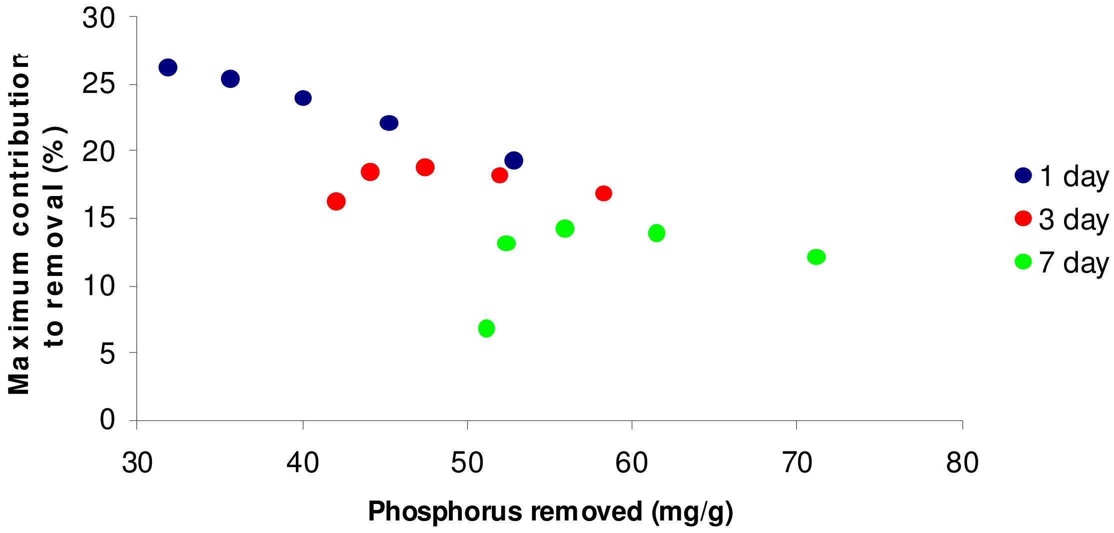


Figure 7.48 Maximum percentage contribution of adsorption to total removal by pellets.

The lowest percentage contribution reported is 7% for the initial concentration of 130mg/l and a phosphorus loading of 51.1mg/g, these values are similar to those found in Figure 7.40 for the tests lasting 1,2 and 3 weeks from Section 7.3.1 where the lowest percentage found was 6%. Again these are the theoretical maximums, due to the decreased surface area of these pellets and the high pHs above the typical range of the point of zero charge suggested by Cornell and Schwertmann (2003) probably retarding adsorption, actual contribution by adsorption is likely to be lower. The dominance of the expected calcium phosphate precipitation can therefore be seen.

A comparison of the batch results presented so far is made in Figure 7.49. This comprises of the results from this section, results from the tests lasting 1, 2 and 3 weeks from Section 7.3.1, the tests lasting 16 hours from Section 7.1.3 and the Freundlich isotherm for the solids from Horden mine water treatment plant from Section 6.2.

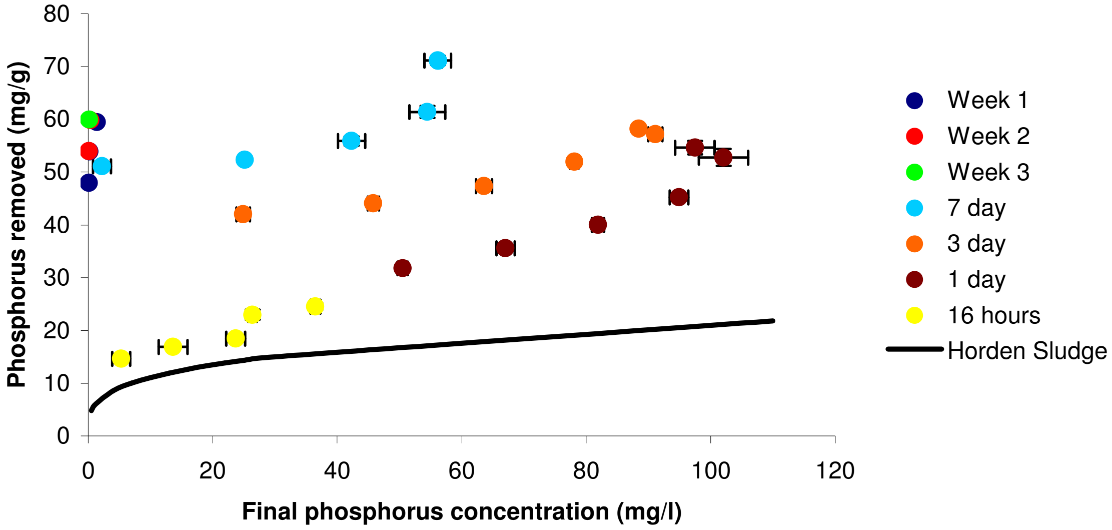


Figure 7.49 Comparison of data for 63-125µm pellets and the Freundlich isotherm solids from Horden.

Figure 7.49 highlights the increase in performance achieved with the increase of test length. The unpelletised solids from Horden have the lowest phosphorus loadings, the improvement as a result of pelletisation can be seen as can the increase in the performance of the pellets with the increase in test length.

7.3.2.3 Rate of removal

To assess the most efficient test length the highest phosphorus loadings (mg/g) achieved from tests from Sections 7.1.3, 7.3.1 and 7.3.3 tests are converted to mg/g/day to show the rate of phosphorous loading onto the pellets. This is plotted against the test length in Figure 7.50.

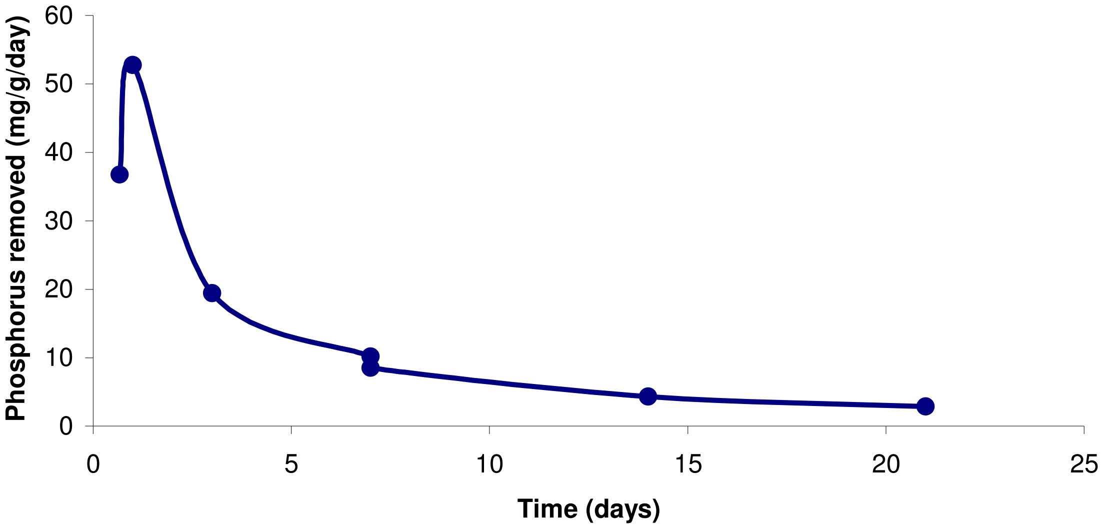


Figure 7.50 Efficiency of removal presented as (mg/g/day) plotted against length of test

Figure 7.50 shows that the shorter test lengths are by far the most efficient. The maximum mg/g/day achieved after 24 hours is higher than that for 16 hours this may be due to the difference in initial concentrations limiting the maximum phosphorus loading achievable. The longer tests are less efficient in terms of the rate of removal but are required to achieve the higher phosphorus loadings. The results for the 7 day test from this section and the week long test from Section 7.3.1 lie directly on top of each other, showing good repeatability.

As discussed in Section 7.2 the most efficient stage of removal is the very early stages. This efficiency is highlighted if the results from the kinetics tests from Section 7.2.1 are converted in the same manner as those in Figure 7.50. The test lasting 1 minute from the tests in Section 7.2.1 is removing the equivalent of 6800mg/g/day compared to the highest value of 52.8mg/g/day from Figure 7.50 however the phosphorus loading achieved at this point was only 4.7mg/g. There is clearly a pay off between short exposures with high removal efficiencies and long exposures with lower efficiencies but that achieve much higher phosphorus loadings.

This section has presented the results for phosphorus removal by pellets for tests lasting 1,3 and 7 days. Removal occurred throughout the week long tests with the highest rate of removal during the initial 0-1 day period. Phosphorus removal was linked to a drop in pH which is indicative of calcium phosphate precipitation and the potential contribution of adsorption to removal was shown to be minimal.

7.3.3 Tests lasting up to one week – relationship between phosphorus and calcium concentrations

This section presents the results of tests identical to those of Section 7.3.2 but which were analysed for both phosphorus and calcium. Initial concentrations of 130-230mg/l were therefore used with 0.1g of pellets in 40ml solutions (2.5g/l solids concentration).

7.3.3.1 Phosphorus removal

The final phosphorus concentrations found are plotted against the relevant initial phosphorus concentrations in Figure 7.51.

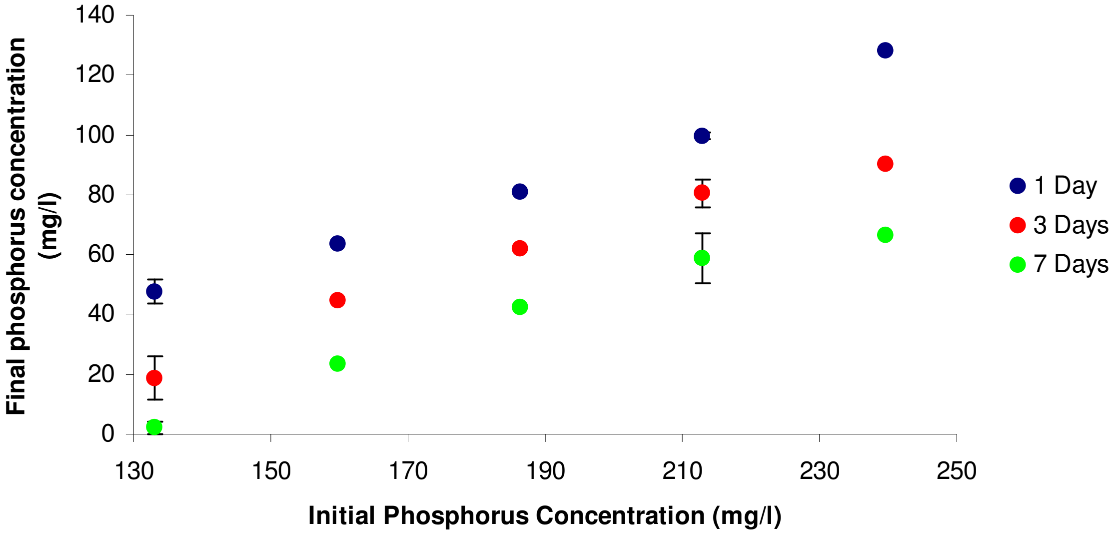


Figure 7.51 Results for the second set of phosphorus removal tests on 63-125µm pellets

This test is performing very closely to that reported on in Section 7.3.2. Taking the 7 day results as an example in the test reported in this section the 130-

230mg/l initial concentration range has been reduced to 2-66mg/l, in the test from Section 7.3.2 the same initial concentrations were reduced to 2-56mg/l. These are results for two separate tests on two separate batches of pellets and show good repeatability for both pellet production and experimental procedure. This similarity was found for all three test lengths. These results are presented in Figure 7.52 with phosphorus removed (mg/g) plotted against residual phosphorus concentration (mg/l).

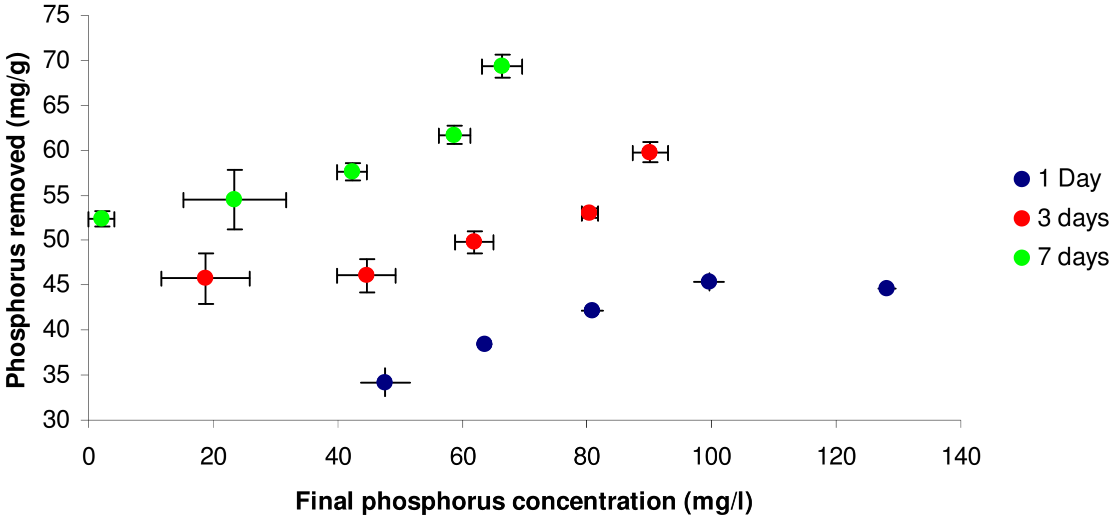


Figure 7.52 phosphorus loading results 63-125µm pellets

The results in Figure 7.52 can be compared to those from Section 7.3.2. The 7 day results in this section show 52.4-69.3mg/g removed across the final concentration range of 2.1-66.4mg/l. Section 7.3.2 found 51.1 to 71.1mg/g at 2.2-56.2mg/l showing good repeatability. A comparison between all test lengths for the results of both sections is made in Figure 7.53, averages between the two tests are also plotted as lines.

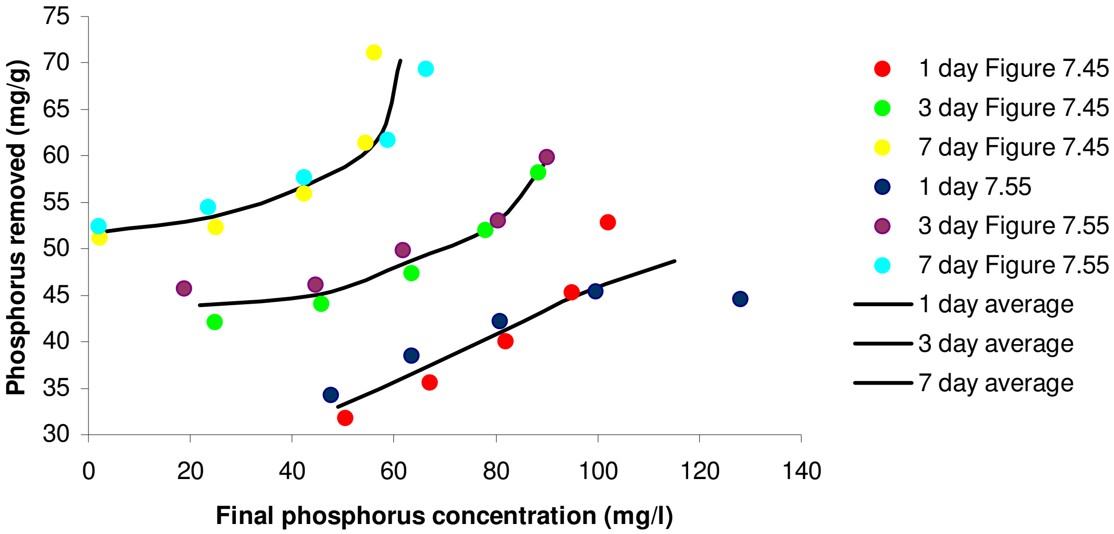


Figure 7.53 Comparison of phosphorus loading results for the data from Figures 7.45 and 7.55.

The tests from the current section are performing to a very similar standard to those of Section 7.3.2. This shows the repeatability of these tests and the consistency in pellet production. No further analysis of the phosphorus removal is presented for this data as it will be just repetition of the analyses presented in Section 7.3.2. The pH values for the tests from the current section are now discussed, the same initial phosphorus concentrations as Section 7.3.2 were used and so the relationship between initial concentration and initial pH is the same as shown in Figure 7.44. Figure 7.54 presents the relationship between final pH and initial pH.

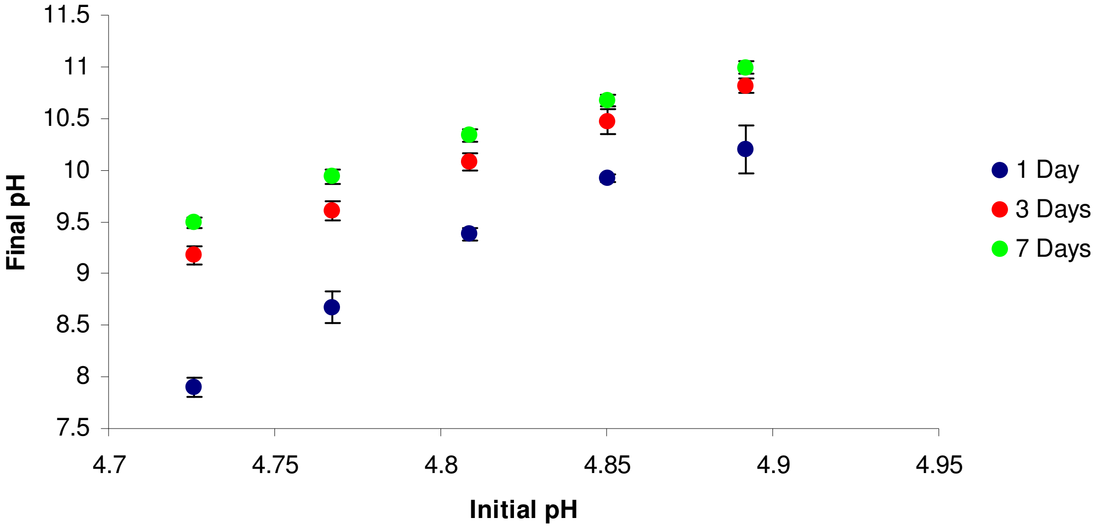


Figure 7.54 Variation of final pH with initial pH

All test lengths showed a slight positive correlation between initial and final pH. The development of pH is believed to follow the following pattern, the higher initial concentrations result in lower initial pHs, the addition of the pellets raise these pHs due to leaching of the hydroxide ions from the cement and then the precipitation of HAP is expected to consume some of these hydroxide ions to leave the resultant final pH. The 7 days results range from 9.5-11.0, the 3 day results 9.2-10.8 and the 1 day results 7.9-10.2. The similarity between the results shown in this section and those from Section 7.3.2 can be seen in Figure 7.55 where the variation of phosphorus removed with final pH from both sections is plotted alongside the average values represented by lines.

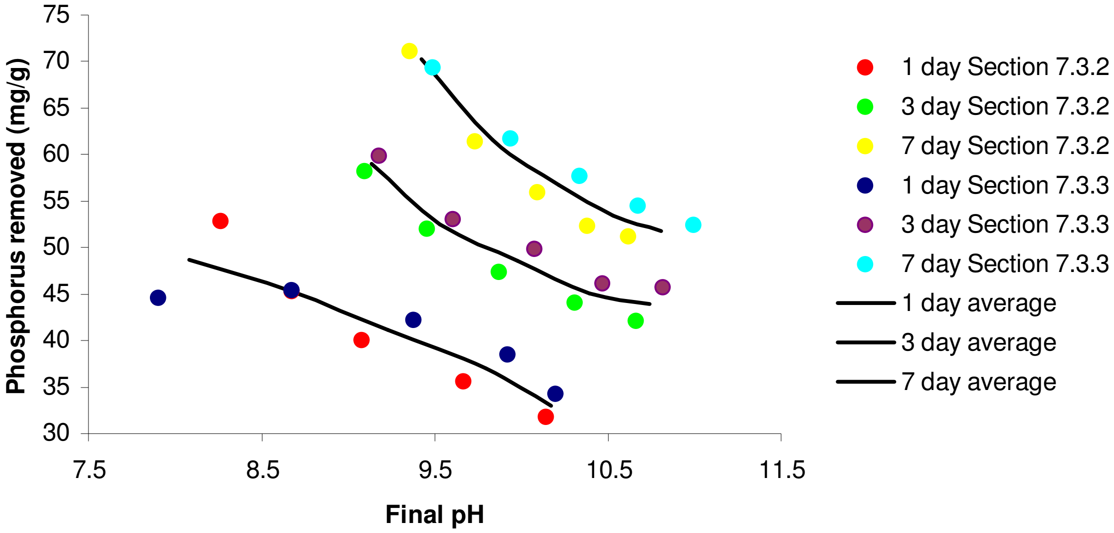


Figure 7.55 Comparison of phosphorus removal and pH data for the tests from this section (7.3.3) and Section 7.3.2

The results from this section are very similar to those of Section 7.3.2. Again the correlation of lower pHs with higher phosphorus removals can be seen. The similarity between the two sets of results again shows the repeatability of these tests and the consistency in the production of pellets.

7.3.3.2 Calcium analysis

The amount of calcium released by pellets in each test was determined by adding 0.1g of pellets to 40ml of deionised water. These were then shaken alongside the tests containing phosphorus for 1, 3 and 7 days, this was carried out in triplicate. The results for these tests are shown in Figure 7.56 with the concentration of calcium released from the pellets plotted against the length of test.

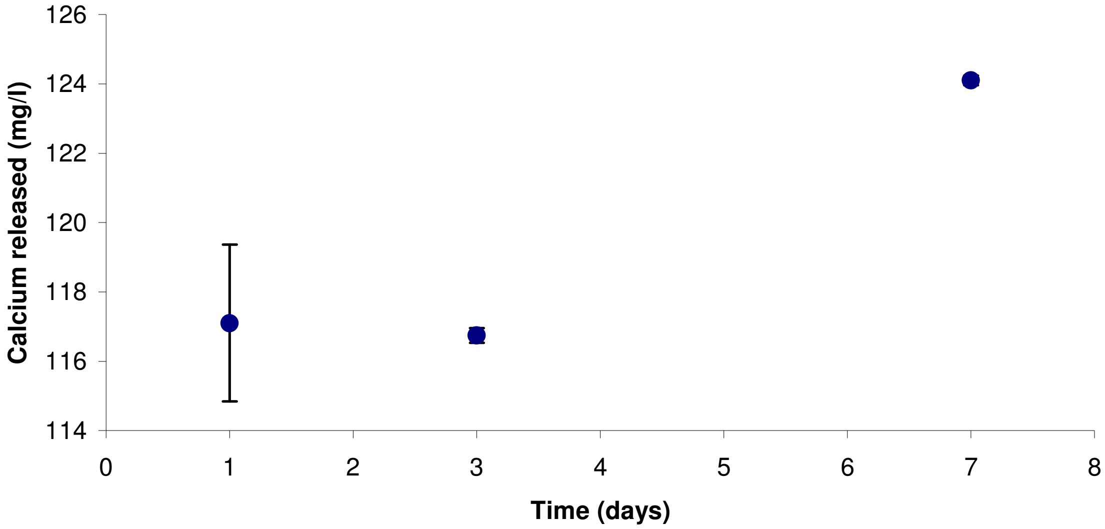


Figure 7.56 The release of calcium with time by 0.1g of pellets in 40ml of deionised water. Tests lasted 1,3 and 7 days.

Figure 7.56 shows that after both 1 and 3 days 117mg/l of calcium had been released into the deionised water, this is equivalent to 47mg/g (milligram of calcium per gram of pellet), this rises to 124mg/l after 7 days which is equivalent to 50mg/g. Thus between 3 and 7 days 7mg/l is further released just a 6% increase. The release of calcium by pellets is shown to be relatively rapid, this is the same conclusion is in Section 7.2.2.2. Assuming that the Portland cement contained 2/3rds CaO and knowing that the pellets contained 30% cement the expected calcium content would be 14.3% (143mg/g). These tests found up to 50mg/g was released, around a third of the total calcium.

The pH of these tests with pellets in deionised water was measured. The tests lasting 1 day had an average pH of 11.2, the 3 day 11.3 and the 7 day 11.4. This shows there is a very slight increase in both calcium concentration and pH with time, but results are very close for all test lengths. All of the final pHs for the test containing phosphorus as reported in Figure 7.54 are lower than these values found, this fits in with the findings of Lu *et al.* (2009) and Johansson and Gustafsson (2000) who both saw this reduction of pH as partial evidence of calcium phosphate precipitation. The reduction of pH is explained by the consumption of hydroxide ions in the precipitation of HAP as explained in

Section 7.2.2. The phosphorus removal (mg/g) is plotted against the final calcium concentrations found in Figure 7.57.

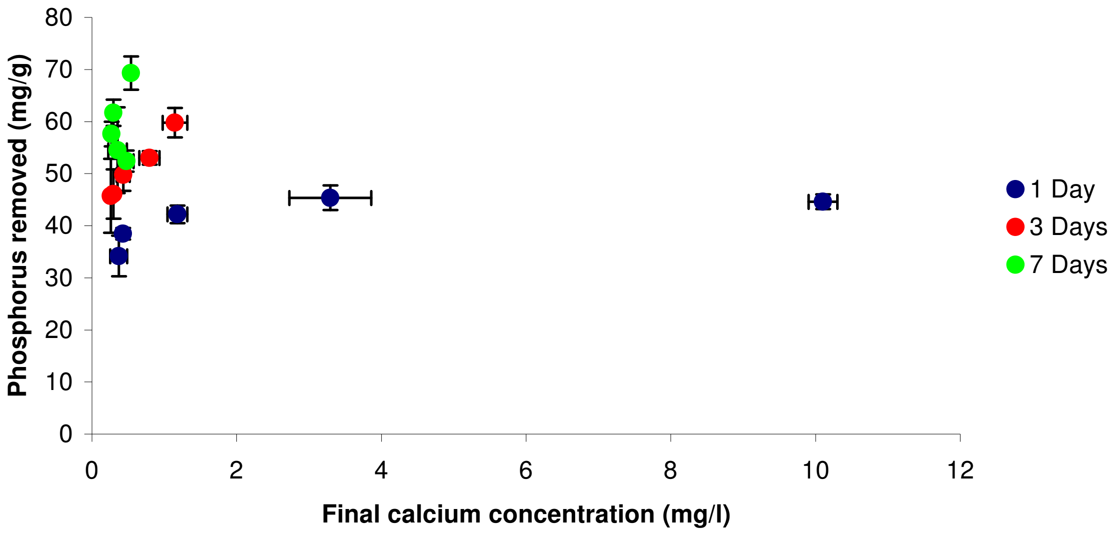


Figure 7.57 Variation of phosphorus removed with residual calcium concentration

Residual calcium concentrations ranged from 0.3-10.1mg/l, the majority being below 2mg/l, a large reduction from the 117-124mg/l found released by the pellets. The results for the test lasting 1 day have residual concentrations from 0.37 up to 10.1mg/l, the 3 day 0.26-1.15mg/l and the 7 day 0.27-0.54mg/l, the longer the test, the lower the residual calcium concentrations which ties in with the higher phosphorus removal achieved. This relationship is investigated through a plot of change in phosphorus concentration against change in calcium concentration in Figure 7.58. The change in calcium concentration is calculated from subtracting the residual calcium concentrations from Figure 7.57 from the appropriate calcium concentrations from Figure 7.56

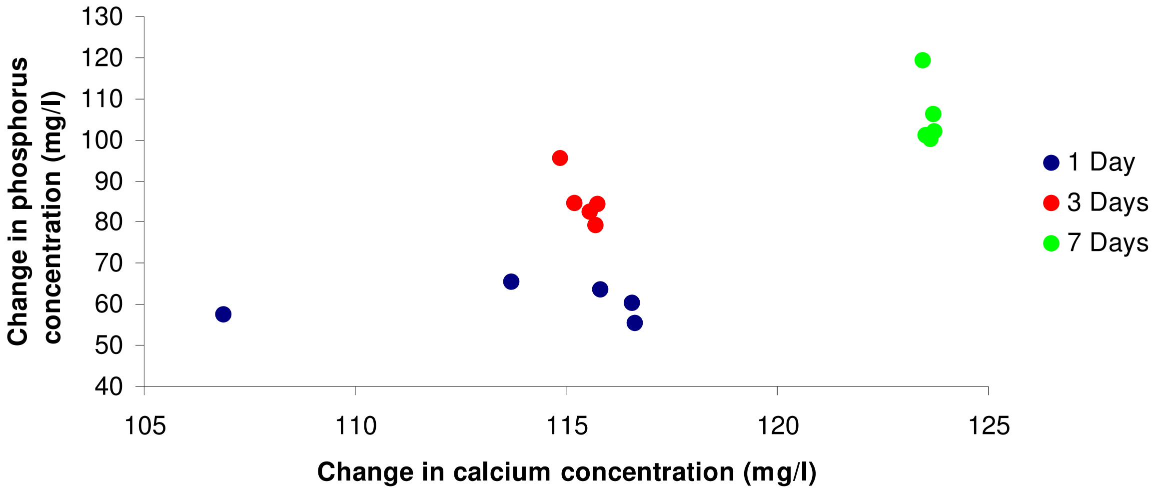


Figure 7.58 Change in phosphorus concentration versus change in calcium concentration

An increase in the change in calcium concentration is correlated with an increase in the change in phosphorus concentration, therefore suggesting the combination of these elements in some form of calcium phosphate precipitation. The data appears to approximately follow a linear pattern and therefore are combined into one data set in Figure 7.59. The data are also converted to moles by converting the mg/l values into absolute grams and then dividing this by the atomic weight of the relevant element.

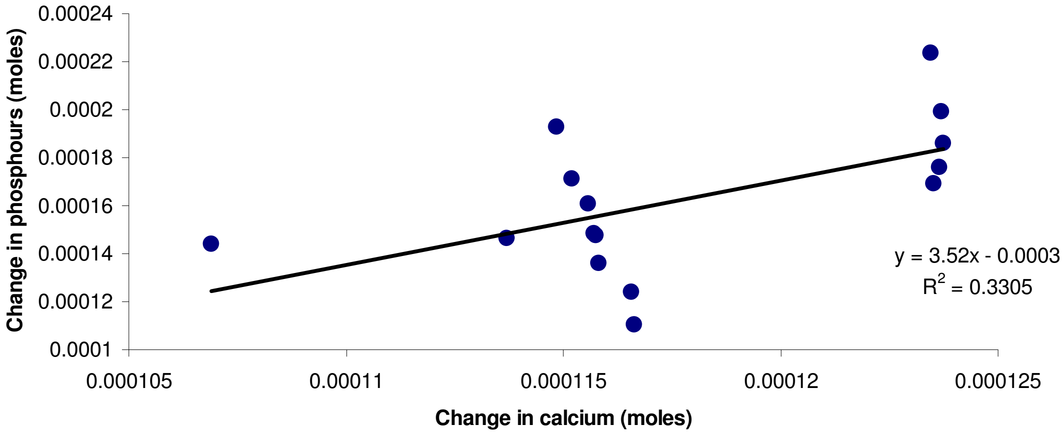


Figure 7.59 Change in phosphorus versus change in calcium in moles for the combined data range of all tests on 63-125µm pellets lasting 1,3 and 7 days.

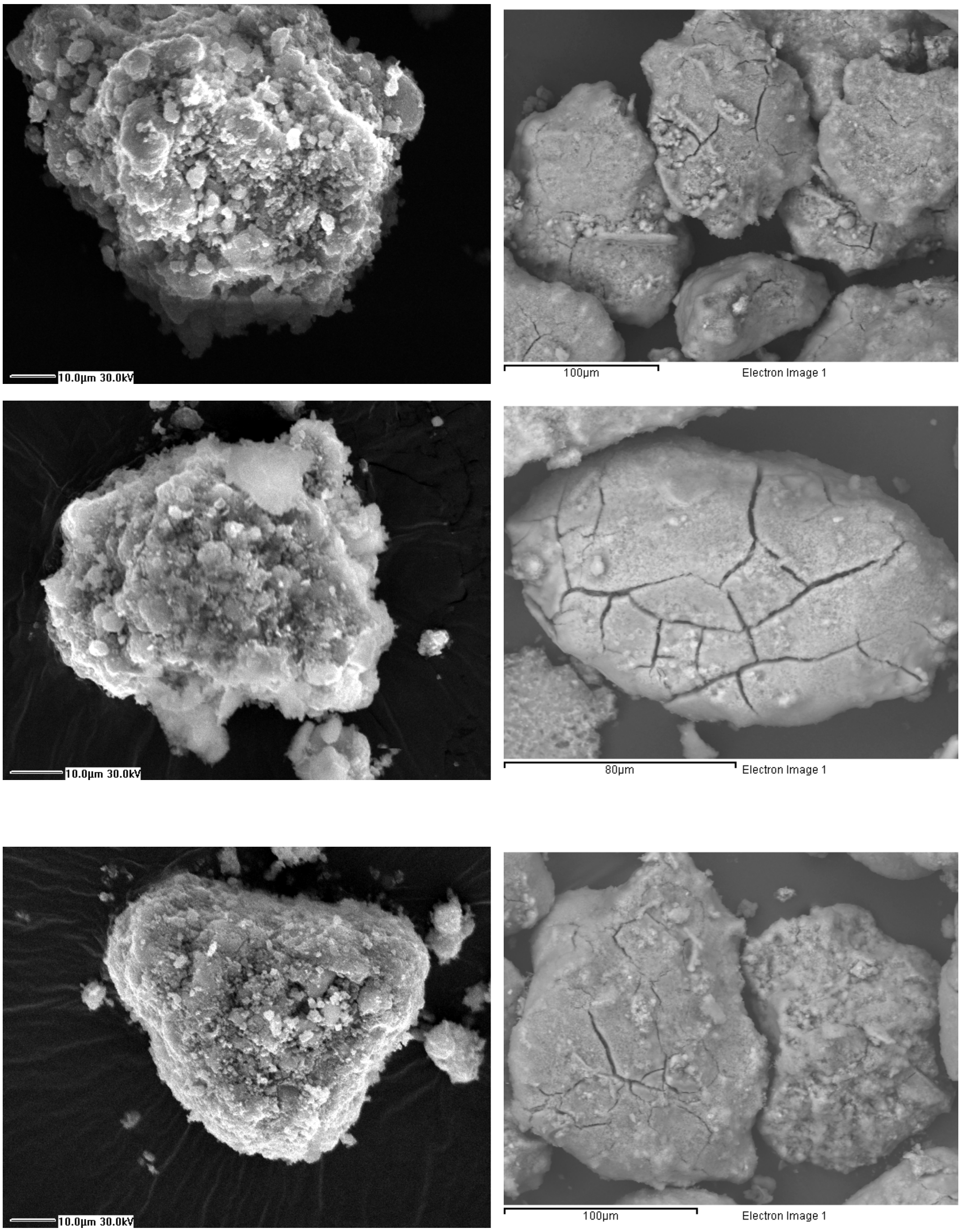
There is a general pattern of increasing changes in phosphorus correlated with increasing changes in calcium but the coefficient of determination of the line of best fit is poor at 0.3305. The inverse of the differential of the line of best fit gives an average Ca:P ratio of 0.29, this is far from the 1.67 ratio for HAP, which the literature review suggests would be the most likely end product of calcium precipitation. Tests reported on in Section 7.3.4 report a much higher release of calcium per gram of pellet, suggesting that the change in calcium may be higher than reported in Figure 7.59, this is fully explored once the results are presented in Section 7.3.4. It is clear that simultaneous removal of calcium and phosphorus is occurring which is a strong piece of evidence that calcium phosphate precipitation is dominating removal.

7.3.3.3 Morphology and surface chemistry of used pellets

This section uses Scanning Electron Microscope (SEM) micrographs to study the morphology of both used and unused pellets. The SEM was then used in conjunction with Energy Dispersive X-ray spectroscopy (EDX) to provide analysis of the surface chemistry of the used pellets.

7.3.3.3.1 Comparison of virgin and used pellet morphology

The pellets used for the 7 day test with an initial phosphorus concentration of 240mg/l from Section 7.3.3 (66mg/l final concentration and 69mg/g loading) were analysed using SEM-EDX. The analysis was carried out in conjunction with Cardiff University School of Earth and Ocean Sciences. Once the phosphorus removal tests had completed, the solutions were filtered, the pellets from this specific test were retained on the filter papers, then air dried and supplied to the School of Earth and Ocean Sciences. SEM micrographs of these used pellets (right hand side column) are compared in Figure 7.60 to the micrographs of unused pellets (left hand side column) which were presented in Section 5.2.4.



(Unused) (Used)

Figure 7.60 Comparison of virgin and exposed 63-125 micron pellets produced from solids from Horden and cement.

Figure 7.60 shows a clear difference in morphology between the used and the unused pellets. The virgin pellets can be seen to be composed of smaller particles providing quite a rough surface as described in Chapter 5. The used pellets are showing much smoother surfaces that could well be as a result of calcium phosphates being precipitated onto the surface and thus reducing the surface area.

Oguz *et al.* (2003) studied phosphorus removal by concrete and found that the surface area of their material was reduced after being used to remove phosphorus. Cracks can be seen on the surface of the used pellets and this will likely be due to the drying of the pellets before the SEM analysis was carried out.

7.3.3.3.2 Surface chemistry of used pellets

The SEM is also capable of chemical analysis using EDX (Energy-dispersive X-ray spectroscopy). The analysis was carried out on the used pellets shown in Figure 7.60. These micrographs are reproduced with the areas of analysis or "spectrum" highlighted. These are presented in Figures 7.65-7.67 alongside the elemental analysis in terms of weight % and atomic %.

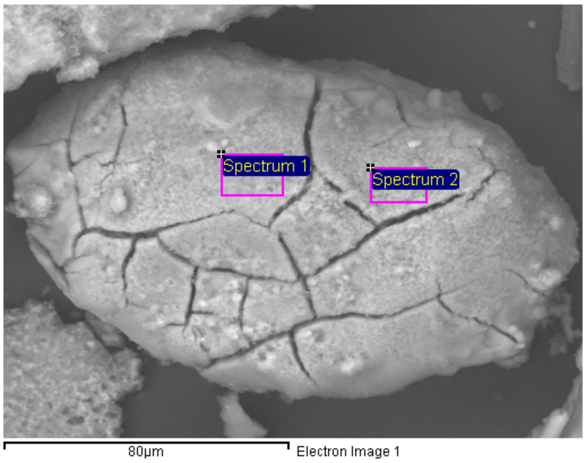


Figure 7.61 SEM micrograph of exposed pellet and the areas of analysis

Table 7.4 Elemental analysis of the areas shown in Figure 7.61 (weight %)

Spectrum	Mg (%)	Al (%)	Si (%)	P (%)	Ca (%)	Fe (%)	O (%)	Total (%)
Spectrum 1	0.78	0.29	0.41	19.51	35.04	2.75	41.21	100.00
Spectrum 2	0.80	0.16	0.20	20.31	35.67	1.18	41.69	100.00
Mean	0.79	0.22	0.30	19.91	35.36	1.97	41.45	100.00
Std. dev	0.01	0.09	0.15	0.56	0.45	1.11	0.34	

Table 7.5 Elemental analysis of the areas shown in Figure 7.61 (atomic %)

Spectrum	Mg (%)	Al (%)	Si (%)	P (%)	Ca (%)	Fe (%)	O (%)	Total (%)
Spectrum 1	0.77	0.26	0.35	15.05	20.88	1.18	61.52	100.00
Spectrum 2	0.78	0.14	0.17	15.54	21.1	0.5	61.77	100.00
Mean	0.77	0.2	0.26	15.29	20.99	0.84	61.65	100.00
Std. dev	0.01	0.08	0.13	0.35	0.15	0.48	0.18	

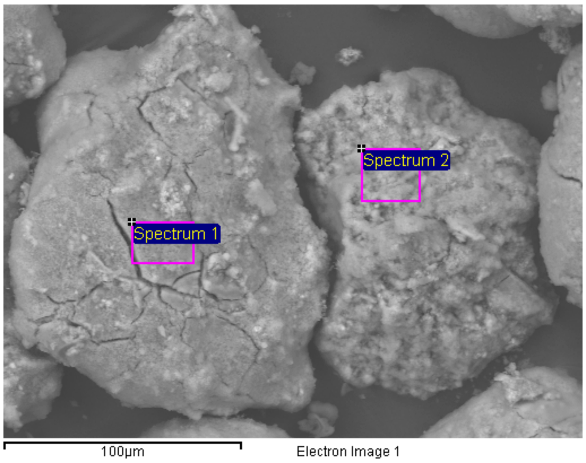


Figure 7.62 SEM micrograph of exposed pellet and the areas of analysis

Table 7.6 Elemental analysis of the areas shown in Figure 7.62 (weight %)

Spectrum	Mg (%)	Al (%)	Si (%)	P (%)	K (%)	Ca (%)	Fe (%)	O (%)	Total
Spectrum 1	0.91	0.56	1.22	19.17	0.45	32.90	3.37	41.43	100.00
Spectrum 2	0.64	0.53	2.27	13.82	1.15	40.45	2.65	38.48	100.00
Mean	0.78	0.54	1.74	16.50	0.80	36.68	3.01	39.95	100.00
Std. dev	0.19	0.02	0.75	3.78	0.50	5.34	0.51	2.09	

Table 7.7 Elemental analysis of the areas shown in Figure 7.62 (atomic %)

Spectrum	Mg (%)	Al (%)	Si (%)	P (%)	K (%)	Ca (%)	Fe (%)	O (%)	Total
Spectrum 1	0.89	0.49	1.03	14.73	0.27	19.53	1.43	61.62	100.00
Spectrum 2	0.65	0.48	1.99	10.98	0.72	24.83	1.17	59.17	100.00
Mean	0.77	0.49	1.51	12.86	0.50	22.18	1.30	60.39	100.00
Std. dev	0.17	0.01	0.68	2.65	0.32	3.75	0.19	1.73	

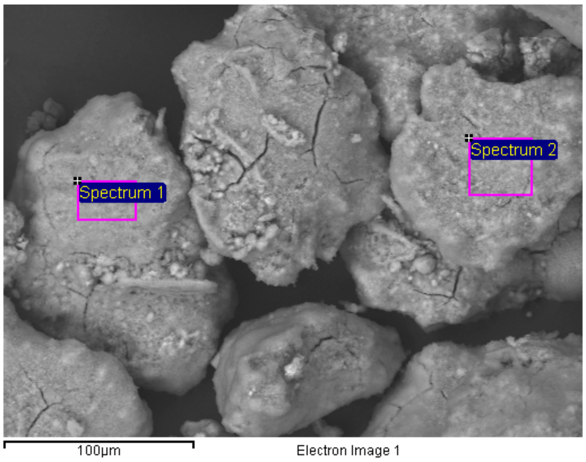


Figure 7.63 SEM micrograph of exposed pellet and the areas of analysis

Table 7.8 Elemental analysis of the areas shown in Figure 7.63 (weight %)

Spectrum	Mg (%)	Al (%)	Si (%)	P (%)	K (%)	Ca (%)	Fe (%)	O (%)	Total
Spectrum 1	0.47	0.19	0.29	16.32	0.48	37.31	6.28	38.67	100.00
Spectrum 2	0.61	0.85	1.03	14.31	0.59	35.46	9.37	37.77	100.00
Mean	0.54	0.52	0.66	15.31	0.54	36.39	7.82	38.22	100.00
Std. dev	0.09	0.47	0.53	1.42	0.08	1.31	2.18	0.63	

Table 7.9 Elemental analysis of the areas shown in Figure 7.63 (atomic %)

Spectrum	Mg (%)	Al (%)	Si (%)	P (%)	K (%)	Ca (%)	Fe (%)	O (%)	Total
Spectrum 1	0.48	0.17	0.25	13.05	0.30	23.07	2.79	59.88	100.00
Spectrum 2	0.62	0.79	0.92	11.60	0.38	22.21	4.21	59.26	100.00
Mean	0.55	0.48	0.59	12.32	0.34	22.64	3.50	59.57	100.00
Std. dev	0.10	0.44	0.47	1.03	0.06	0.61	1.01	0.44	

These results are collated and presented as weight percent averages in Figure 7.64 to allow easier analysis. The error bars represent ± one standard deviation.

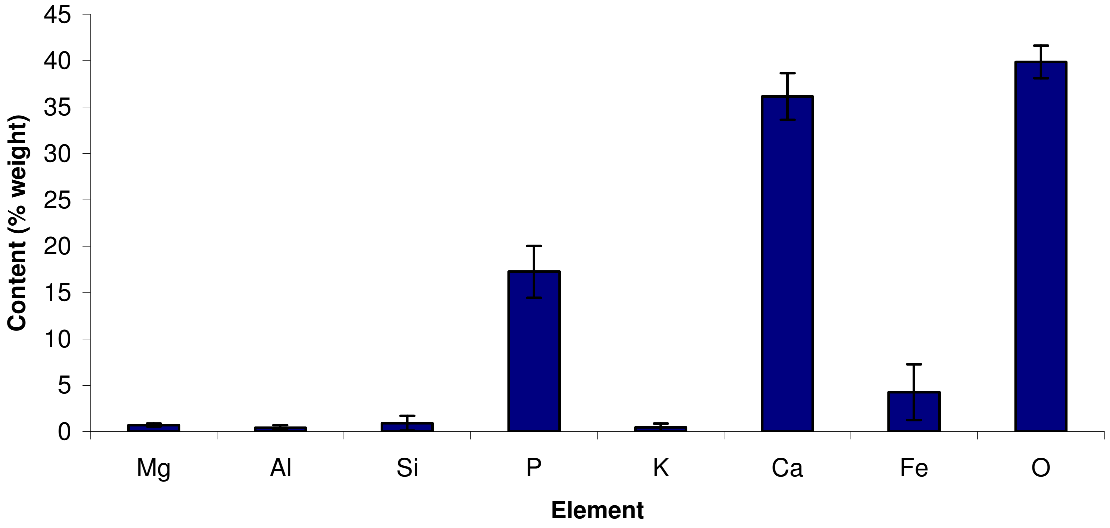


Figure 7.64 Average weight % for elements detected through the SEM-EDX analysis on exposed pellets

Figure 7.64 shows that, aside from oxygen, the dominant constituent is calcium (36%) then phosphorus (17%) and then much lower iron (4%). The rest of the elements make up 2.5%. Potassium represents 0.5% showing that this constituent of the KH_2PO_4 used to make the phosphorus stock solutions is taking no part in the surface chemistry. The SEM-EDX analyses the top four microns of the material, these results show that this top four microns contain 172mg/g of phosphorus, this compares to the experimentally determined 69mg/g for the whole of the pellet, showing the dominance of the surface towards removal.

The average iron weight % reported was 4.3%. The pellets are composed of 48% of the solids from Horden, these solids are 34.8% iron and so from this an iron weight percentage of 16.7% would be expected, four times the value found showing the reduced role iron has in the surface chemistry. The average calcium percentage by weight was found to be 36.1%. Assuming that the Portland cement contained 2/3rds CaO and knowing that the pellets contained 30% cement the expected calcium content would be 14.3% thus under half of the weight percentage found by the SEM-EDX. This highlights the relative importance of iron and calcium towards the final surface chemistry and shows calcium to be the more important, highlighting the expected dominance of calcium phosphate precipitation.

As shown in Tables 7.4-7.9 percentage content in terms of atomic % was also obtained through conversion of the weight percentage by the molar mass of the respective elements. The average values for these are shown in Figure 7.65

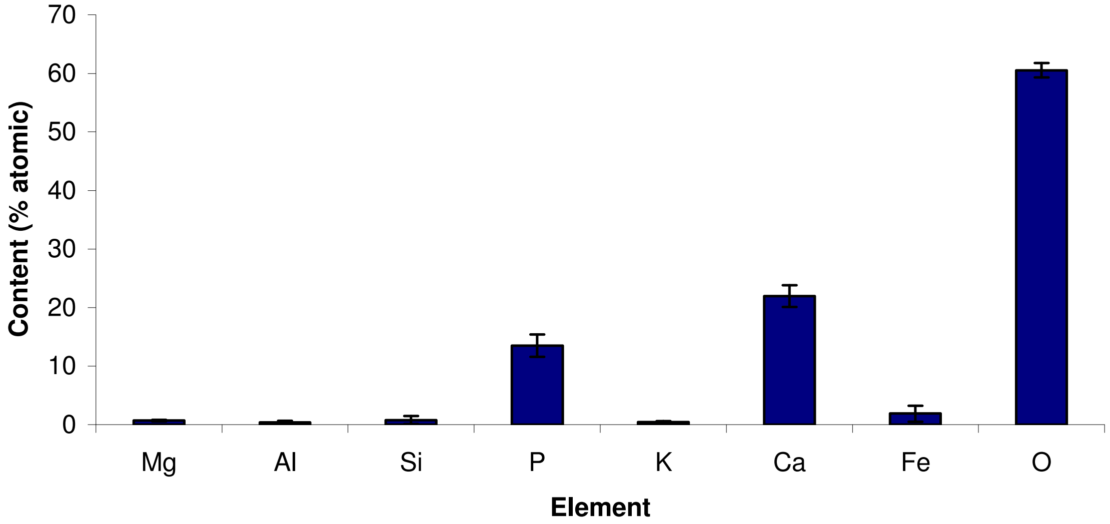


Figure 7.65 Average atomic % for the SEM-EDX results on exposed pellets

The dominance of the surface chemistry by calcium and phosphorus can again be seen. The average Ca:P molar ratio is 1.62 this is very close to the stoichiometric ratio for HAP of 1.67 and would therefore appear to confirm that the formation of HAP is dominating removal. The Ca:P ratios for each pellet are presented in Figure 7.66. The analysis for the pellet in Figure 7.61. is represented by SEM 1 and 2, that in Figure 7.62 SEM3 and 4 and that in Figure 7.63 SEM5 and 6. The stoichiometric ratio for HAP (1.67) is also plotted.

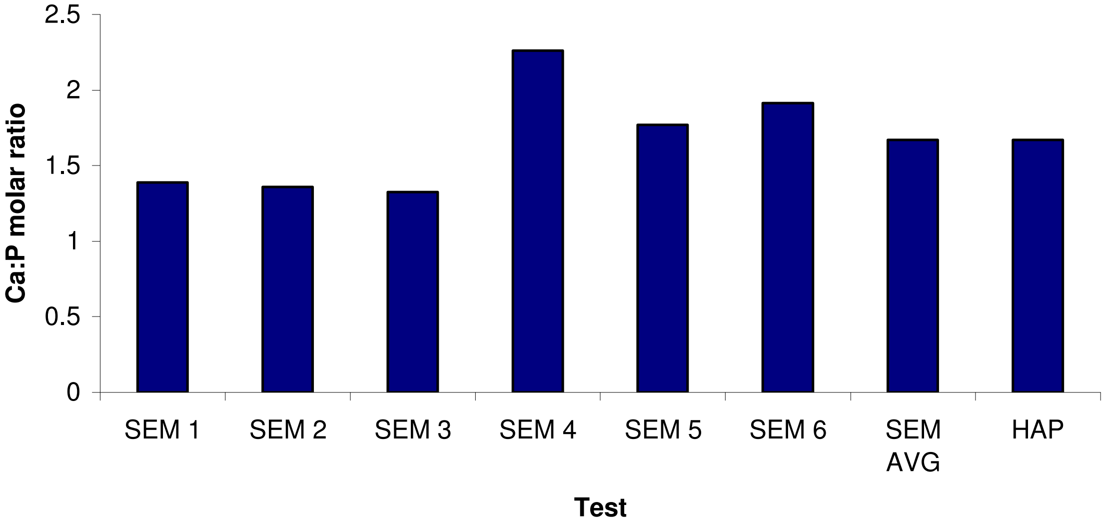


Figure 7.66 Ca:P molar ratio for all the SEM-EDX results, the average and the stoichiometric ratio for HAP are included for comparison

Kim *et al.* (2006) suggest a range of 1.33 and 1.95 wherein HAP precipitation could be occurring. All but one of these spectrums (SEM 4 – 2.26) reported values within that range. This SEM-EDX analysis would appear to confirm HAP as the end product of the calcium phosphate precipitation.

This section has presented results for tests carried out in the same manner as Section 7.3.2 with the addition of calcium analysis. It was shown, that in terms of phosphorus removal and pH the results from this section are very close to those of Section 7.3.2, showing consistency of pellet production and experimental procedure. It has been shown that these pellets release relatively large amounts of calcium when shaken in deionised water and when phosphorus is added these calcium concentrations are dramatically reduced. A correlation between the change in calcium concentration and the change in phosphorus concentration has been identified, this reinforces the theory that calcium phosphate precipitation the dominant removal mechanism. Through SEM-EDX analysis of the used pellets surface an average calcium-phosphorus molar ratio of 1.62 was found and this would appear to confirm HAP precipitation as the major removal mechanism as supported by the conclusions of Lee *et al.* (2009), Johansson and Gustafsson (2000), Can and Yidiz (2006) and many others.

7.3.4 Phosphorus removal by pellets from an influent concentration typical of WWTWs

A set of batch tests was carried out at an initial concentration of 11mg/l in order to asses the pellets performance at these lower initial concentrations, this concentration being typical of influent phosphorus concentrations received by WWTWs. The filtered solutions were analysed for both calcium and phosphorus to investigate their relationship in this situation.

7.3.4.1 Phosphorus removal

Tests were conducted on solutions of 40ml and the weight of pellets added was reduced from 0.1g to the range 0.0044-0.008g so that the ratio of the weight of pellets per litre to the initial phosphorus concentration was kept similar to that of Section 7.3.3, this is shown in Table 7.10

Table 7.10 Ratio of pellet weight per volume to phosphorus concentration

Section 7.3.3			This section		
Initial P conc (mg/l)	Pellet conc (g/l)	Ratio (initial conc: pellet conc)	Initial P Conc (mg/l)	Pellet Conc (g/l)	Ratio (initial conc:pellet conc)
133	2.5	53	11.06	0.20	55
160	2.5	64	11.06	0.17	66
186	2.5	75	11.06	0.14	77
213	2.5	85	11.06	0.13	88
240	2.5	96	11.06	0.11	100

The variation of residual phosphorus concentration is plotted against the weight of pellets added in Figure 7.67. The initial phosphorus concentration (11mg/l) is also plotted as a line.

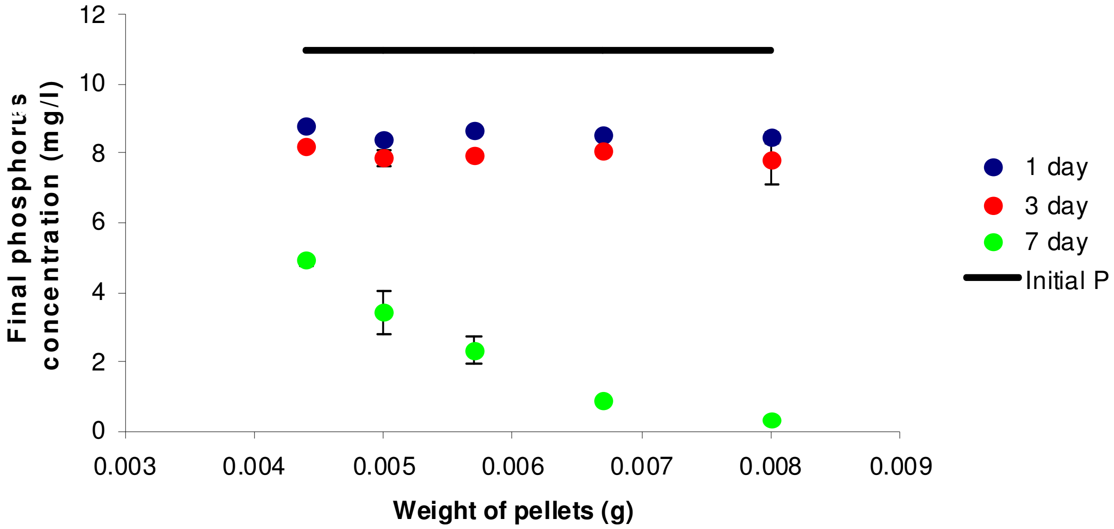


Figure 7.67 Residual phosphorous concentration as affected by weight of pellets added.

The results for the tests lasting 1 and 3 days are performing closely with little phosphorus removal and the results for the 7 day test show phosphorus removed to a considerably lower concentration. This contrasts to the results from Sections 7.3.2 and 7.3.3 where removal was more consistent over the 7 days. The results for the 7 day test follow the expected pattern where an increase in pellet weight has resulted in a lower residual phosphorus concentration. The tests lasting 1 and 3 days surprisingly show no correlation between pellet weight and phosphorus removal, the reasons for this will be explored once all the data for the phosphorus, pH and calcium concentrations have been presented. The reduction of the phosphorus concentration is plotted against time in days in Figure 7.68 to clarify the time dependency of these tests.

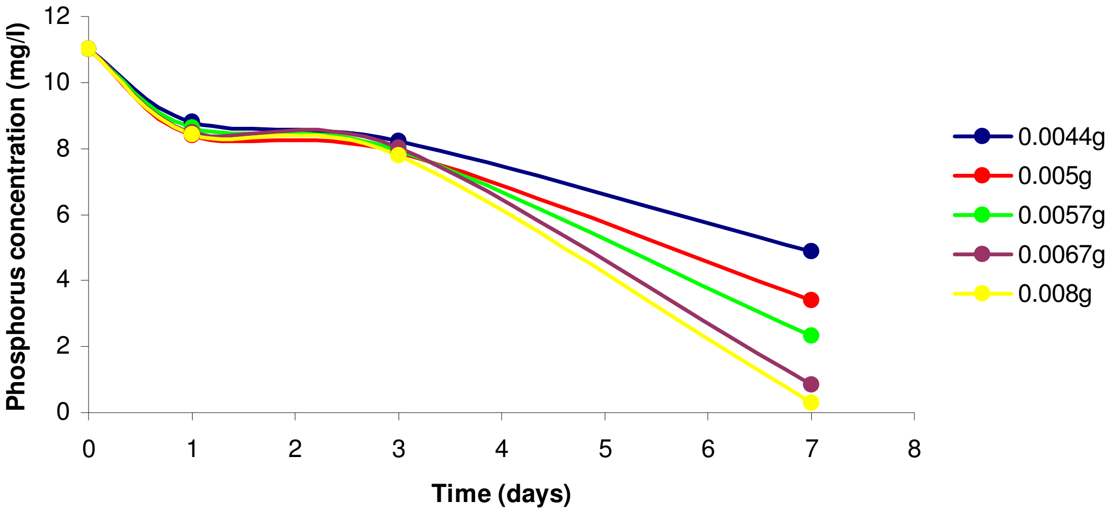


Figure 7.68 Reduction of phosphorus as affected by test length

The reduced rate of removal between days 1 and 3 can again be clearly seen. All test weights are essentially performing to the same level until after day 3 where the difference in weight has an effect and removal begins to be correlated with pellet weight. The rate of change of phosphorus is quantified through analysis of the gradients in Table 7.11 where the relationship between the length of test and the rate of removal is shown.

Table 7.11 Gradient analysis for the data in Figure 7.68

Pellet weight (g)	Gradient day 0-1 (mg/l/day)	Gradient day 1-3 (mg/l/day)	Gradient day 3-7 (mg/l/day)
0.008	2.57	0.32	1.87
0.0067	2.51	0.23	1.79
0.0057	2.36	0.36	1.40
0.005	2.60	0.26	1.12
0.0044	2.21	0.29	0.83
Average	2.45	0.29	1.40
Std Dev	0.17	0.05	0.44

For the periods 0-1 and 3-7 days there is a general trend that the higher the weight of pellet, the higher the rate of removal as would be expected. As with the results from previous sections the initial period of 0-1 days has the highest rate of removal. However there is a large discrepancy in the 1-3 day period in which very little removal occurs after which the gradients increase again. The results are now plotted as phosphorus removed (mg/g) against the residual phosphorus concentration (mg/l) in Figure 7.69.

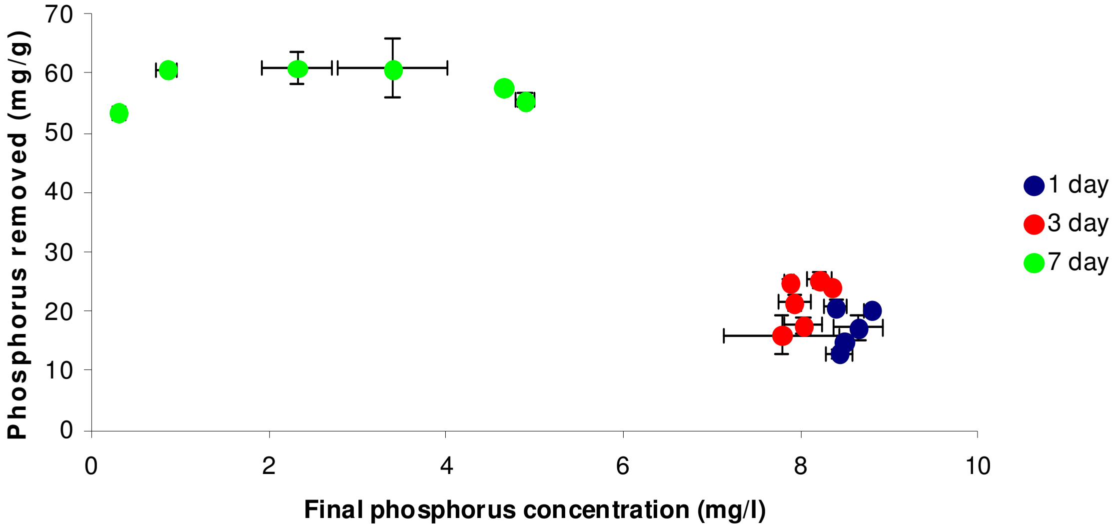


Figure 7.69 Phosphorus loading results for tests with an initial concentration of 11.06mg/l

As expected from the data shown in Figure 7.67, there is a large disparity between the results for 7 days and those for 1 and 3 days. The 7 day test is achieving loadings of between 53.5-60.9mg/g, comparable to the values from Section 7.6 where the pellets removed 52mg/g at similar final concentrations. The 3 day test shows removals of between 16.0 and 25.4 mg/g (45.7-59.8mg/g from Section 7.3.3) and the 1 day test 12.9 to 20.0mg/g (34.2-44.6mg/g from Section 7.3.3). The reasons behind the behaviour of the 1 and 3 days tests will be fully explored once the calcium concentrations and pH values have been analysed. These results are plotted alongside those from Sections 7.1.3 and 7.3.3 to allow an easy comparison.

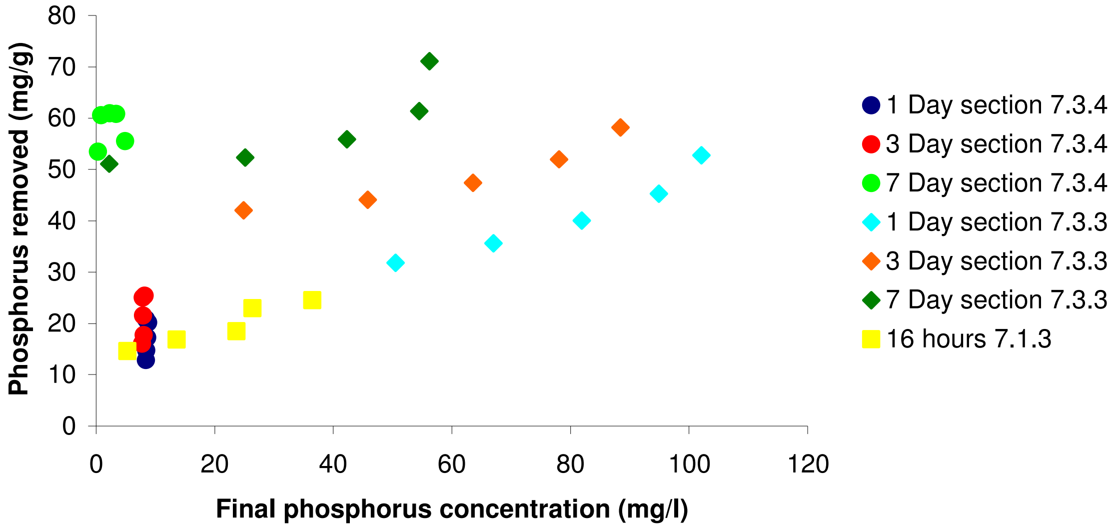


Figure 7.70 Comparison of major pellet data from; this Section (7.3.4), Section 7.3.3 and Section 7.1.3.

Figure 7.70 shows that the data for the 1 day tests for this section fit in with the 1 day results from Section 7.3.3 and the 16 hour tests from Section 7.1.3. As expected from the discussion above the results for the tests lasting 3 days are not performing in the same fashion as the 3 day results from Section 7.3.3. The 7 day results however are close to the tests from Section 7.3.3. The pH was monitored for these tests, the data for this is initially presented in Figure 7.71 as the final pH as affected by the weight of pellets. As the initial concentration was a constant 11.06mg/l, the initial pH was a constant 5.08.

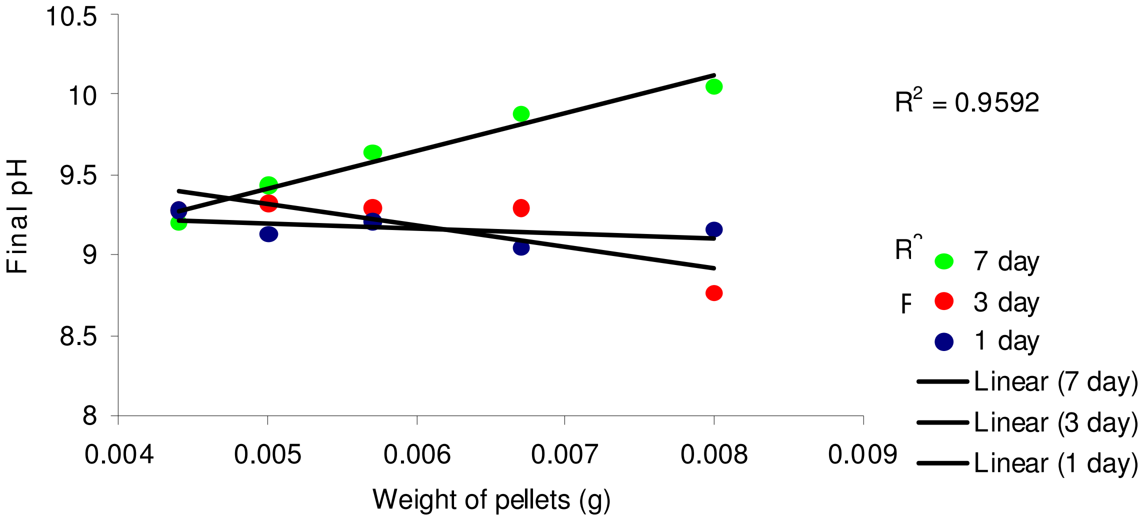


Figure 7.71 Final pH as affected by the weight of pellets used

Figure 7.71 shows that in terms of pH there is again a clear difference between the results for tests lasting 1 and 3 days and those lasting 7 days. For tests lasting 1 and 3 days the relationship between final pH and pellet weight are essentially flat with a very slight negative correlation, an increase in weight of pellets used resulting in a slight decrease in pH (0.27 and 0.64 R^2 respective values). This contrasts with the results for the 7 day test where there is a strong positive correlation (0.96 R^2 value) where an increase in weight of pellets results in a higher final pH. This is the same pattern to phosphorus removal shown in Figure 7.68. The fact that the final pH follows a similar pattern as removal suggests that this could be reflecting a governing factor for removal. The final pH for the test lasting 1 day is in the range 9.0 to 9.3, this compares to the range of between 7.9 and 10.2 for the 1 day results from Section 7.3.3 For the 3 day test these results show a range of 8.8 to 9.3 compared to 9.2 to 10.8 for the results from Section 7.3.3. The 7 day results show 9.3-10.0 compared to 9.5 to 11 for the results from Section 7.3.3. Johansson and Gustafsson (2000) state that pHs above 9 are required for efficient calcium phosphate precipitation, all but one final pHs are above this. The phosphorus loadings achieved are plotted against the final pH on Figure 7.72

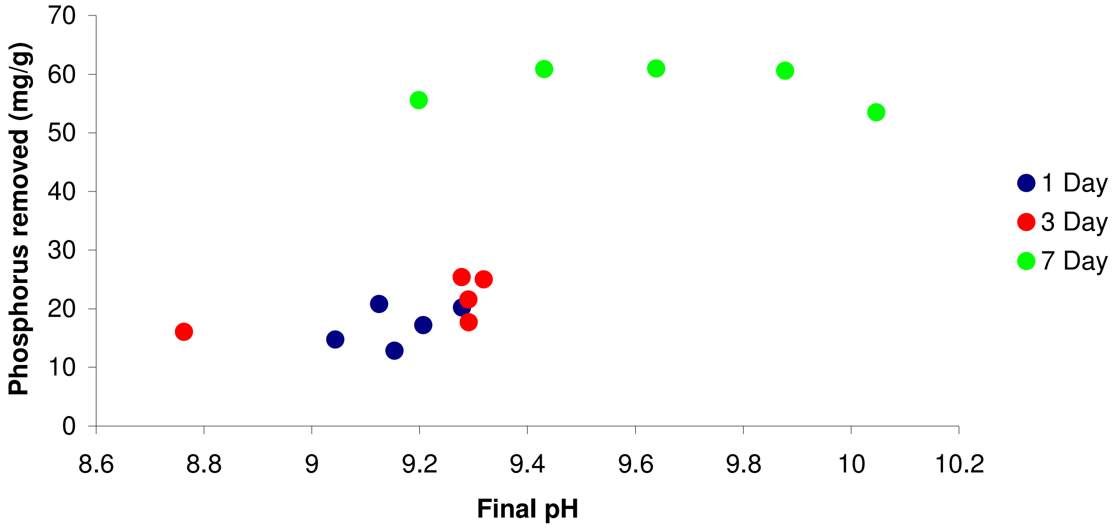


Figure 7.72 Relationship between final pH and phosphorus removed (mg/g)

The differences in final pH and phosphorus loading for the 7 day test are clear. There is one data point for the 7 day results that has the same final pH as those from 1 and 3 days aside from this both the range of pHs and the phosphorus loadings are higher. Previous tests have shown for each test length, higher phosphorus removal was tied in with lower final pHs, this is not the case here with the 7 day results showing a flat relationship. The 1 and 3 day results appear to be showing slight variation across effectively one data point with little variation in either final pH or phosphorus loading. The 7 day results fit in with the findings of Johansson and Gustafsson (2000) who found that pHs over 9 were required for efficient calcium phosphate precipitation. This cannot be the only factor here however due to the overlap of pH with the 1 and 3 days tests which found much lower phosphorus loadings. The reason that these tests are not following the same pattern between pH and phosphorus removal as the previous tests and the findings by Johansson and Gustafsson (2000) is likely due the variation in the pellet weights used for this test. In the previous tests carried out in support of this thesis the weight of pellets used was kept constant and the phosphorus concentration was varied, for the tests presented in this section it is the pellet weight that is varied. The supply of hydroxide ions from the pellets is therefore not constant across the tests but varied with pellet weight.

The maximum percentage contribution by adsorption to removal is plotted against the phosphorus loading in Figure 7.73. The contribution by adsorption is calculated from the loading provided by the Freundlich isotherm for the solids from Horden at the relevant equilibrium concentration.

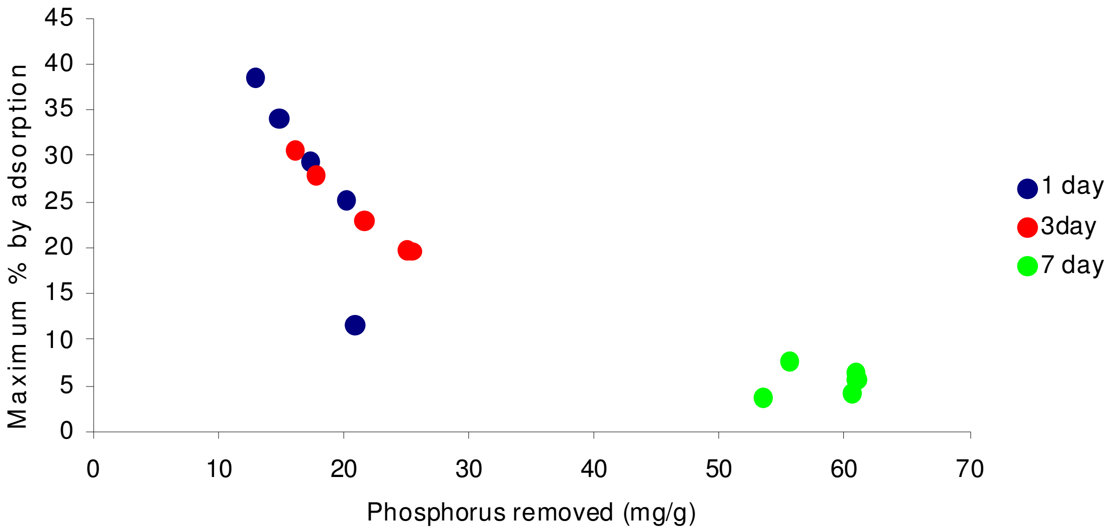


Figure 7.73 Maximum percentage contribution of adsorption to total removal by pellets

Figure 7.73 shows that for the 7 day results adsorption can be accounting for a maximum of around 5% of removal, this ties in with the percentage found from Section 7.3.3 where adsorption was found to potentially contribute as little as 6%. The reduction in surface area due to pelletisation and the high final pHs likely above the point of zero charge mean that this minimal contribution by adsorption, is itself likely to be an overestimation.

7.3.4.2 Calcium analysis

The supernatant solution from these tests was analysed for calcium as well at phosphorus. As with Section 7.3.3.2 pellets were shaken in deionised water so as to determine the calcium released by the pellets. This was carried out for three pellet weights 0.0044, 0.0057 and 0.008g and interpolation was used for the intermediate weights. These results are shown in Figure 7.74

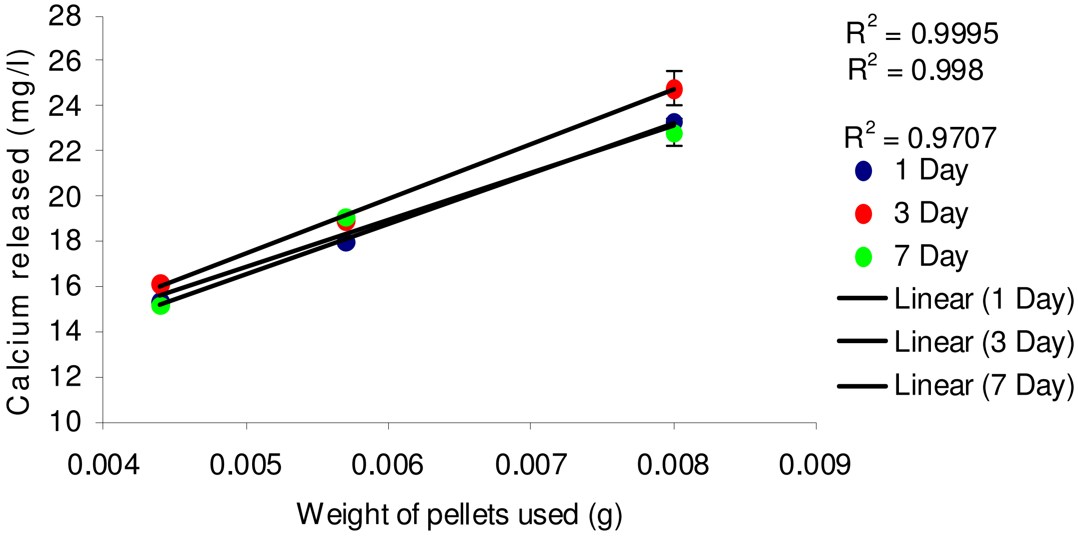


Figure 7.74 Release of calcium as affected by weight of pellets for tests lasting 1,3 and 7 days

The calcium released ranges from 15.13mg/l to 24.765mg/l. As expected for all three test lengths there is a strong correlation between the calcium concentration and the weight of pellets used and therefore interpolation to determine the calcium released from intermediate pellet weights can be carried out with confidence. Figure 7.74 shows that effectively all of the calcium that will be released is released after 1 day as the results for all tests lengths are near identical, this ties in with the results from Section 7.3.3 where there was little increase in calcium released across the three test lengths. If all three data sets shown in Figure 7.74 is combined into one data series and fitted with a line of best fit, the line of best fit has the equation y=2240x+5.7589 with a R^2 value of 0.9668, this equation was used to determine the calcium released by intermediate weights of pellets.

If these results are converted to milligrams of calcium released per gram of pellet, these tests are releasing in the order of 114-146mg/g this contrasts to the 46-49mg/g for the pellets from Section 7.3.3. As discussed in Section 7.3.3, the theoretical solubility of $Ca(OH)_2$ results in a calcium concentration of 959mg/l, the rise in mg/g of calcium released is therefore not explained by concentrations approaching saturation yet there is a significant difference in the calcium released. Assuming that the Portland cement contained 2/3rds CaO and knowing that the pellets contained 30% cement the expected calcium content would be 14.3% or 143mg/g thus showing that for these tests the majority of the calcium in these pellets appears to be leaching out and available in solution. Figure 7.74 does not offer a direct explanation as to the stalling of removal between 1 and 3 days as it is clear that all calcium has been released by this point.

The pH of the tests charting calcium released was also monitored, this is shown in Table 7.12 and compared to the final pHs for tests containing phosphorus.

Table 7.12 Comparison of pHs for calcium release tests and those containing phosphorus.

Test length (days)	Background pH range (from tests with just deionised water)	Final pH range (from the actual tests containing phosphorus)
1	10.5-10.5	9.0-9.3
3	10.5-10.7	8.8-9.2
7	10.5-10.6	9.2-10.0

Table 7.12 shows that for all tests the introduction of phosphorus has reduced the final pH. This fits in with the results found by Lu *et al.* (2009) and Johansson and Gustafsson (2000) who both saw this pattern as contributory evidence of calcium phosphate precipitation. The equation of HAP precipitation shown in Section 7.2.2 shows the consumption of hydroxide ions and the results shown in Table 7.12 are reflecting this. The phosphorus loadings are plotted against the residual calcium concentrations in Figure 7.75.

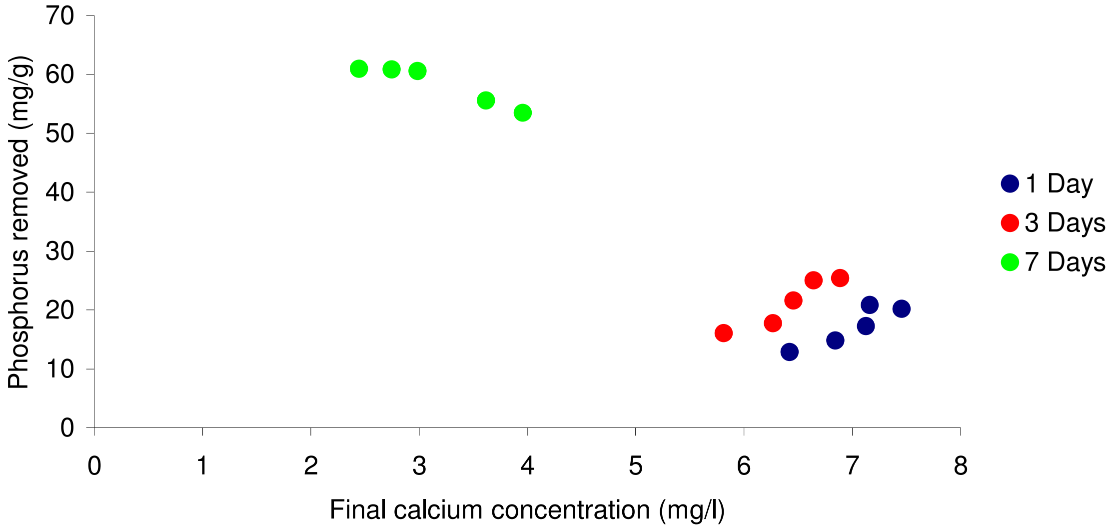


Figure 7.75 Variation of phosphorus removed with residual calcium concentration for tests with an initial phosphorus concentration of 11mg/l

Figure 7.75 shows the variation of phosphorus removed with the residual calcium concentrations. As with phosphorus removal and pH the results for the 7 day test are clearly different to those for the 1 and 3 day tests. The 7 day results have much higher phosphorus loadings (53.5-60.9mg/g) and lower final calcium concentrations (2.4-4.0mg/l). The 1 and 3 day results are again similar. The 3 day phosphorus loadings range from 16.1-25.4mg/g and the final calcium concentrations 5.8-6.9mg/l. the 1 day loadings ranged from 12.9-20.2mg/g and the calcium concentrations 6.4-7.5mg/l.

The change in phosphorus concentration is plotted against the change in calcium concentration in Figure 7.76. The change in calcium concentration is obtained by subtracting the residual concentration from Figure 7.75 from the values in Figure 7.74. The values are presented as the absolute change in moles

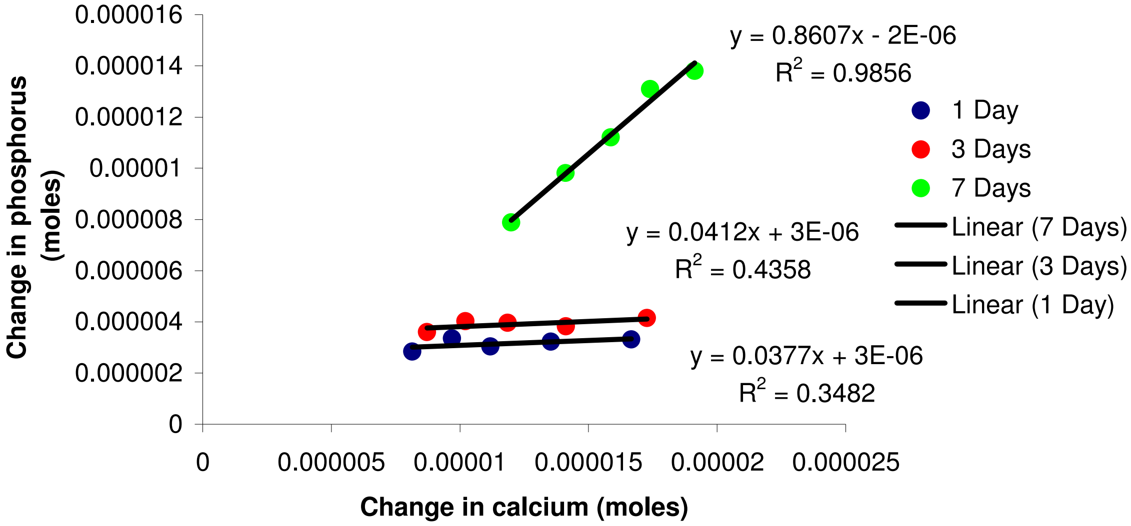


Figure 7.76 Change in phosphorus versus change in calcium in moles

Figure 7.76 shows that for the 7 day results there is a clear and strong correlation between changes in moles of both calcium and phosphorus with an R^2 value of 0.9856. The inverse of the gradient from the line of best fit gives an average Ca:P ratio of 1.16. This value is closer to the expected HAP ratio of 1.67 than the 0.29 from Section 7.3.3, yet is still too low. The increase in molar ratio is due to the higher proportion of calcium released as shown in Figure 7.59.

There is clearly a relationship between calcium and phosphorus concentrations here. The stalling of phosphorus removal between the 1 and 3 day tests ties in with a minimal change in calcium concentration between these test lengths. The seven day results do have a generally higher pH than the shorter tests and this is known to assist with calcium phosphate precipitation. At lower supersaturation levels nucleation of crystals/precipitates takes longer and the poorer removals found early on could be reflecting an increased period of induction for the tests presented in this section (Khomskii 1969). This effect was studied using the PHREEQCI software to calculate saturation indices (SIs) for both this section and Section 7.3.3. Saturation indices are calculated from the equation

$$SI = LOG\left(\frac{IAP}{Ksp}\right) \qquad \text{Equation 7.9}$$

Where SI = the saturation index, IAP is the Ion activity product and Ksp is the solubility constant. The ion activity product is the product of activity of the ions present and the solubility constant is a measure of how soluble a substance is. When the ratio of the IAP to the Ksp is 1 and therefore the SI is 0 the solution is saturated and no precipitation is predicted. A SI of above 0 represents a supersaturated solution where precipitation is predicted. A SI of below 0 represents an under saturated solution where precipitation will not occur. A higher SI represents higher supersaturation and a higher likelihood that precipitation will occur. The assumed initial conditions from this section and those from Section 7.3.3 were inputted (see Table 7.13) and the effect of these on the saturation index of HAP determined, these results are shown in Figure 7.77. The prediction of HAP as a precipitate by PHREEQCI reinforces the conclusions made in Section 7.3.3.

Table 7.13 input conditions for PHREEQCI

Section	Section 7.3.3	Section 7.3.4
Initial P concentration (mg/l)	133-240	11
Initial Ca concentration (mg/l)	117	15.6-23.7
Initial pH	11.2	10.6

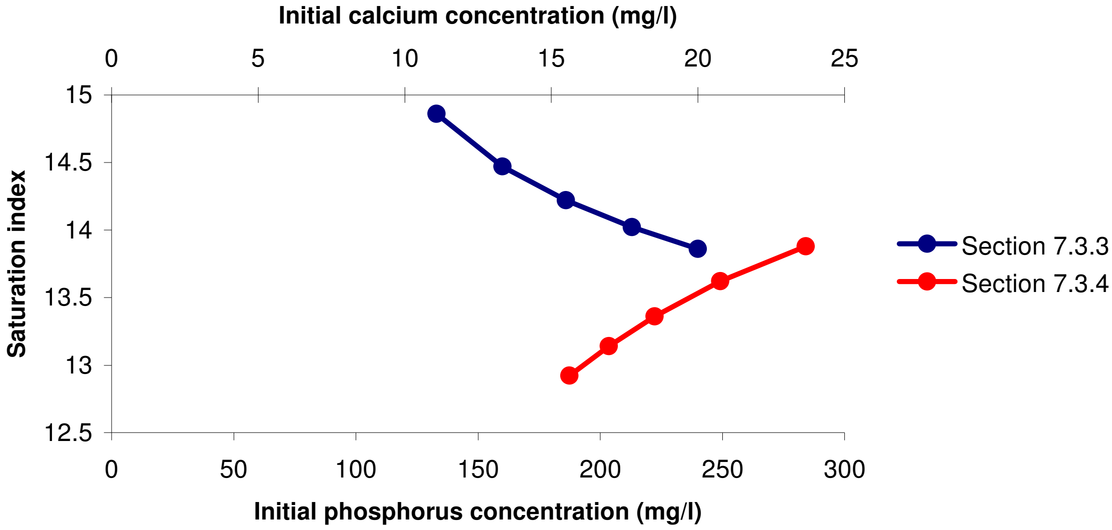


Figure 7.77 Saturation indices for initial conditions for Sections 7.3.3 and 7.3.4

The test reported in the current section generally has lower SIs than the test from Section 7.3.3 but that here is an overlap and so perhaps the degree of supersaturation does not explain the difference in the kinetics of removal. PHREEQCI is further used in Section 8.5 to investigate a range of initial conditions.

This section has shown that for the lower phosphorus and pellet concentrations studied the same high phosphorus loading after 7 days found in Section 7.3 can be achieved. The 7 day results show correlation between removal and pellet weight whereas the 1 and 3 day tests do not this is perhaps due to the lower levels of supersaturation resulting in slower rates of nucleation for these tests.

7.4 Pellets without Horden solids

This section presents the results of tests carried out on pellets completely absent of the solids from Horden. Tests were carried out where the dry Horden solids were directly replaced by crushed sand. This was to investigate the contribution the solids from Horden make towards the total removal. Tests were also performed on a sample of concrete waste to investigate the potential of this material for phosphorus removal as cement appears to be the main active ingredient in cementitious pellets.

7.4.1 Horden solids replaced by crushed sand

Sections 7.3.3 and 7.3.4 have shown the dominance of calcium phosphate precipitation towards removal. Tests were performed on pellets where the Horden solids were replaced by crushed sand to further investigate this dominance, the crushed sand assumed essentially inert in term of phosphorus removal. Arias *et al.* (2001) found quartz sand to remove a maximum of 0.27mg/g up to equilibrium concentrations in excess of 300mg/l. The batch tests carried out on the pellets produced with crushed sand in the current section mirrored those carried out in Section 7.3.3, 63-125µm pellets were produced, the test volume was 40ml and 0.1g of pellets was used (2.5g/l solids concentration), initial concentrations ranged from 130-240mg/l. The full details of the pellet production can be found in Section 5. The filtered solutions were analysed for both phosphorous and calcium.

7.4.1.1 Phosphorus removal

The final phosphorus concentrations are plotted against the initial concentrations in Figure 7.78.

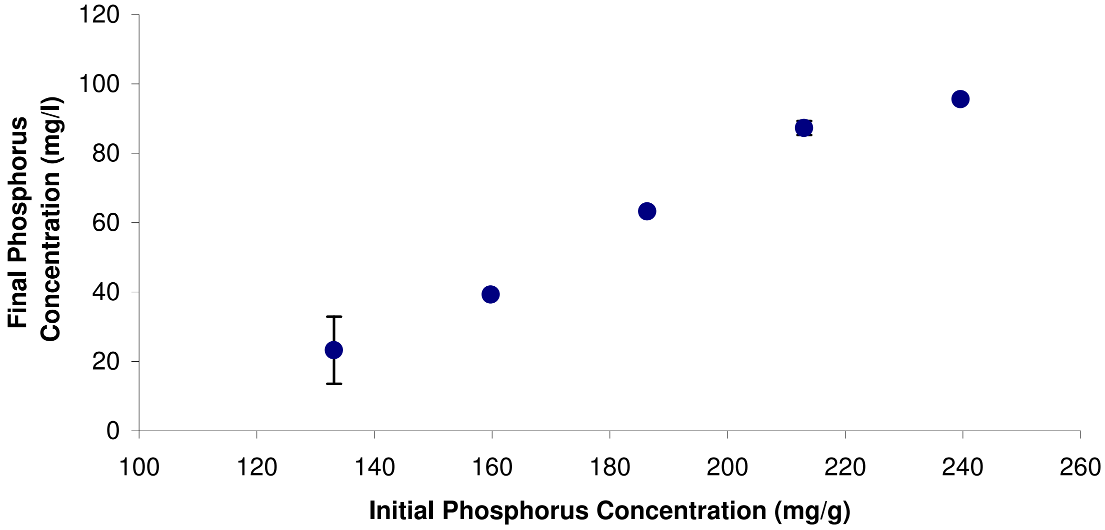


Figure 7.78 Results for the phosphorus removal tests carried out on pellets produced from crushed sand and cement.

For the range of initial concentrations of 130-240mg/l the final phosphorus concentrations range from 23.2 to 95.5mg/l. This compares to 2-66mg/l for the 7 day results from Section 7.3.3 which had identical initial concentrations. Therefore these pellets are not performing as well as those from Section 7.3.3 made with the solids from Horden though they are, however, still removing phosphorus well. The phosphorus loadings achieved by these pellets are plotted against the final concentrations in Figure 7.79.

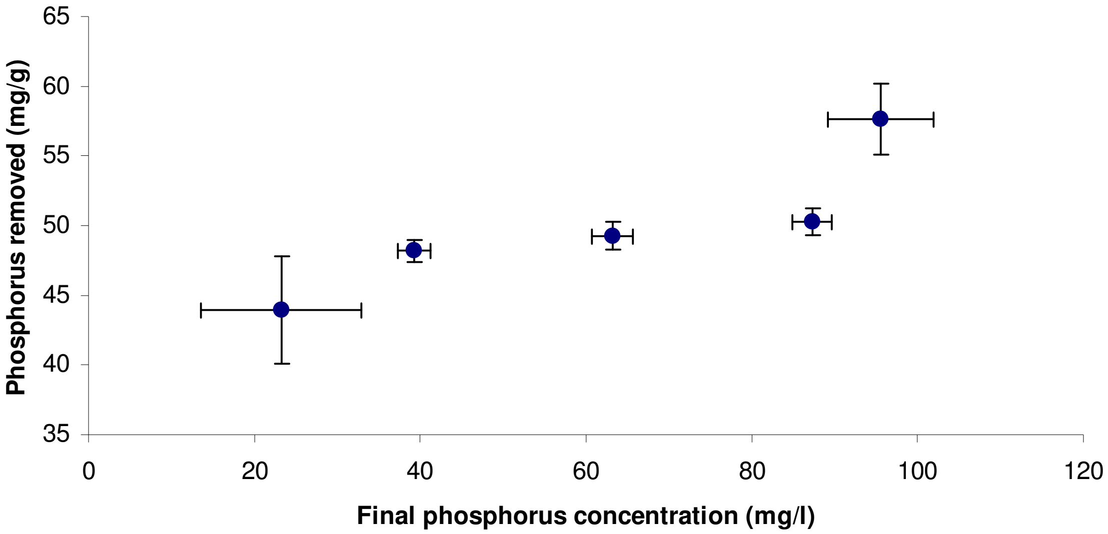


Figure 7.79 Phosphorus removed by 63-125μm pellets made from crushed sand, cement and water.

Figure 7.79 shows that these pellets are removing 44-58mg/g over the final concentration range of 23-96mg/l. This compares to 51-71mg/g over the final concentration range of 2-66mg/l for the pellets from Section 7.3.3. The difference in performance is not large and shows that when the solids from Horden are removed from the pellet mix, these pellets are still performing well. This is therefore another piece of evidence supporting the importance of calcium phosphate precipitation and the redundant nature of the Horden solids. The phosphorus loadings for these pellets are directly compared to those for the pellets from Section 7.3.3 in Figure 7.80.

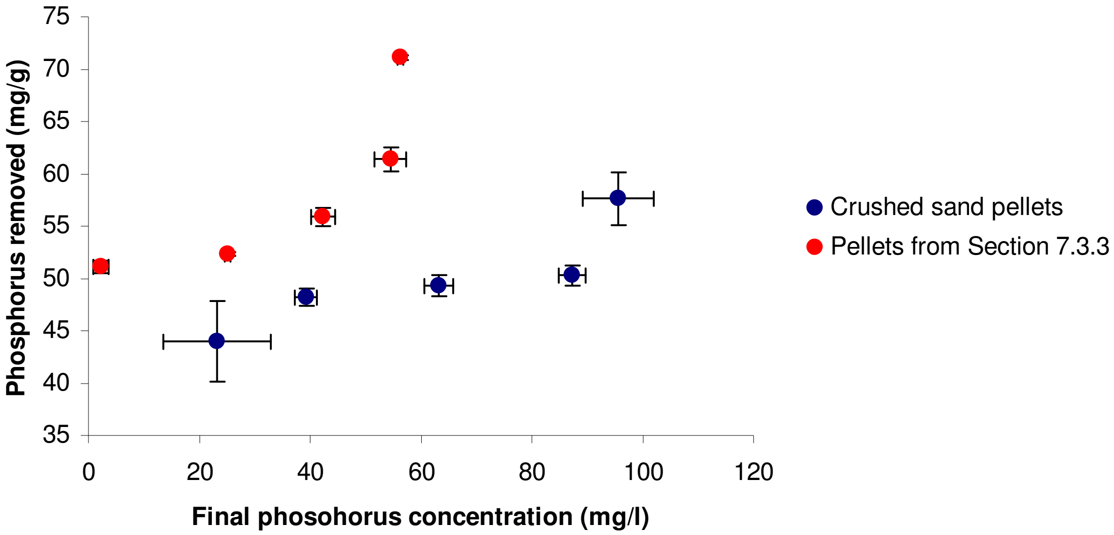


Figure 7.80 Comparison of phosphorus loading for the pellets made from the solids from Horden and those made from crushed sand.

Figure 7.80 suggests that the cement fraction of the pellets must be responsible for the vast majority of removal. The reasons behind the slightly poorer performance of these crushed sand pellets is explored below through calcium and pH analysis. The initial phosphorus concentrations used are the same as those used in Section 7.3.2 and so the relationship between initial concentration and initial pH is the same as shown in Figure 7.44, Figure 7.81 shows the relationship between final pH and initial

pH.

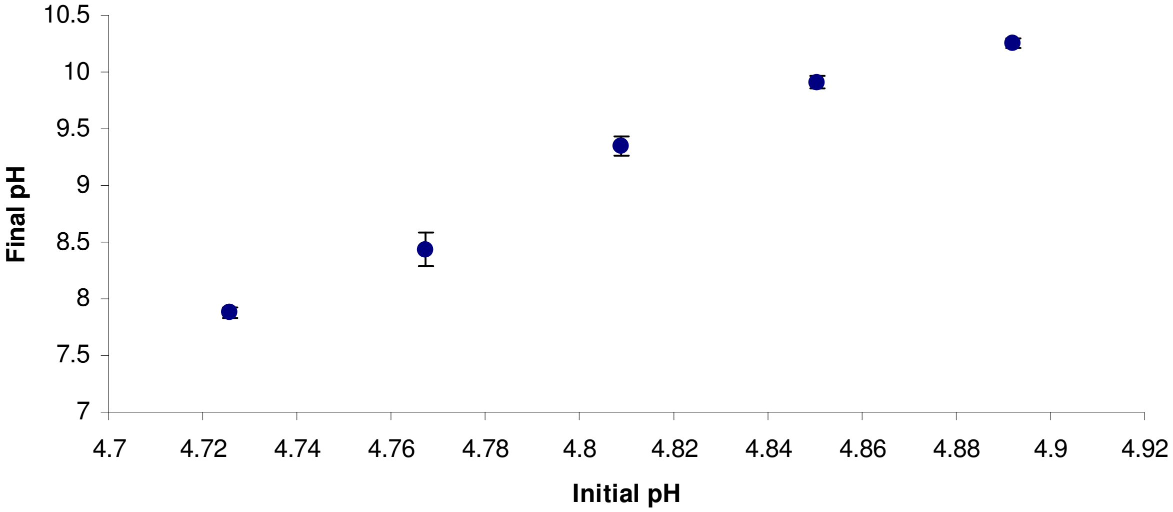


Figure 7.81 Variation of final ph with initial pH

Figure 7.81 shows that the final pHs range from 7.88 to 10.26, this compares to the 7 day results from Section 7.3.3 where final pHs ranged from 9.49 to 11.0. The pH values for the pellets studied in this section are significantly lower than those from Section 7.3.3 and this could offer a partial explanation towards the slightly poorer performance of these pellets. The phosphorus loadings achieved by these pellets are plotted against the final pH in Figure 7.82, the results from Section 7.3.3 are included as a comparison.

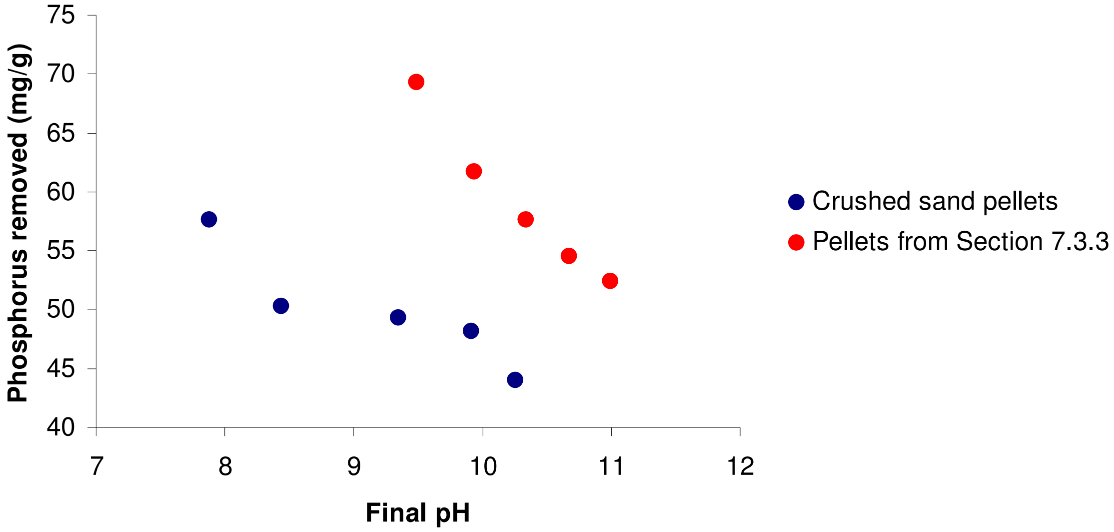


Figure 7.82 Comparison of pH and removal for pellets made from crushed sand and those from Section 7.3.3

The final pH values for the test reported in the current section are in the range of 7.9-10.3. There is an inverse relationship between the final pH and the phosphorus removed, this is the general pattern that all pellet results have taken and is indicative of calcium phosphate precipitation due to the consumption of hydroxide ions in the formation of HAP. The results for the current section have both a lower range of removal (44.0 to 57.6 compared to 52.4 to 69.3mg/g) and final pH (7.9 to 10.3 compared to 9.5 to 11.0) compared to the results from Section 7.3.3.

7.4.1.2 Calcium analysis

As with the tests from Sections 7.3.3 and 7.3.4 these tests were analysed for calcium as well as phosphorus. 0.1g of the pellets was shaken in 40ml of deionised water to determine the release of calcium. This found an average of 89mg/l released for the three tests with a standard deviation of 6mg/l. This compares to 124mg/l for the 7 day tests from Section 7.3.3. Therefore the lower phosphorus removal found for these crushed sand pellets compared to those from Section 7.3.3 can be linked to the pellets studied in this section releasing less calcium as well as the lower range of final pHs they produced, both these factors being instrumental in calcium phosphate precipitation. The pellets studied in the current section could be releasing less calcium as the result of the extra silica from the sand forming calcium silicates which then fix the calcium within the cement.

The pH of these calcium released tests was again monitored, this showed an average value of 11.4, this compares to the range of 7.9-10.3 for the tests containing phosphorus. As with the previous sections, the tests containing phosphorus are showing the concurrent consumption of phosphorus, calcium and pH. This is again following the pattern mentioned by Lu *et al.* (2009) and Johansson and Gustafsson (2000) who both suggest this shows that calcium phosphate precipitation is occurring. An average pH of 11.4 matches the value found for the 7 day calcium release test from Section 7.3.3. The phosphorus removed (mg/g) is plotted against the residual calcium concentration in Figure 7.83.

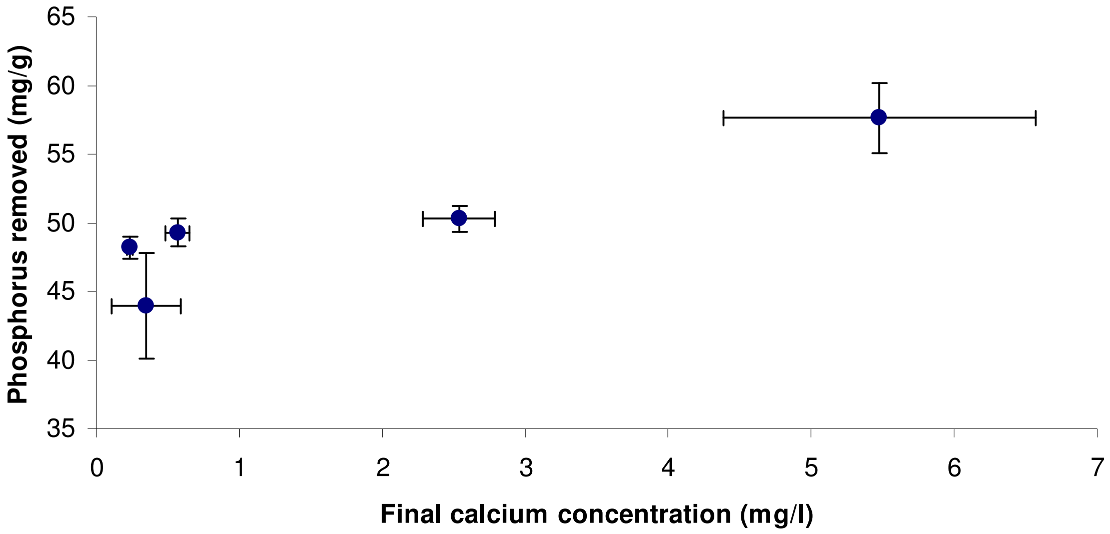


Figure 7.83 Phosphorus removed (mg/g) variation with final calcium concentration (mg/l)

The final calcium concentrations range from 0.2mg/l to 5.5mg/l and there is a slight positive correlation between phosphorus removed and final calcium concentration. This is unexpected for the calcium phosphate precipitation theory where higher phosphorus removal should relate to higher calcium removal. The range of residual calcium concentrations is however very small compared to the calcium found to be released (89mg/l) and this could effectively be viewed as variation across one data point. Figure 7.84 plots the change in phosphorus against the change in calcium, both are expressed as total moles.

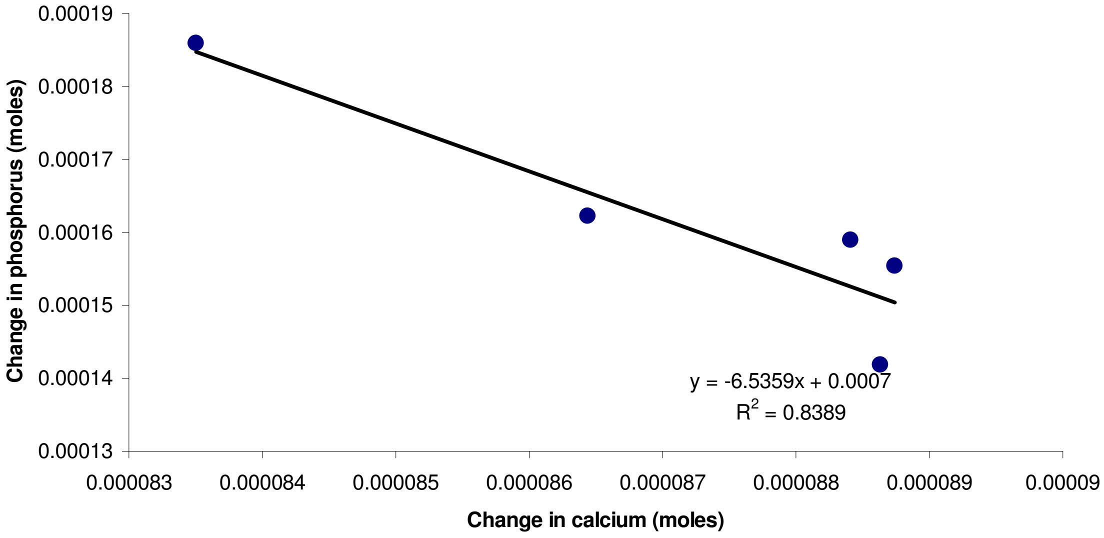


Figure 7.84 Variation of change in phosphorus with change in calcium

There is a negative correlation between changes in the two elements in Figure 7.84, however the data for both the y and x axis are for relatively small ranges. A range of 0.00002 moles for change in phosphorus (13% of average value) and 0.000005 moles for the change in calcium (6% of average value). Figure 7.84 could therefore be showing slight variation for what is effectively one data point as the phosphorus removed and residual calcium levels for all tests are very similar. These results are compared to those from Section 7.3.3 and 7.3.4 in Figure 7.85.

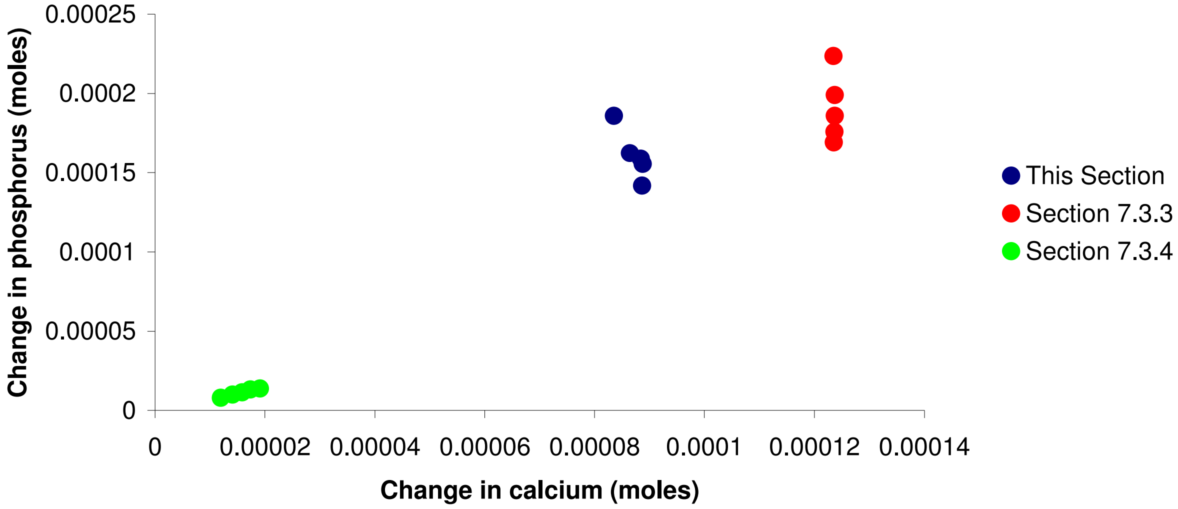


Figure 7.85 comparison of change in calcium and phosphorus in moles for 3 Sections; the pellets from this Section, Section 7.3.3 and Section 7.3.4.

Between the three experiments reported here there appears to be a consistent correlation between the change in calcium and the change in phosphorus. Therefore these results are plotted as one data stream and fitted with a linear line of best fit in Figure 7.86.

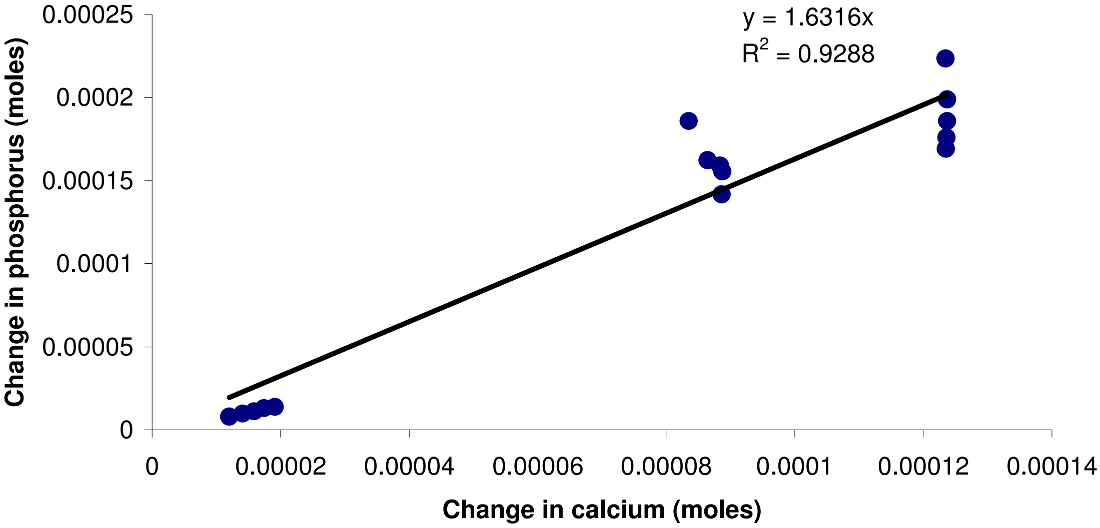


Figure 7.86 Comparison of change in calcium and phosphorus in moles for this Section, Section 7.3.3 and Section 7.3.4.

Figure 7.86 suggests that the results from the three tests can be directly compared. The line of best fit has a R^2 value of 0.93 showing good correlation. The line of best fit was forced through the intercept, thus assuming no phosphorus removal without a change in calcium concentration, Taking the inverse of the equation of the line of best gives an average Ca:P ratio of 0.61. This is not the stoichiometric ratio for HAP of 1.67 but the strong correlation shows a definite consistency in the relationship between reductions in calcium and phosphorus. The presence of HAP was confirmed by SEM-EDX in Section 7.3.3 and also predicted through the PHREEQCI analysis and by many papers in the literature review. The fact that the data from this section, where no solids from Horden were used, fits in with the data from the other two tests suggests again that the cement is by far the most important constituent of these pellets and the solids from Horden play little or no part in the removal of phosphorus.

This section has shown that replacing the solids from Horden in the pellets has little effect on the phosphorus removal capacity of the pellets. The dip in performance can be explained by the lower pH values and calcium concentrations that the pellets made from crushed sand released. A consistency in the relationship between calcium and phosphorus across several experiments has been shown.

7.4.2 Concrete pellets

A sample of concrete was obtained from the concrete laboratory at Cardiff University's School of Engineering. This was a cured piece of concrete that had been used in an unconfined compression test. The concrete was crushed to produce 63-125μm pellets. Tests lasting 7 days were carried out with 0.1g of pellets and a test volume of 40ml (2.5g/l solids concentration). Tests were performed in triplicate and with initial concentrations of 130-234mg/l, therefore being directly comparable to the results in Section 7.3.3 and 7.4.1.

7.4.2.1 Phosphorus removal

Figure 7.87 plots the final phosphorus concentrations against their initial concentrations.

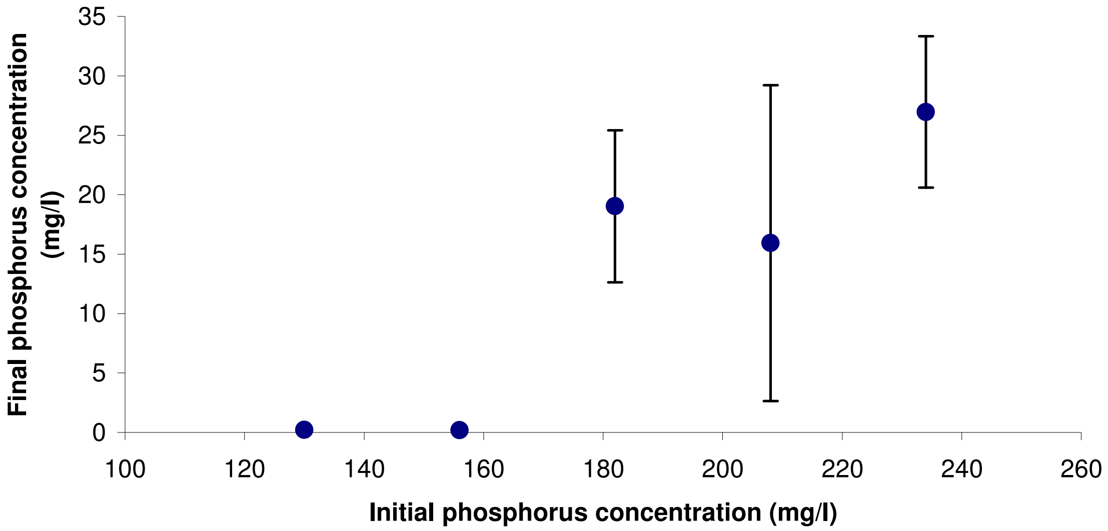


Figure 7.87 Phosphorus removal by 63-125μm concrete waste pellets.

The two lowest initial concentrations (130 and 156 mg/l) were both reduced to 0.2mg/l. The three higher data points can be seen to have large standard deviations. In the case of the tests with 182 and 208mg/l initial concentrations this is due to a single outlier. This variance is particularly apparent for the test with an initial concentration of 208mg/l where final concentrations of 25.7, 20.5 and 1.7mg/l were found. Such variability is surprising as through the crushing and sizing of the pellets, the material would be expected to be completely mixed and therefore offer consistent results.

The final concentrations found for these tests range from 0.2 to 27.0mg/l. Tests reported on in Section 7.3.3 with the same initial concentrations on pellets produced from the addition of cement to the sludge from Horden found final concentrations of 2.1 to 66.4mg/l. The pellets tested in this section are therefore performing to a higher standard than those containing Horden solids. The phosphorus loadings achieved by the concrete pellets are plotted against the final concentrations in Figure 7.88.

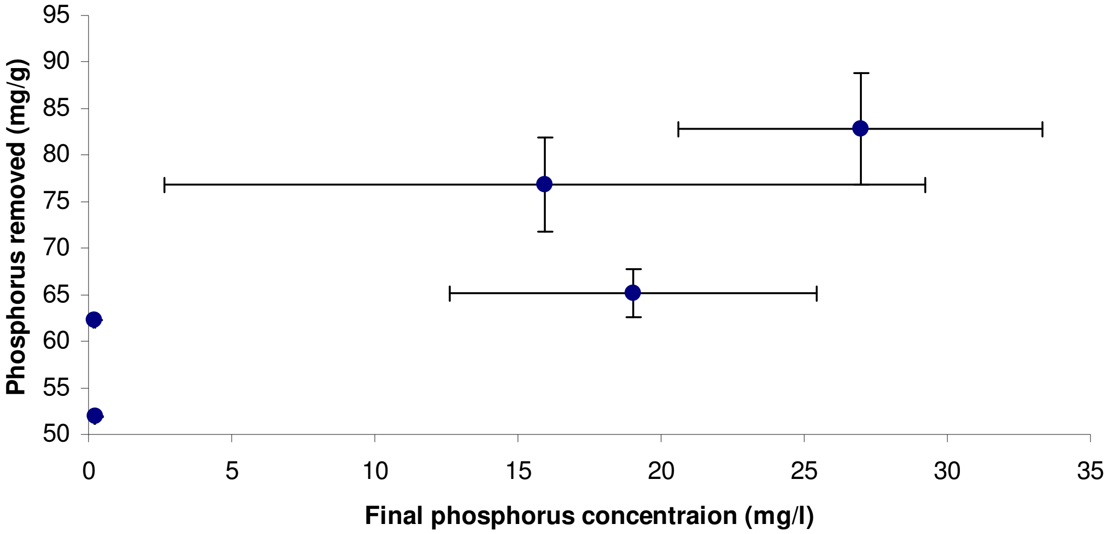


Figure 7.88 Phosphorus loading results for 63-125µm concrete pellets

Figure 7.88 shows that these pellets were found capable of removing between 51.9mg/g and 82.8mg/g with the final concentrations ranging from 0.2 to 82.8mg/l. This compares to the loading range of 52.4mg/g to 69.3mg/g for the 7 day test on pellets in Section 7.3.3. The comparison between these concrete pellets studied in this section and those containing Horden solids from Section 7.3.3 is shown in Figure 7.89.

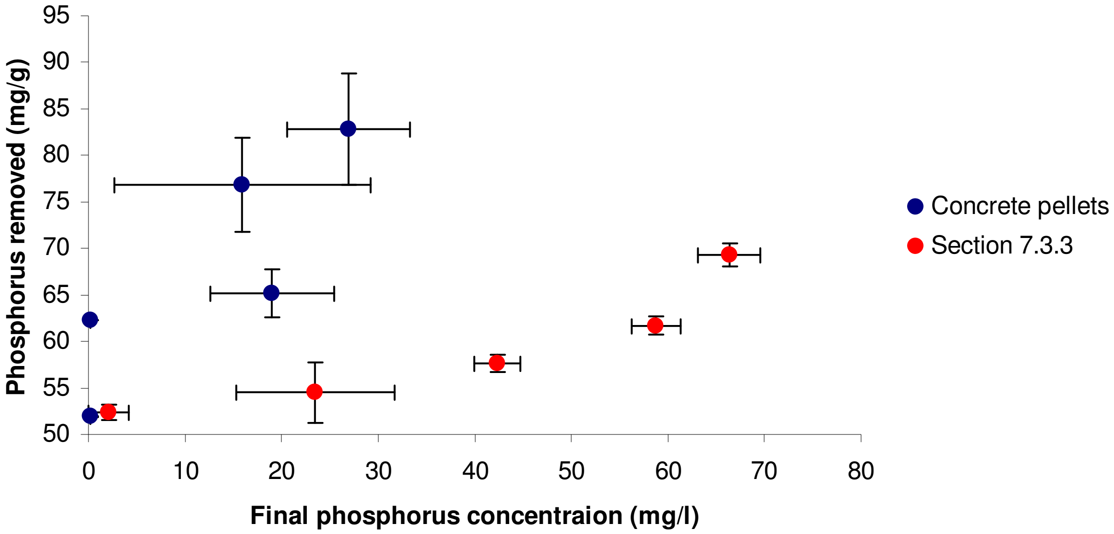


Figure 7.89 Phosphorus loading results for 63-125µm concrete pellets and the 63-125µm pellets from Section 7.3.

The concrete pellets studied in this section are outperforming those produced from the addition of cement to the sludge from Horden studied by identical tests in Section 7.3.3. These results and those from Section 7.4.1 further highlight the redundant nature of the solids from Horden in removal by pellets composed of them. Figure 7.90 also suggests that phosphorus removal could be a potential use of construction/concrete waste. Again the same range of initial concentrations was used and therefore the relationship between these and the initial pH values is the same as shown in Figure 7.44. The final pHs of the filtered solutions are plotted against the initial concentrations in Figure 7.90

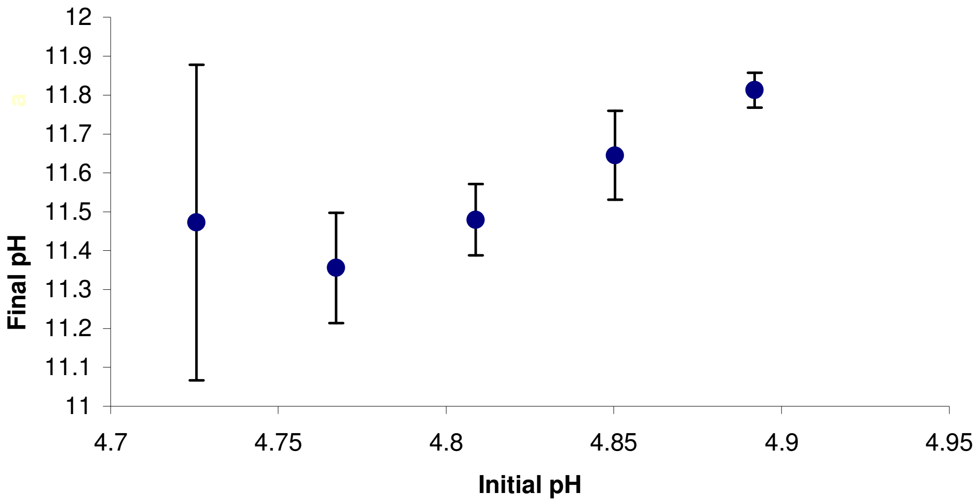


Figure 7.90 Variation of final pH with initial pH for concrete pellets

Figure 7.90 shows a general trend of higher final pHs with higher initial pHs, this is not true for the lowest initial pH which was found to have a large standard deviation. Final pHs ranged from 11.4 to 11.8, this compares to a range of 9.5 to 11.0 for the results from Section 7.3.3, these pellets are therefore reaching significantly higher pHs, this could be a contributing factor towards the superior removal found by these concrete pellets. Figure 7.92 plots the phosphorus removed (mg/g) against the final pH.

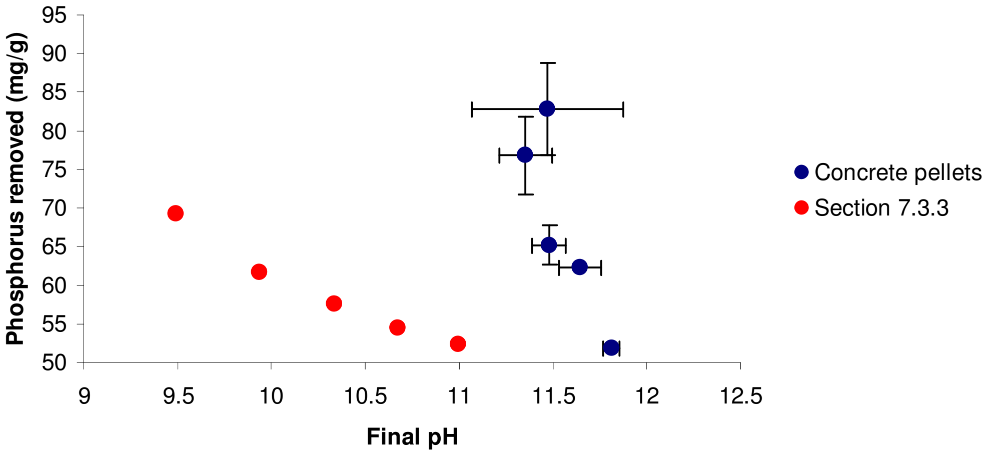


Figure 7.91 Variation of phosphorus loading with final pH for concrete pellets.

The higher phosphorus removals are correlated with the lower pH values for the concrete pellets studied in this section. This is the same pattern found in Sections 7.3.3 and 7.4.1 and this is also the pattern found by Lu *et al.* (2009) and Johansson and Gustafsson (2000) among others who found this to be indicative of calcium phosphate precipitation.

7.4.2.2 Calcium analysis

The filtered solutions were analysed for calcium as well as phosphorus. Figure 7.92 shows these results through the plotting of the phosphorus removed (mg/g) against the final calcium concentrations found. Tests on the pellets shaken for 7 days in just deionised water found a release of 123.8mg/l with a standard deviation of 19.3. This value of 123.8mg/l is equivalent to 49.5mg/g, the pellets studied in Section 7.3.3 released 124.1mg/l equivalent to 49.6mg/g, thus these pellets are releasing very similar amounts of calcium. The phosphorus loadings achieved are plotted against the final calcium concentration found in tests containing phosphorus in Figure 7.92.

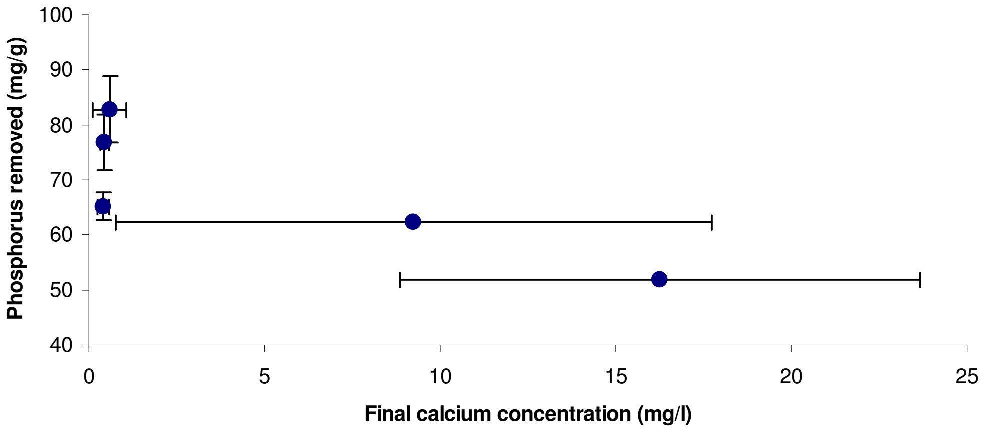


Figure 7.92 Variation of phosphorus loading with final calcium concentration

The three highest phosphorus loadings found occurred at very low calcium concentrations (0.4-0.6mg/l). These are particularly low in comparison to the 123.8mg/l that these pellets were found to release. The two tests with the lower phosphorus loadings found final calcium concentrations of 9.2mg/l and 16.3mg/l. These concentrations were found to have large standard deviations for the three tests. The change in phosphorus is plotted against the change in calcium in Figure 7.93. The change in phosphorus is the difference between the initial phosphorous and the final phosphorus present. The change in calcium is calculated by subtracting the final concentration from the 123.8mg/l found released by pellets. Both elements are expressed in terms of the total moles present

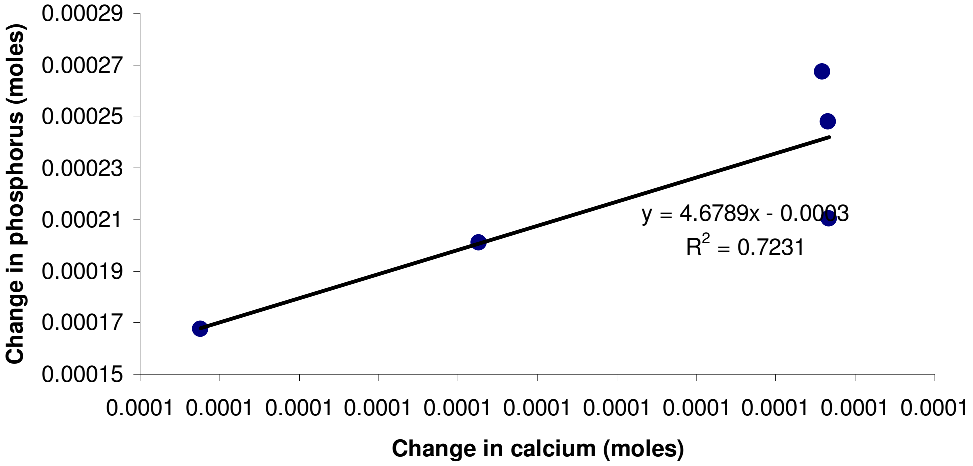


Figure 7.93 Variation of change in phosphorus with change in calcium for 63-125μm concrete pellets.

Figure 7.93 shows that there is a relationship between higher changes in calcium resulting in higher changes in phosphorus. This is indicative of calcium phosphate precipitation and is what would be expected of concrete as discussed by (Berg *et al.* 2005) and (Oguz *et al.* 2003) among others. The results from Figure 7.94 are plotted alongside those from Figure 7.87 from Section 7.4.1 in Figure 7.94. The intercept of the line of best fit is set to zero, thus assuming no change in phosphorus concentration unattributed to a change in calcium

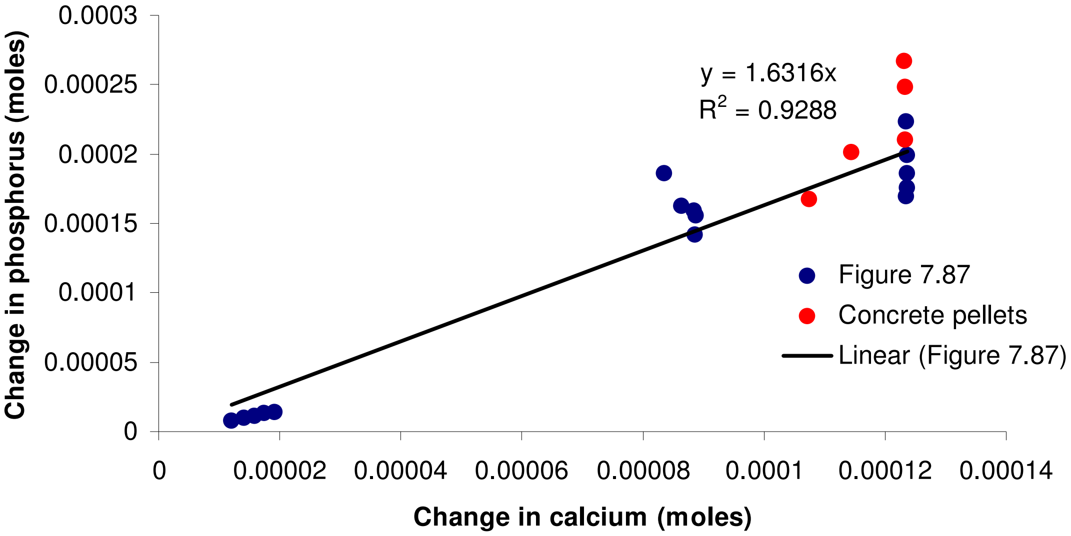


Figure 7.94 Combination of Figure 7.87 and Figure 7.93

Figure 7.94 shows that the results from this section follow the same pattern of those from Sections 7.3.3, 7.3.4 and 7.4.1. These sections include results for pellets containing solids from Horden and those where those solid were replaced by crushed sand. Figure 7.94 therefore suggests that for all these tests the relationship between calcium and phosphorus is the most important rather than any interaction with the solids from Horden. The results from this section are particularly close to those from Section 7.3.3, the experimental conditions were identical for these two sections and again show the negligible influence of the solids from Horden on phosphorus removal in these cases.

This section has shown that crushed concrete has a relatively high ability to remove phosphorus, higher than pellets composed of solids from Horden and cement. The removal mechanism of these concrete pellets has been shown to be calcium phosphate precipitation, this was indicated through higher phosphorus removal being linked to consumption of pH and calcium. The relationship between changes in calcium and phosphorus were found to agree with those of previous sections showing the consistent domination of calcium phosphate precipitation as a removal mechanism throughout this chapter.

7.5 Chapter summary

Chapter 7 investigated the removal of phosphorus by AMD and cement based pellets. This chapter was split into four sections, a summary of each is provided below.

7.5.1 Section 7.1 summary

Section 7.1 showed the improvement in phosphorus removal with a reduction pellet size. Pellets from 2.8-4mm down to 45-63µm were tested. The 2.8-4mm pellets removed a maximum of 23.5mg/g at a high final concentration of 362mg/l, the 45-63µm removed up to 45.7mg/g at a final concentration of 54mg/l. As the removal achieved increased, so did the range of final pH values, the 2.8-4mm had a range of final pHs of 6.7-7.9 and the 45-63µm pellets 9.9-10.6. This is believed to be as a result of the increased surface areas of the smaller pellets facilitating dissolution of hydroxide ions from the cement. All subsequent tests were performed on 63-125µm pellets as these were found to perform closely to 45-63µm pellets and were easier to produce. Pellets in the 45-63µm and 63-125µm outperformed the unpelletised solids from Horden, this is an unexpected pattern if adsorption is the dominant removal mechanism, as the surface area is reduced (64 m^2/g down to 1.77m^2/g for the 45-63µm pellets) and the pH was increased which is not conducive to anionic adsorption. This pattern is explained by calcium phosphate precipitation being the dominant removal mechanism and this theory was further explored throughout this chapter.

7.5.2 Section 7.2 summary

The results for kinetic tests on pellets were presented in Section 7.2. Two tests were performed, one lasting up to one hour and the second lasting up to sixteen. The test lasting one hour was performed on 45-63µm and 63-125µm pellets. This test showed that, as with the batch tests from Section 7.1, these two pellet sizes performed in a very similar manner with the 63-125µm removing the initial concentration of 11mg/l to 6.56mg/l after an hour and the 45-63µm 5.19mg/l. It was shown that over this period of an hour, the first minutes had by far the highest rate of removal. For the 63-125µm pellets the time period 0-1 minutes had a removal rate of 1.78mg/l/min and the period 40-60mins had effectively a rate of zero. The progression of pH for the three tests followed an unexpected pattern with the test with higher solids concentration showing lower pHs. Comparing these results to those of the 16 hour tests is, perhaps, slightly limited due to the varying solids and phosphorus concentrations but it can be seen that the majority of removal after 16 hours occurs with in the first hour.

The second kinetics test studied the performance of 63-125µm pellets up to 16 hours. Again there was an initial period with the highest rate of removal up to 30 minutes, the rate of removal then was dramatically reduced up to a period of 5 hours. Between 5 and 8 hours there was in fact a further increase in the rate of removal. Throughout this the pH of the solution was steadily increasing and it could be that the initial removal could be attributable to adsorption which the rising pH thereafter inhibits and calcium phosphate precipitation becomes the major removal mechanism. The progression of the calcium concentration was also studied and this showed it to rapidly increase initially, stagnate and then begin to decline, this pattern is believed to be a result of the balance between calcium being released from the pellets and its consumption from solution by calcium phosphate precipitation.

7.5.3 Section 7.3 summary

Section 7.3 reported on long term batch tests with contact times up to thee weeks, Section 7.3.1 detailed the results of tests lasting 1,2 and 3 weeks, these were carried out to investigate the potential of a long term removal mechanism and ensure that the maximum phosphorus removal capacities were being reported. These tests found removal occurring up to the maximum test length of 3 weeks with phosphorus loadings as high up to 59.9mg/g at a final concentration of 0.17mg/l found compared to 30.5mg/g at the lowest final concentration of 5.3mg/l for the 16 hour pellet test. The final pHs of these tests was found to be very high ranging from 10.8 to 11.3 after 3 weeks. The pellets easily outperforming the dry Horden solids at these high pHs showed that adsorption is not the major removal mechanism in this case and in fact likely has a negligible contribution to removal.

This increase in performance with a large increase in contact time up to 3 weeks was thought to be a result of slow calcium phosphate crystallisation and tests lasting 1,3 and 7 days were performed to monitor the progression of phosphorus removal for these times. Two sets of identical tests were performed the second being a repeat of the first but with the addition of the solutions being analysed for calcium as well as phosphorus. In terms of phosphorus removal and pH the two tests sets performed near identically highlighting the repeatability of the pellet production and laboratory tests. The period of 0-1 days had by far the highest rate of removal whereafter the rate became a more gradual one and this pattern is typical of crystal growth. Taking data from the repeat test, after 1 day the phosphorus loading achieved ranged from 34.2-44.6mg/g, after 3 days 45.7 - 59.8mg/g and after 7 days 52.4 - 69.3mg/g comparable to those levels found in Section 7.3.1. The final pH of these tests increased slightly throughout the tests from 7.9-10.2 after 1 day to 9.2-10.8 after 3 and 9.5-11.0 after 7 days. For the repeat test pellets were shaken in deionised water to gain an appreciation of the levels of calcium they were releasing. This found a calcium concentration of 117mg/l after 1 and 3 days with a slight increase to 124mg/l after 7 days. These high concentrations contrast with the calcium concentrations found with the tests containing phosphorus which found 0.37 - 10.1mg/l after 1 day 0.26-1.15mg/l after 3 days and the 7 day test 0.27-0.54mg/l. A pattern between increasing changes in both phosphorus and calcium concentrations was identified, strongly indicative of calcium phosphate precipitation especially when combined with the final high pHs. The pellets from the second test with the highest initial concentration were analysed using SEM-EDX and this found an average calcium to phosphorus ratio of 1.62, this is very close to the ratio of the expected end product, hydroxyapatite which has a stoichiometric ratio of 1.67. Thus this is a strong piece of evidence that the expected end product, hydroxyapatite is being formed.

Section 7.3.4 reported on tests lasting 1, 3 and 7 days with a fixed initial phosphorous concentration of 11mg/l and varying weights of pellets used. These tests were performed to investigate the performance of these pellets at a phosphorus concentration closer to those that could be expected at a WWTWs. As with previous tests the early stages were found to have the highest rate of removal but for the 1-3 day period little removal was found, the exact reasons for this were uncertain. After 1 day phosphorus loadings of 12.9 to 20.0mg/g were found, after 3 days between 16.0 and 25.4 mg/g and after 7 days 53.5-60.9mg/g. After 7 days the loadings achieved were comparable to those from Section 7.3.3. These tests were again analysed for calcium as well as phosphorus. Shaking the pellets in just deionised water found 114-146mg/g calcium released, this compares to 46-49mg/g from section 7.3.3. The solubility of Portandlite could not explain this difference. The difference in the progression of removal and in the calcium released by pellets between the tests in Section .7.3.4 and 7.3.3 could not be fully explained and remain areas of uncertainty.

7.5.4 Summary of Section 7.4

Section 7.4 reported on tests performed on pellets containing no solids from Horden. The first test replaced the Horden solids with crushed sand, this test was carried out to further investigate the redundant nature of the Horden solids in the removal of phosphorus by cemented pellets. The test lasted 7 days and found phosphorus loadings of between 44-58mg/g, slightly lower than those found in Section 7.3.8. These lower loadings were explained by the lower levels of calcium released by these crushed sand pellets (89mg/l compared to 124mg/l from section 7.3.3). As well as lower calcium concentrations, lower final pH values were also found (7.88 to 10.26) both of these factors would reduce the effectiveness of calcium phosphate precipitation and so explain the lower phosphorus loadings found.

Tests were also performed on a sample of concrete crushed into the 63-125μm size range. The tests again lased 7 days and phosphorus loadings of between 51.9mg/g and 82.8mg/g were found, higher than those found for the pelletised Horden solids in Section 7.3.3. Final pHs ranged from 11.4 to 11.8, this compares to pH values of 9.5 to 11.0 for the results from Section 7.3.3 the higher range of pHs tied in with the higher range of phosphorus loadings. When shaken in deionised water these crushed concrete pellets released 124mg/l calcium identical to those pellets from Section 7.3.3.

A consistent relationship between changes in calcium and phosphorus concentrations was found for the tests from sections 7.3.3, 7.3.4, 7.4.1 and 7.4.2 again strongly supporting the theory that calcium phosphate precipitation is the major removal mechanism. The calcium to phosphorous ratio found in the change in calcium vs change in phosphorus graphs was not the stoichiometric 1.67 for HAP. The difference is likely due to the calcium released being more of an approximation and in the tests containing phosphorus calcium phosphate precipitates may be retarding the further release of calcium from the pellets.

8. Phosphorus removal by pellets in column tests: results and discussion

This chapter presents the results and discussion for the continuous column tests carried out using pellets produced from the addition of cement to the treated sludge from the Horden minewater treatment plant. The full details of these columns can be found in Section 5.3. Three identical columns were used, each had an internal diameter of 10cm and a total bed depth of 30cm. Sampling ports were placed every 10cm and each 30cm column was therefore viewed as three 10cm columns in series. The columns were run with average flow rates of 0.28, 0.60 and 0.87 l/hr. Effluent phosphorus, calcium and pH values for each column are presented and discussed and then comparisons are drawn between the three columns. The PHREEQCI software is used to determine the effect of various influent conditions on precipitates. Finally the up scaling models described in Section 4.3.2 are calculated and sizing calculations carried out for real world situations.

8.1 Column 1

Column 1 was run at the lowest flow rate of all three columns with an average flow rate of 0.28l/hr (35.65l/hr/m^2) with a standard deviation of 0.1. The total pore volume was found to be 194ml and this resulted in a contact time of 13.8 minutes for the bottom 10cm, 27.7 minutes for the bottom 20cm and 41.5 minutes for the whole 30cm column. The linear flow rate for the column was 0.43m/hr, as with all columns, the total test time was 937 hours and this column was sampled twice weekly. The variation of flow rate with test length for this column is shown in Figure 8.1

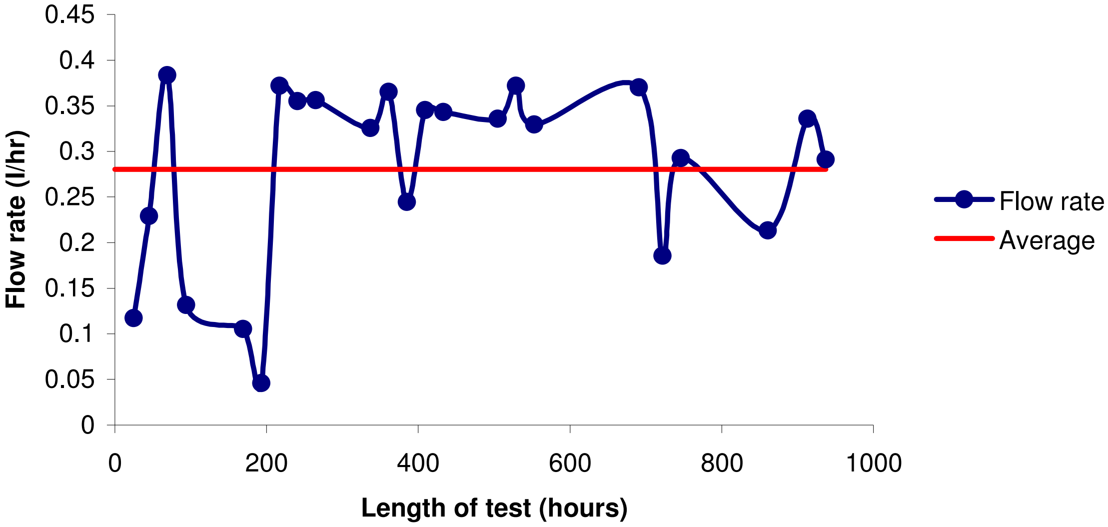
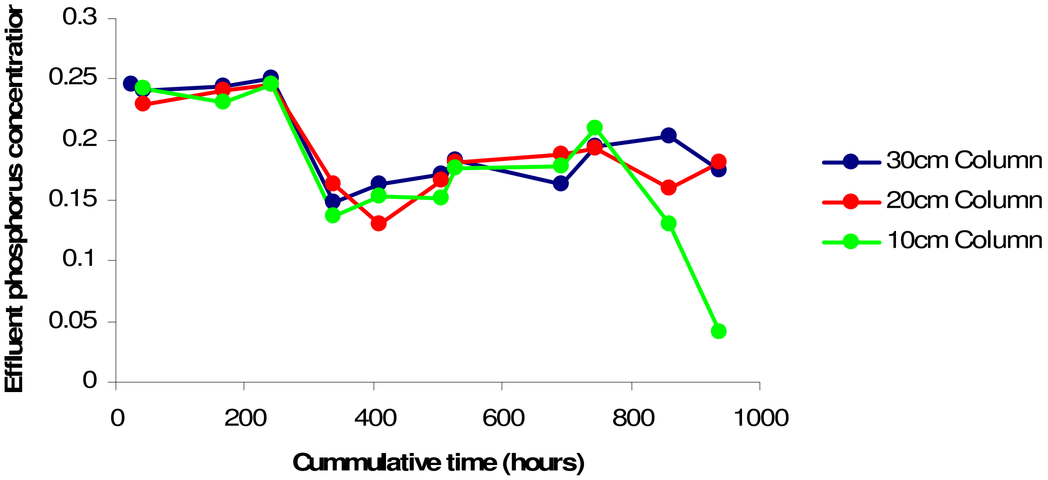
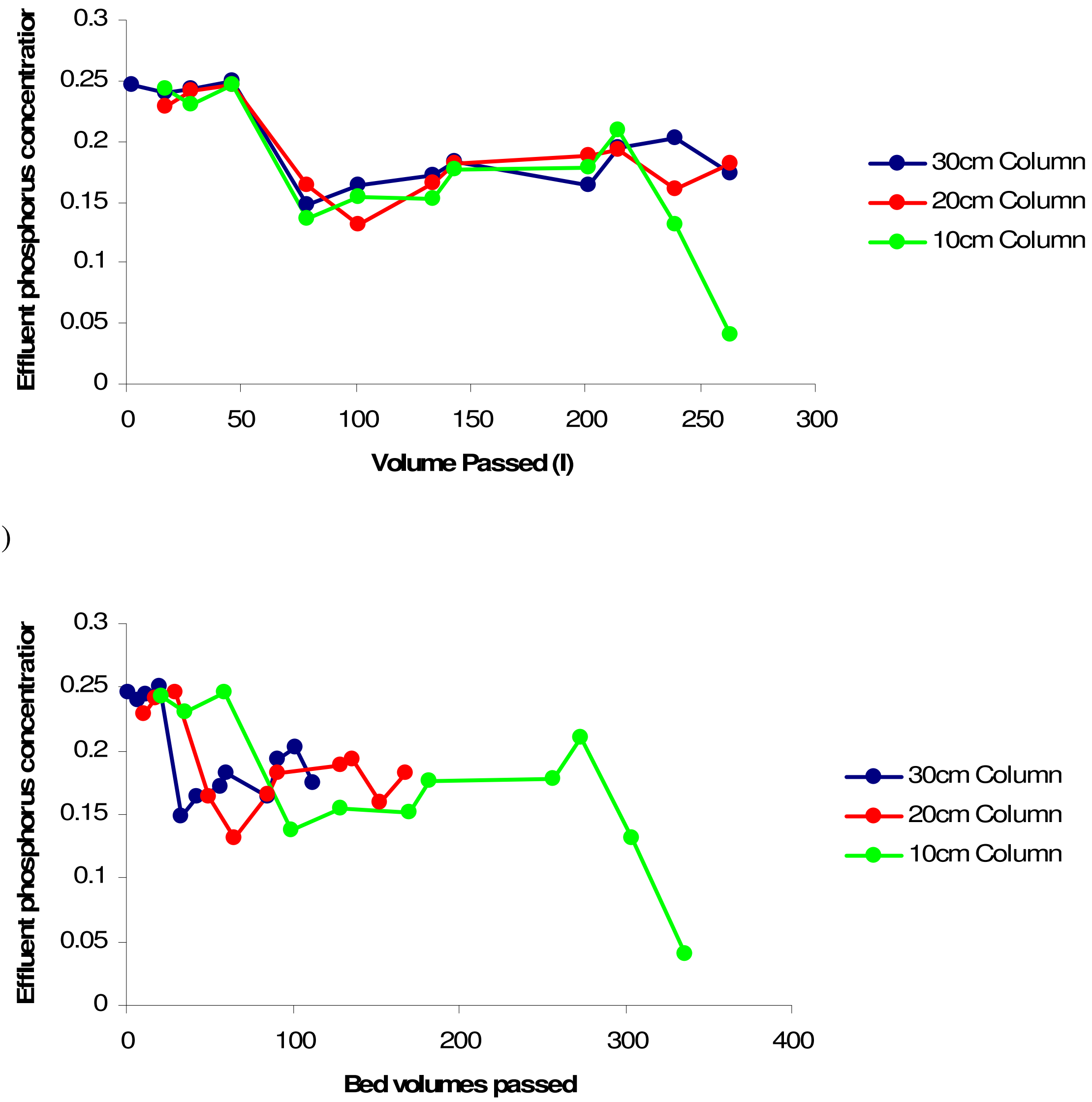


Figure 8.1 Variation of flow rate with test length for Column 1. The mean flow rate of 0.28l/hr is also plotted

Flow rates were relatively variable with the standard deviation of 0.1 representing 36% of the mean value. Variation in flow is to be expected and the flow rates in Figure 8.1 are distinctive from those of the other two columns. In Figure 8.2 the effluent phosphorus concentrations are plotted firstly against the length of test in hours (Figure 8.2a), the volume treated in litres (Figure 8.2b) and thirdly against the number of bed volumes treated (Figure 8.2c). Here bed volumes are considered as the total volume of the bed, i.e. the cross-sectional area of the column multiplied by the bed depth.



(a)



(b)

(c)

Figures 8.2 (a), (b) and (c) Effluent phosphorus concentration versus (a) time in hours and water treated in (b) litres and (c) bed volumes for column 1. The influent phosphorus concentration was 11.23mg/l

Data is presented for the bottom 10cm of the column, the bottom 20cm of the column and the total 30cm deep bed. All three column lengths removed the influent phosphorus concentration of 11.23mg/l consistently below 0.25mg/l. The total volume treated by these three column lengths was 263 litres, equivalent to 112 bed volumes for the 30cm length, 168 bed volumes for the 20cm length and 336 bed volumes for the 10cm length. Apart from the last data point for the

30cm length the three column lengths are reducing phosphorus to very similar effluent concentrations. Therefore, in this situation, no benefit is found for the longer column lengths. The anomalous final data point for the 10cm column length is at 0.04mg/l, this is below the 0.1mg/l that the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was calibrated to and so full confidence cannot be placed in this value. The chosen breakthrough concentration for these columns was 1mg/l as this is viewed as a likely discharge limit for WasteWater Treatment Works (WWTWs). As none of the column lengths came close to this concentration no strong conclusions regarding the service time can be made from the results of this column. It can be said that at the shortest residence time of 13.8 minutes the 10cm column length is capable of treating in an excess of 263 litres or 336 bed volumes before breakthrough.

Column 1 treated 263 litres in total, at the influent concentration of 11.23mg/l this is an overall input of 2.951g of total phosphorus. Through the integration of Figure 8.2(b) it was calculated that of this the 30cm column length removed 2.901g of total phosphorus or 98%. This is a phosphorus loading of 1.09mg/g (phosphorus/pellets) for the total 30cm deep bed equivalent to 8.24 kg/m^3 (phosphorus/pellets) based upon the average packed bed density of 1.129 tonnes/m^3. This is a fractional capacity of 1.8% of the highest removal found from the batch tests at low final concentrations (59.9mg/g at 0.17mg/l from the 3 week test in Section 7.3.1). The 20cm column length removed 2.903g, this is 1.64mg/g, 1.85kg/m^3 or 2.7% of the maximum capacity. The 10cm Column removed 2.907g, equivalent to 3.28mg/g, 3.70 kg/m^3 or 5.5%.

After three weeks of operation all three columns were taken offline, drained and rested for a week, for column 1 this was after 134 litres had been passed. As the column was running at its maximum phosphorus removal efficiency at this point, no benefit for column 1 was realised from this break.

The effluent was analysed for calcium as well as phosphorus so as to investigate their relationship in this situation. Figure 8.3 shows the effluent calcium concentration (mg/l) plotted against the volume treated.

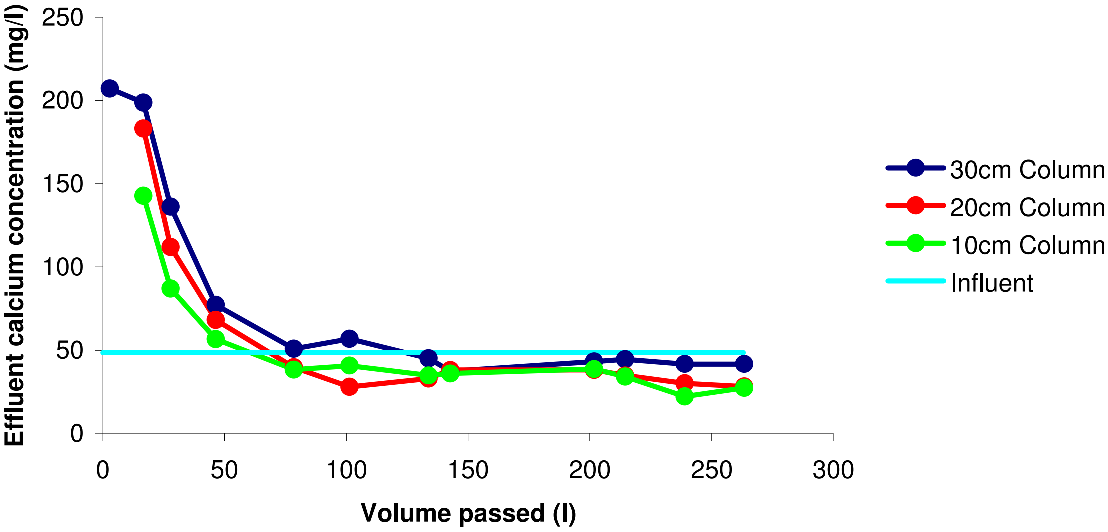


Figure 8.3 Effluent calcium concentration versus volume treated for column 1, the influent calcium concentration is also shown (48.7mg/l).

At the early stages of the test, the calcium concentration was as high as 207mg/l for the 30cm column length. There is a general trend of the longer bed depths resulting in higher effluent calcium concentrations this is expected due to the increased contact with the pellets. At the early stages these differences are quite pronounced, after 16.7 litres have been passed the calcium effluent concentration was 198.7, 183.2 and 142.6mg/l (30cm, 20cm, 10cm bed depth). The effluent calcium concentration quickly reduces and after 78.5 litres were treated all three column lengths have an effluent calcium concentration approximately equal to that of the influent. The influent concentration was 48.67mg/l and is the background calcium level found in Cardiff tap water.

The effluent calcium concentrations dropping below that of the influent suggests that due to the raising of the pH by the pellets the calcium present in the influent tap water was becoming involved in the precipitation of phosphorus. Lee *et al.* (2009) studied phosphorus removal by oyster shells, which due to the levels of calcium in their influent water acted primarily as a source of hydroxide ions, the pellets studied in the current thesis could be showing similar behaviour.

This concurrent reduction of both calcium and phosphorus was reported in Chapter 7 of the current thesis and also by Lu *et al.* (2009) and Johansson and

Gustafsson (2000) amongst many other papers where it is cited as evidence of calcium phosphate precipitation.

The average influent calcium concentration of 48.67mg/l is relatively high. The stoichiometric molar ratio for the expected end product, hydroxyapatite (HAP), is 1.67 (Ca:P). Comparing the influent calcium and phosphorus concentrations (48.67 and 11.23mg/l) results in a molar ratio of 3.37:1 (Ca:P), the influent therefore contains sufficient calcium to precipitate all of the influent phosphorus. The calcium and phosphorus concentrations were found to be stable in the influent reservoir, this was at a pH of 7.9, therefore showing the requirement of elevated pHs for the calcium phosphate precipitation.

A crust was found to have formed on the top of column 1 as shown in Figure 8.4, X-Ray Diffraction (XRD) analysis (shown in Figure 8.5) showed this to be calcite ($CaCO_3$). Mayes *et al.* (2009) who used similar pellets to these in column tests to remove zinc from minewater also found that a calcium carbonate crust formed atop of their columns.

Figure 8.4 Calcite crust on the top of column 1

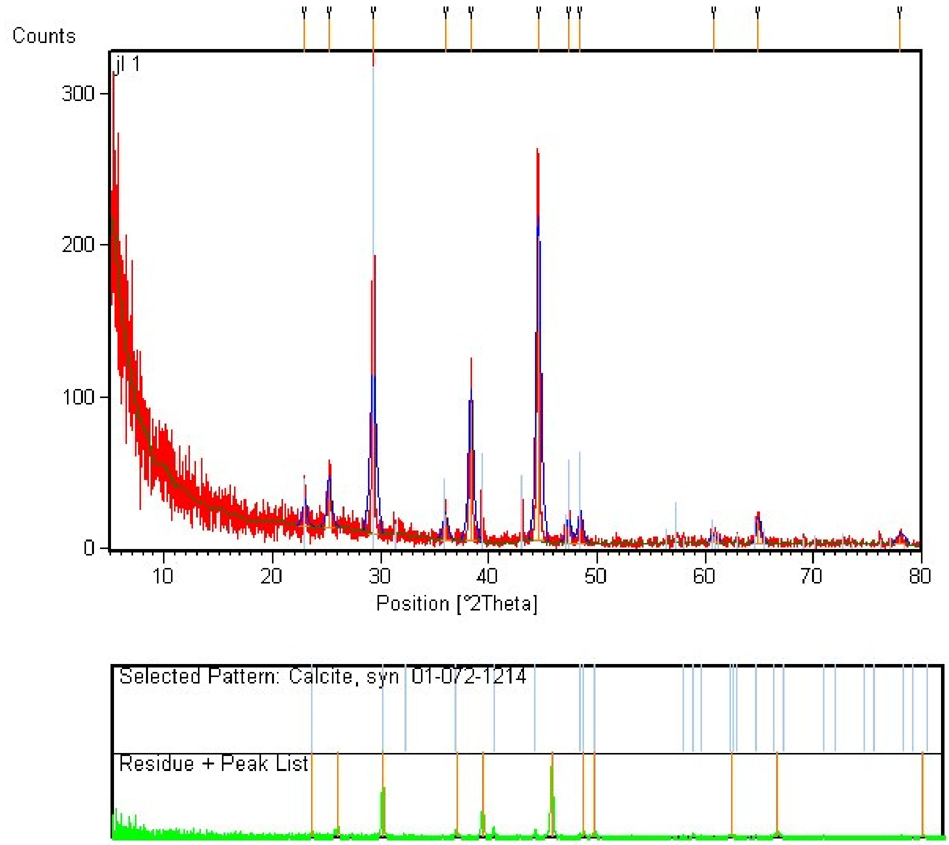


Figure 8.5 XRD trace of the crust on top of column 1 and comparison to that of calcite

The pH of the effluent from all three bed depths are plotted against the volume treated in Figure 8.6. The influent pH of 7.9 is also plotted.

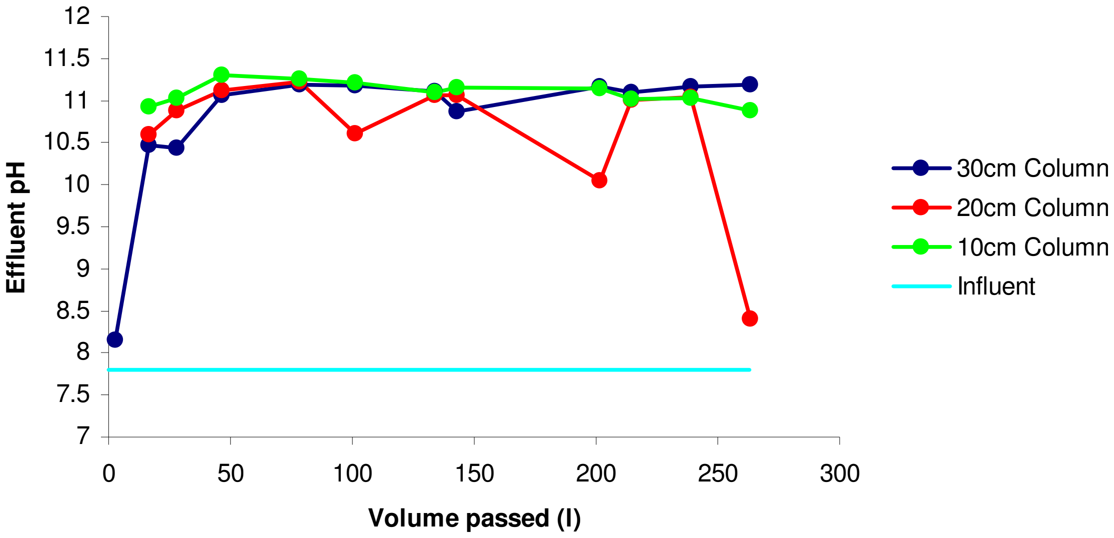


Figure 8.6 Effluent pH versus volume treated for column 1, the influent pH of 7.9 is also shown.

Aside for a few outliers, the effluent pH values for all three columns lengths were very close and remained constant throughout the experiment. Removing the three obvious outliers for the 20cm column (101, 202, 263 litres passed) and the first data point for the 30cm column, the mean pH value for all three column lengths is 11.03 with a standard deviation of just 0.21. This shows that at this flow rate after 263 litres had been treated the pellets are still consistently raising the effluent to a high pH. These results also show that even after the pellets had been aged for three months they still retained their ability to raise pH, these highly elevated pHs, although instrumental in removal, could however well be problematic for implementation of this technology.

In the discussion of the subsequent columns the effluent calcium and pH will be compared to the effluent phosphorous concentration. However the consistently high phosphorus removal efficiency by this column means that no relationships are able to be identified for this column.

8.2 Column 2

Column 2 was operated at the mid range flow rate of the three columns with an average flow rate of 0.60l/hr (76.38 l/hr/m^2) with a standard deviation of 0.21. The total pore volume was found to be 196ml and this resulted in contact times of 6.6 minutes for the bottom 10cm, 13.1 minutes for the bottom 20cm and 19.7 minutes for the whole 30cm column. The linear flow rate for the column was 0.91m/hr and this column was sampled thrice weekly. The variation of the flow rate with test length for this column is shown in Figure 8.7

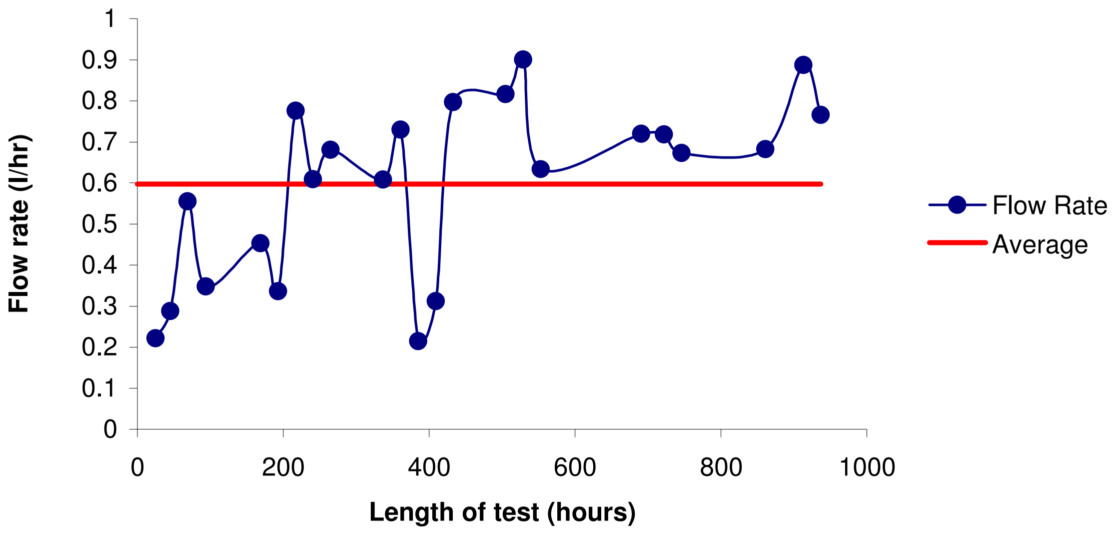
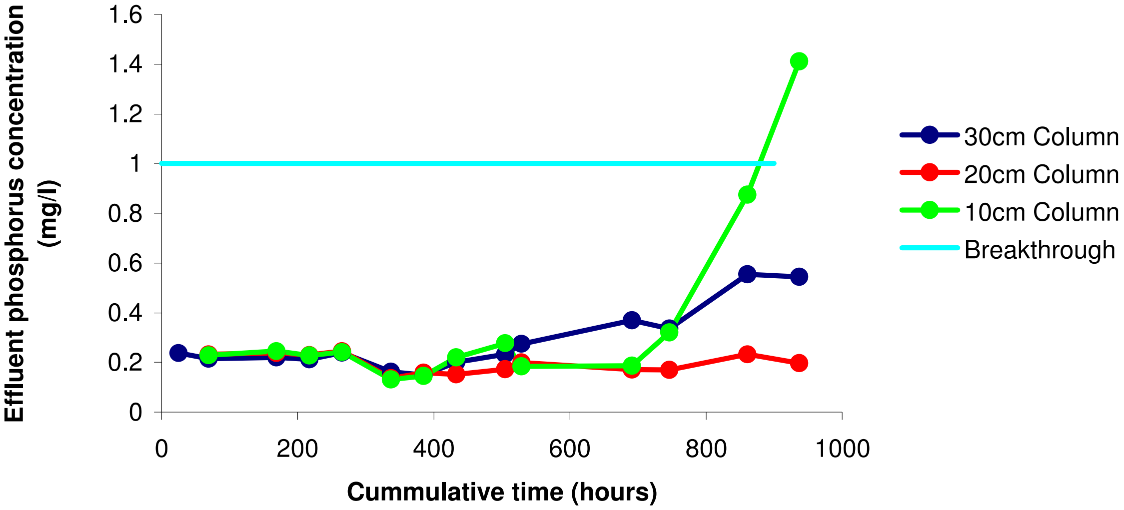
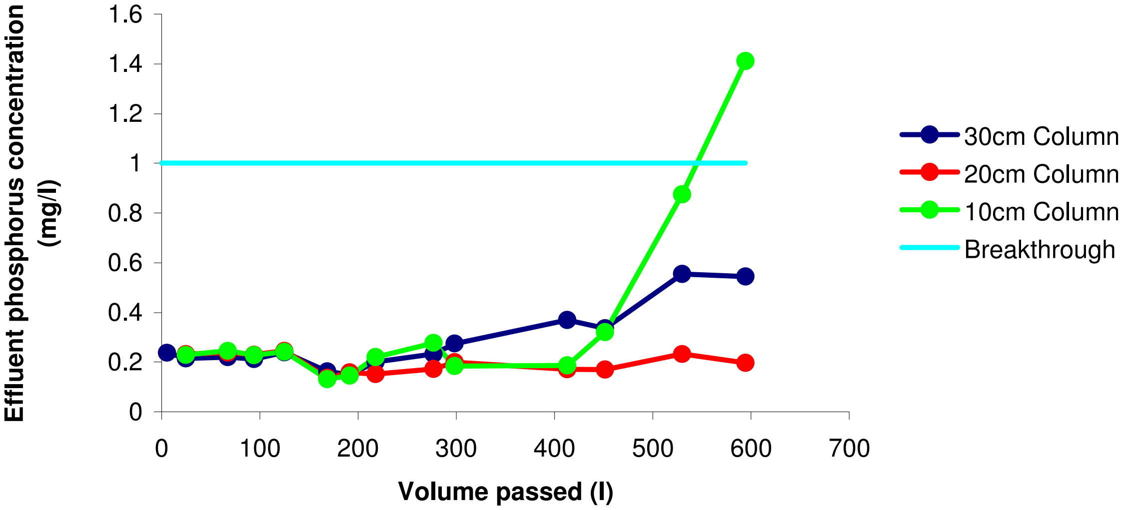


Figure 8.7 Variation of flow rate with test length for Column 2. The average value of 0.60l/hr is also plotted.

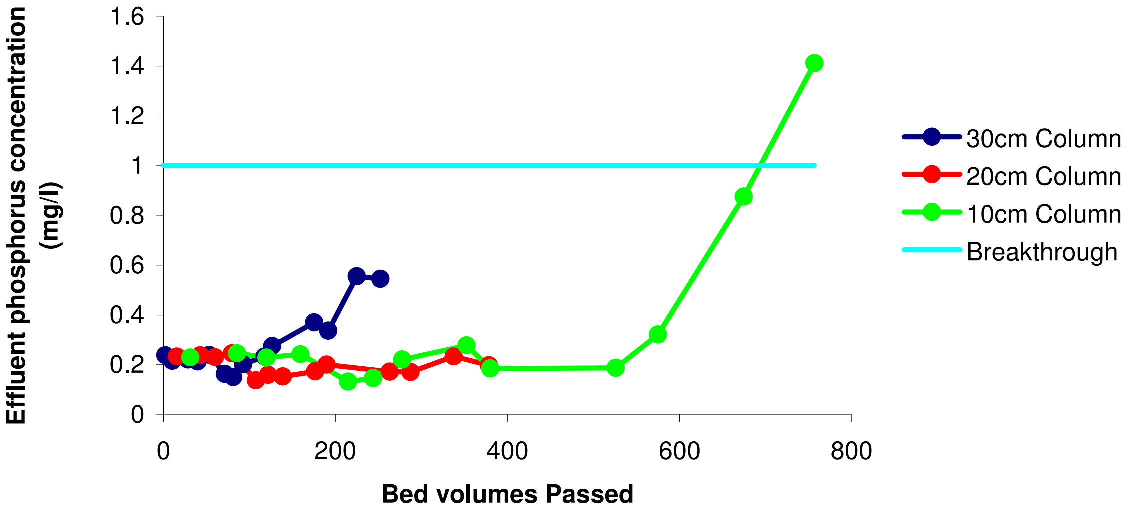
Figure 8.7 shows the variation of flow rate for column 2 throughout the experiment. The standard deviation of the flow rates was 0.2, representing 36% of the mean. As with the results for Column 1 the effluent phosphorus concentration is plotted against the test length and the volume treated in litres and also in bed volumes. The chosen breakthrough concentration of 1mg/l is also plotted upon these charts.


Effluent phosphorus concentration (mg/l)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
1000
Cummulative time (hours)
30cm Column
20cm Column
10cm Column
Breakthrough

(a)


Effluent phosphorus concentration (mg/l)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
600
700
Volume passed (l)
30cm Column
20cm Column
10cm Column
Breakthrough

(b)



(c)

Figures 8.8 (a), (b) and (c) Effluent phosphorus concentration versus (a) test length in hours and water treated in (b) litres and (c) bed volumes for column 2. The influent phosphorus concentration (11.23mg/l) and breakthrough concentration of (1mg/l) are also plotted.

After 451 litres had been treated the effluent phosphorus concentration from the 10cm column length starts to rise and quickly rises to above the breakthrough concentration of 1mg/l. This breakthrough occurs after 550 litres have been treated, equivalent to 701 bed volumes. At the end of the test the 10cm column had an effluent phosphorus concentration of 1.41mg/l. The 20cm column length consistently removed phosphorus below 0.25mg/l directly comparable to the results from column 1 where all effluent concentrations were below 0.25mg/l.

Unexpectedly the effluent phosphorus concentration for the 30cm column rises above that of both the 20cm and 10cm column lengths after 293 litres had been treated. There is a consistent rise and so cannot be considered anomalous. These results suggest that phosphorus is being released by the pellets in the top 10cm rather than removed. The reasons for this will be fully discussed once the effluent calcium and pH results have been presented.

For column 2, in total 594 litres of water were passed, at the influent concentration of 11.23mg/l this is equivalent to 6.657g of total phosphorus. Over the whole test length the 30cm column length removed 6.475g of this, representing 97% removal and 2.43mg/g or 2.74kg/m^3, a fractional capacity of 4.1%. The 20cm length removed 6.544g of total phosphorus, this is 98% removal and a phosphorus loading of 3.69mg/g (4.17kg/m^3) which is a fractional capacity of 6.2%.

Over the whole test length the 10cm column removed 6.443g of total phosphorus representing 97% removal and 7.3mg/g (8.24kg/m^3), a fractional capacity of 12%. At breakthrough, 550 litres had been passed, a total influent of 6.160g of phosphorus. At breakpoint the phosphorus loading was 6.77mg/g (7.68kg/m^3) and this is a fractional capacity of 11%.

The higher flow rates used with column 2 compared to column 1 (0.60 vs 0.28l/hr) have exposed the pellets in column 2 to much more phosphorus, which all three column lengths still achieving 97% removal, marginally lower than the 98% removal from column 1. At breakpoint the 10cm length of column 2 had removed 6.77mg/g, compared to the 3.27mg/g achieved by the 10cm length of column 1, although as column 1 did not reach break point its actual capacity will be larger than this.

When the column was taken offline and rested for a week, 277 litres had been passed, the effluent concentrations for the three column lengths were in the region of 0.2mg/l, where they remained after the break. The break therefore had no effect on effluent phosphorus concentrations as the columns were already operating at their maximum removal.

The variation of effluent calcium concentration with the volume of water treated is presented in Figure 8.9 with the influent value of 48.67mg/l also plotted.

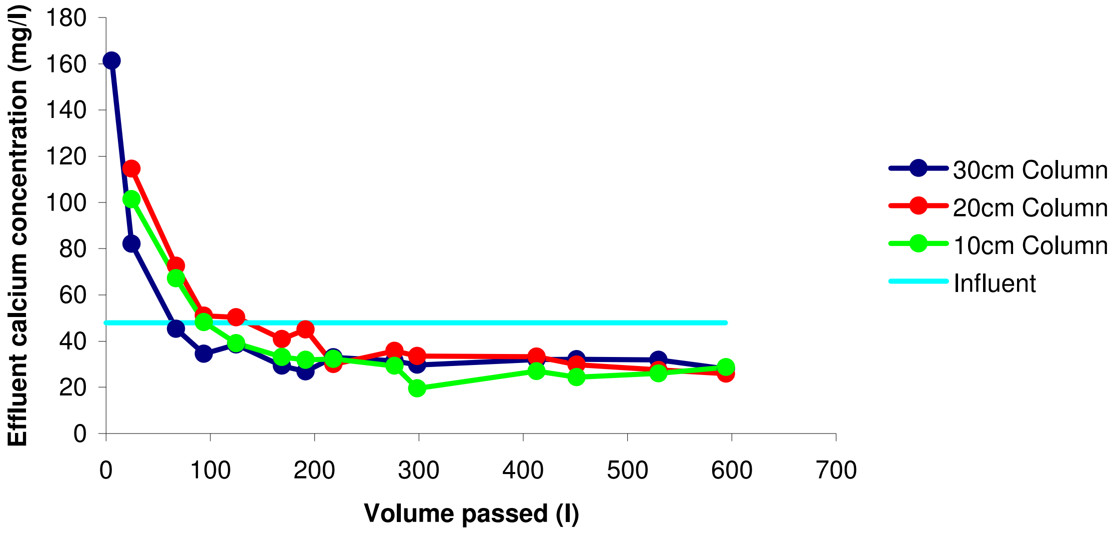


Figure 8.9 Effluent calcium concentration versus volume treated for column 2, the influent calcium concentration is also shown (48.7mg/l).

The calcium concentrations for all three column lengths follow a similar pattern to that of column 1 in so much as that the effluent concentration is initially high and then rapidly drops below that of the influent. Unexpectedly the 2nd, 3rd and 4th data points for the 30cm column length are all below that for the 20cm and 10cm lengths. This is the opposite to what may be expected and could offer the start of an explanation of the higher phosphorus concentrations that were found for this column length. After 125 litres had been treated the effluent calcium concentration for the 10cm and 20cm lengths was essentially at the influent level and the 30cm length reached the influent level after 67 litres had been treated. This compares to 79 litres treated at the same point for all lengths of column 1. Aside from the 30cm length this makes sense as a longer contact time should allow more dissolution of calcium from the pellets. As with the results for column 1, once the effluent calcium concentrations dipped below the influent calcium concentration, the effluent concentrations remained thus. When the 10cm column length broke through after treating 550 litres the effluent calcium concentration was 26.9mg/l. The calcium carbonate crust found in column 1, was present to a much lesser extent in column 2, with just a couple of flecks visible, this could be as a result of the lower effluent calcium concentrations found for this column.

After 298 litres had been treated, unexpectedly the 30cm column effluent phosphorus concentration began to rise above that of the 20cm column. The calcium analysis does not offer an absolute explanation for this, as over the period where the 30cm phosphorus effluent was higher, the calcium effluent concentrations for both the 20 and 30cm column lengths were equal.

The progression of the effluent pH with volume of water treated is shown in Figure 8.10.

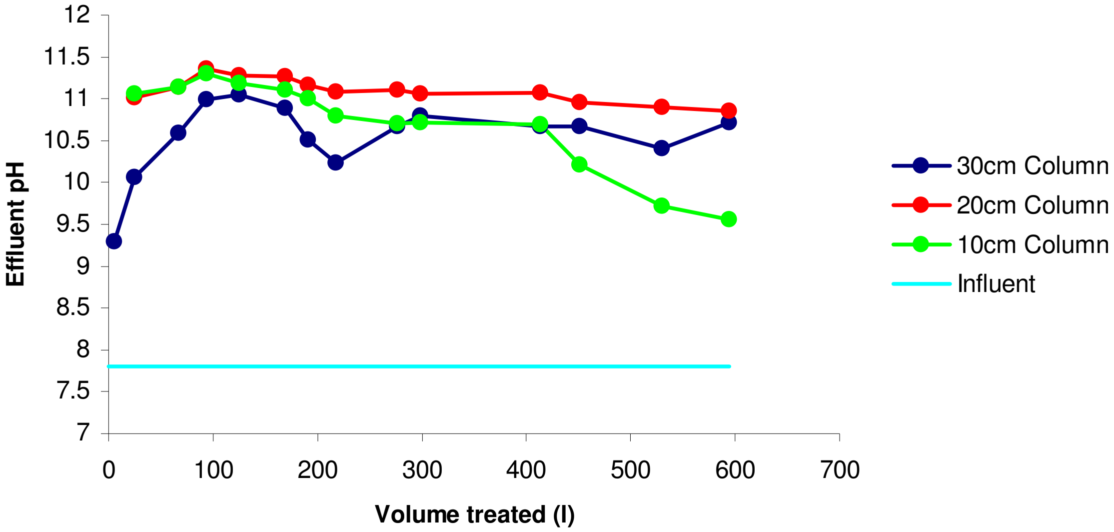


Figure 8.10 Effluent pH versus volume treated for column 2, the influent pH (7.9) is also shown.

In the early stages of the test, the 10cm and 20cm lengths had a similar effluent pH. After 218 litres had been treated the effluent pH of the 10cm length began to dip below that of the 20cm length. This becomes particularly apparent after 451 litres have been treated, this is the point at which the effluent phosphorus concentration for the 10cm length rose above the effluent phosphorus concentration for the 20cm column length. The phosphorus concentration for the 10cm length rose from 0.186mg/l to 0.321mg/l as the pH dropped from 10.867 to 10.212, showing a drop in the reactivity of the pellets. This supports the calcium phosphate precipitation mechanism theory as higher pHs are preferential for this removal mechanism. At the final data point (594 litres treated) the effluent pH for both the 30cm and 20cm column lengths was 10.85 (phosphorus effluent concentration 0.55 and 0.18mg/l respectively), this compares to a pH of 9.56 and a phosphorus concentration of 1.4mg/l for the 10cm column. The effluent phosphorus concentration and pH are clearly linked, this is further investigated in Section 8.5 where the PHREEQCI software is used to predict the effect of pH on saturation indices.

The pH analysis does offer some explanation as to why the phosphorus effluent for the 30cm rises above that of the 20cm length. For the whole of the test the 30cm column length reported pHs lower than those for the 20cm column. This ties in with the higher effluent phosphorus concentrations and supports the calcium phosphate precipitation theory. These lower pHs are therefore correlated with higher phosphorus concentrations. The exact reasons for why this happened however are unclear.

Now that the results for phosphorus, calcium and pH have been presented, relationships between the effluent phosphorus concentration and the effluent calcium and pH will be explored. Firstly all the effluent phosphorus concentrations for column 2 will be plotted against the relevant effluent calcium concentrations in Figure 8.11

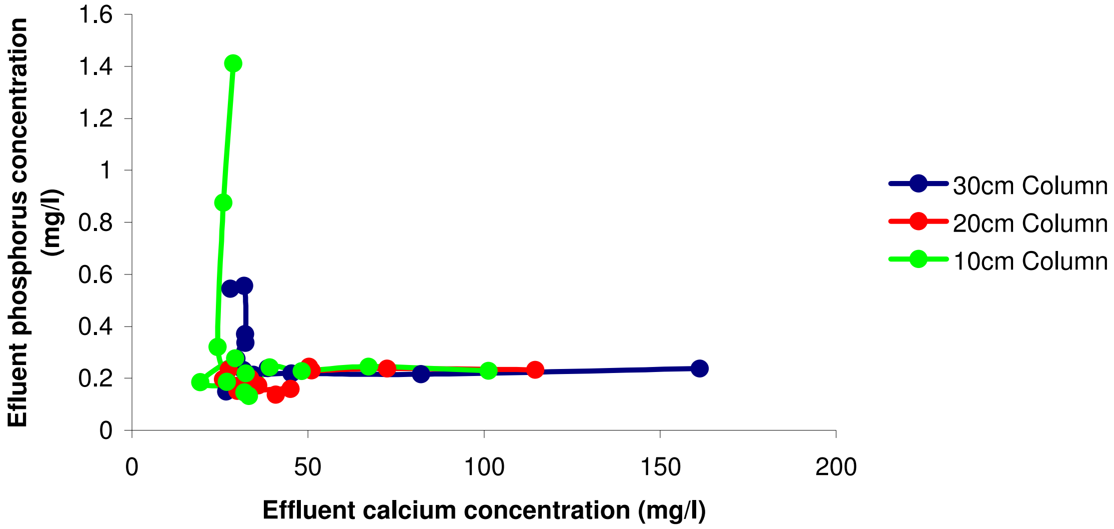


Figure 8.11 Relationship between effluent calcium and phosphorus concentrations for column 2

The effluent phosphorus concentration remains below 0.25mg/l across a wide range of calcium concentrations (30-161mg/l). Particularly for the 10cm column, but also to an extent for the 30cm column, the increasing phosphorus concentrations tie in with lower calcium concentrations. After the calcium concentration drops to 24.38mg/l for the 10cm length and 32.25mg/l for the 30cm length the phosphorus concentration begins to rise with little or no change in effluent calcium concentration. The pattern, particularly for the 10cm column length, again suggests calcium phosphate precipitation as the major removal mechanism. When the calcium levels drop to a lower level, the phosphorus concentration begins to rise, thus highlighting the important role that calcium plays in phosphorus removal here. The PHREEQCI software was used to predict the importance of calcium concentration in the precipitation of HAP, this is reported in Section 8.5.

The effluent phosphorus concentrations are plotted against the corresponding pH in Figure 8.12

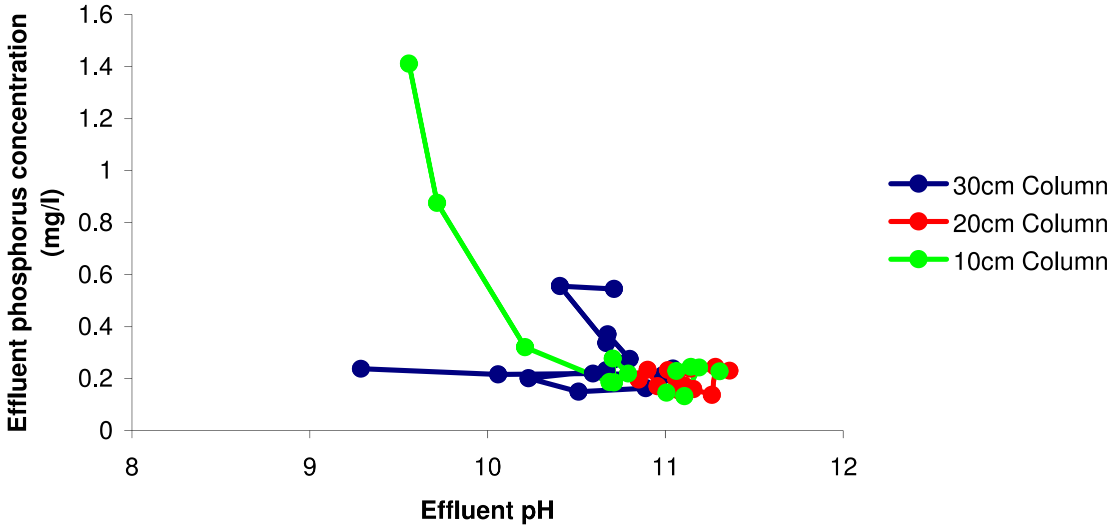


Figure 8.12 Relationship between effluent pH and phosphorus concentrations for column 2

For the 10cm column length, the point where the effluent phosphorous concentration began to rise above that of the 20cm column length (451 litres treated) occurs at the pH of 10.212. The pH then drops to 9.717 and 9.559, these three data points occur at effluent phosphorous concentrations of 0.321, 0.875, 1.411 respectively, the relationship between effluent pH and phosphorus can therefore be seen. The effluent pH for the 20cm length remains in a small range, across a very small range of phosphorus concentrations. The results for the 30cm length are more confused with some low phosphorus concentrations found at low pHs and there is also the start of the same pattern as the 10cm length with higher phosphorus concentrations linked to an increase in pH.

8.3 Column 3

Column 3 was operated with the highest flow rate with an average of 0.87l/hr (110.76 l/hr/m^2) and a standard deviation of 0.25. The total pore volume was found to be 204ml, this resulted in a contact time of 4.7 minutes for the bottom 10cm, 9.4 minutes for the bottom 20cm and 14.1 minutes for the whole 30cm column. The linear flow rate for the column was 1.27m/hr. This column was sampled every weekday. The variation of the flow rate with test length for this column is shown in Figure 8.13

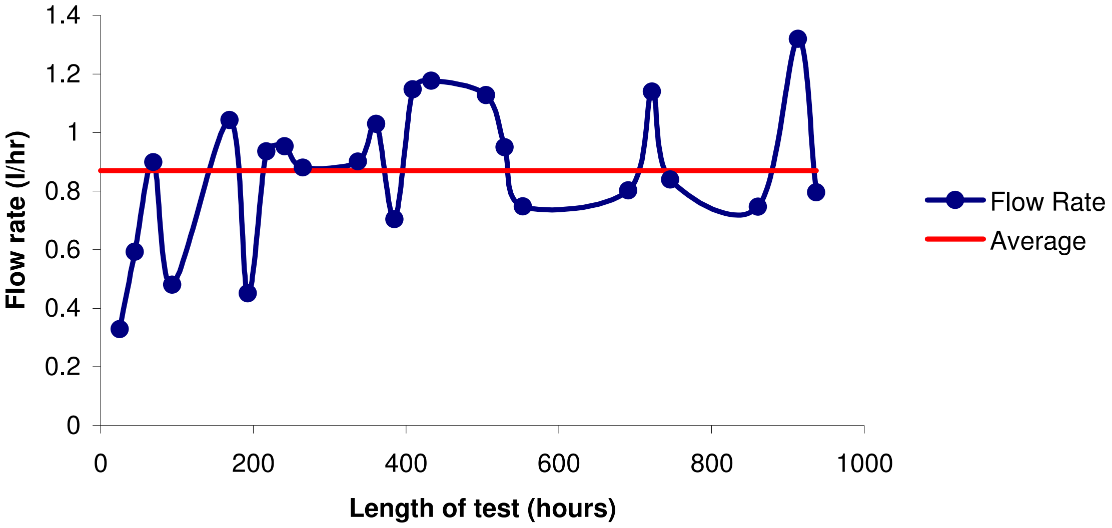
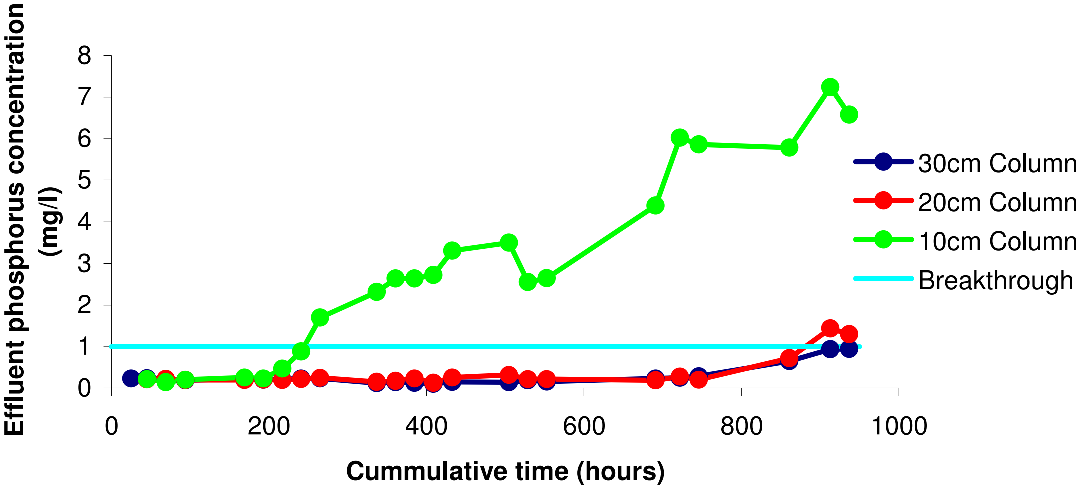


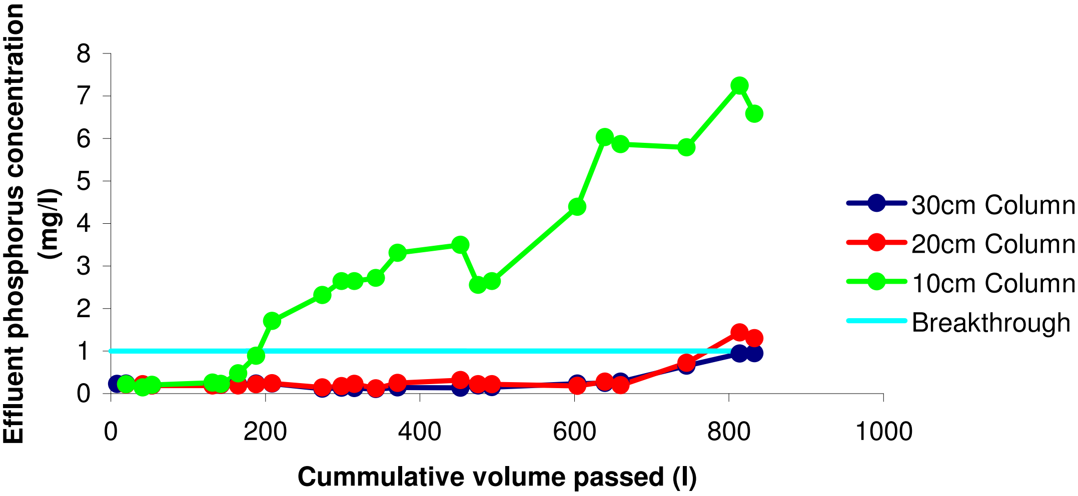
Figure 8.13 Variation of flow rate with test length for Column 3

As with the previous columns, there is variation in flow, but the flow rates remain distinctive from the previous two columns.

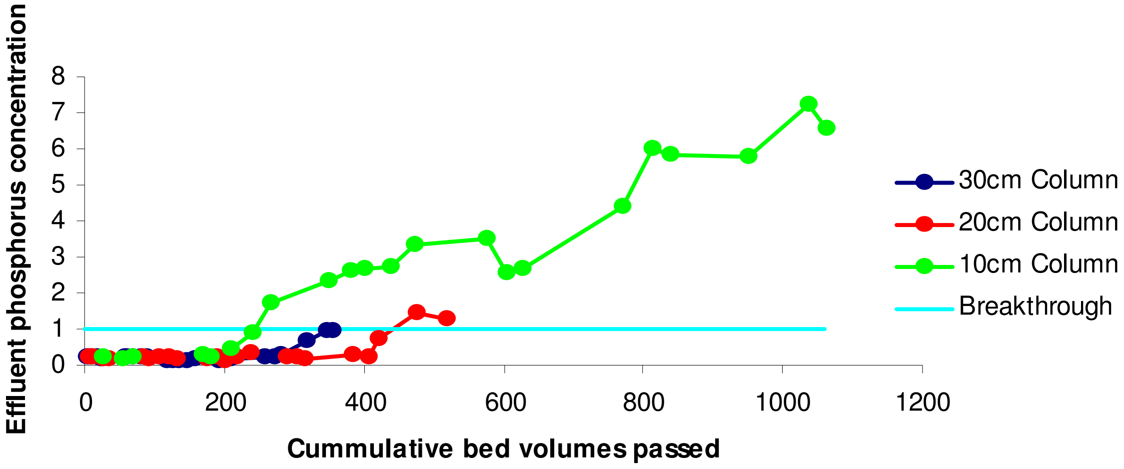
The variation of effluent phosphorus concentration with test length (hours) and volume treated in both litres and bed volumes are shown in Figures 8.14 (a), (b) and (c).



(a)



(b)



(c)

Figures 8.14 (a), (b) and (c) Effluent phosphorus concentration versus (a) length of experiment and water treated in (b) litres and (c) bed volumes for column 3. The influent phosphorus concentration was 11.23mg/l. The breakthrough concentration of 1mg/l is also plotted.

For all three lengths of column 3 the breakthrough concentration of 1mg/l was reached, the final concentration of the 30cm column length was 0.949mg/l, but for the sake of later calculations this will be taken as having achieved breakthrough at this point. The 30cm long column therefore reached breakthrough after 830 litres had been treated, this is equivalent to 352 bed volumes. The 20cm long column broke through after treating 770 litres, equivalent to 531 bed volumes. The 10cm column length achieved breakthrough after 190 litres was treated equivalent to 242 bed volumes. Although the 30cm column treated more litres than the 20cm column it treated far less bed volumes. The 20cm column, with double the weight of pellets and contact time than the 10cm length treated four times the volume of water and twice the number of bed volumes. These results suggests an optimum bed depth exists, as pellets above the mass transfer zone are taking no part in the removal of phosphorus but are still having their calcium and hydroxide ions washed out, thus reducing their reactivity. This would not be the case if adsorption was the dominant removal mechanism as when the phosphorus had been reduced to a low concentration these low concentrations would have little interaction with the material above the MTZ. The 10cm column from column 2 broke through after treating 550 litres equivalent to 701 bed volumes. This is over double the volume treated by the

10cm length of column 3 before breakthrough and highlights the importance of contact time. Dobbie *et al.* (2009) who studied similar materials in a similar situation also found that increasing the contact time with pellets improved the phosphorus removal performance, the kinetic studies discussed in Section 7.2 also show this.

For column 3, 833 litres were treated in total, at the influent concentration of 11.2mg/l this is equivalent to a total exposure of 9.329g of total phosphorous. Through integration of Figure 8.14(b) it was calculated that for the 30cm column length 9.098g of total phosphorus was removed, 98% removal over the whole test length of. This 9.098g removed results in a phosphorus loading of 3.42mg/g (3.86kg/m^3). Of the 59.93mg/g removal found from Section 7.3.1 this is a fractional capacity of 5.7%. Breakthrough occurred at this final point.

For the 20cm column length, in total 9.052g of total phosphorus was removed, 97% removal over the total length of test. This is equivalent to 5.10mg/g (5.76 kg/m^3), a fractional capacity of 8.5%. At breakpoint 8.420g had been removed, this is equivalent to 4.75mg/g, (5.36kg/m^3) a fractional capacity of 7.9%.

In total the 10cm column removed 6.692g of total phosphorus, this is 72% removal over the total length of the test and equivalent to 7.55mg/g or 8.52kg/m^3, a fractional capacity of 15%. At breakpoint 2.053g of total phosphorus had been removed, 2.32 mg/g, 2.62kg/m^3 or 4.5% fractional capacity.

The progression of the phosphorus effluent for the 10cm column length after breakpoint is shown in Figures 8.14 (a),(b) and (c). After breakthrough the pellets continue to remove phosphorus down to relatively low concentrations. Breakthrough occurred after 190 litres had been treated, at the end of the experiment, 833 litres had been passed, a further 643 litres from breakpoint and at this point the effluent phosphorus concentration had risen to just 6.579mg/l therefore the pellets were still removing 41% of the influent phosphorus. Between breakpoint and the completion of the experiment the 10cm column length removed a further 4.71g or 5.32mg/g. These columns are therefore capable of lots of phosphorus removal between breakpoint and exhaustion.

Exhaustion was not found for any columns but the progression of phosphorus concentration between breakpoint and exhaustion is shown to be slow.

The column was taken offline, drained and allowed to rest for a week, this occurred after three weeks when 453 litres had been treated (192, 237 and 576 bed volumes). At this point the phosphorus concentrations for the 30cm and 20cm column lengths were already low at around 0.2mg/l and remained so after the rest period. The effluent phosphorus concentration of the 10cm column length was at 3.50mg/l. The first data point after the rest, after a further 22.8 litres had passed through the column was at 2.55 mg/l. Therefore initially there does appear to be some benefit to this resting of the column. Through interpolation it was found that an additional 95 litres had been passed before the phosphorus concentration had risen back up to 3.50mg/l. Considering that the volume treated until breakpoint was 190 litres, this treating of a further 95 litres (121 bed volumes) is not insignificant. This is however just one data point and so cannot be viewed as conclusive proof of a regenerative phenomenon. Sibrell (2007) who also report a resting/rejuvenation phenomenon suggested equal exposure and rest times, ideally 12 hours. Sibrell found that phosphorus removal was high after 80 hours of exposure where the columns were rested, whereas with continuous exposure the phosphorus removal ceased after 15 hours. This setup would however require double the area required for filters and therefore higher capital expenditure. Drizo *et al.* (2002) is a commonly cited paper dealing with the regeneration of similar materials. Drizo *et al.* (2002) studied a calcium rich electric arc furnace slag, whose main removal mechanism was thought to be precipitation. Drizo suggests that due to the draining of the columns, the local pH was elevated which drew calcium and iron to the surface of the slag. Pratt *et al.* (2009) studied physical techniques for the regeneration of slags including drying and crushing. Crushing was found to be the most effective due to exposure of fresh material, but even so the benefit found was minimal. There therefore seems to be some confusion in this area with Sibrell (2007), Drizo *et al.* (2002) and to an extent the results in this thesis finding some regeneration through the resting of the materials yet the mechanisms of this regeneration are not fully understood.

The effluent calcium concentrations are plotted against the volume treated in Figure 8.15.

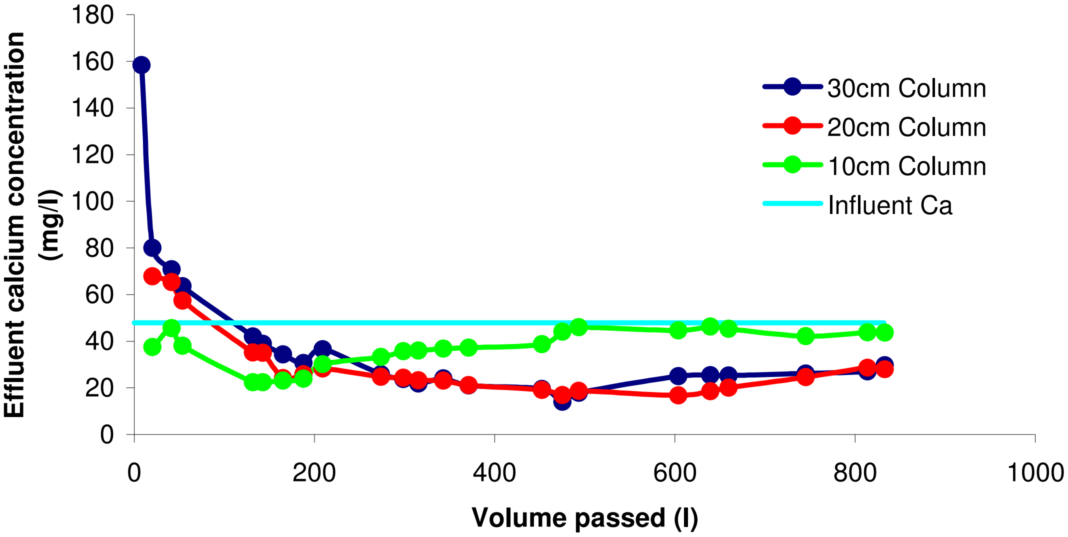


Figure 8.15 Effluent calcium concentration versus volume treated for column 3, the influent calcium concentration is also shown (48.7mg/l).

The results for the 30cm and 20cm column follow a similar pattern to the results for columns 1 and 2, with the relatively high early calcium concentrations soon dropping below the influent calcium concentration where they remain. As with the results for columns 1 and 2 the early differences in calcium concentration are more pronounced. After 20 litres had been treated the effluent calcium concentrations were 80.02, 67.81 and 37.41mg/l (30, 20 and 10cm column lengths). The 10cm column never produced an effluent calcium concentration above the influent. The 20cm column calcium effluent dropped to the influent concentration after 90 litres had been treated and the 30cm column after 120 litres. Between 604 and 833 litres being treated the effluent calcium concentration for the 20cm length rose from 16.66 to 27.88mg/l, during this period the phosphorus concentration rose from 0.18mg/l to 1.31 mg/l. This relationship is more apparent for the 10cm length. The phosphorus concentration for this column length rose from 0.23mg/l after 142 litres were treated to 6.58mg/l after 833 litres were treated, over the same period the effluent calcium concentration rose from 22.27 to 43.69mg/l, ending just below the average influent concentration of 48.7mg/l. Therefore as the ability of the pellets to remove phosphorus drops the effluent calcium concentration rises and approaches the influent concentration due to less of the calcium being taken out of solution by calcium phosphate precipitation. This relationship again shows the importance of the pellets as a source of hydroxide ions and the importance of the influent calcium to removal. The calcium carbonate crust found atop column 1 was not present for column 3.

After the break where the column was taken offline for a week, there was a slight increase in the effluent calcium concentration for the 10cm column from 38.7mg/l to 44.1mg/l, this is more clearly explored below in Figure 8.17. There was negligible effect on the other two column lengths.

The variation of effluent pH with volume of water treated for all lengths of column 3 is shown in Figure 8.16

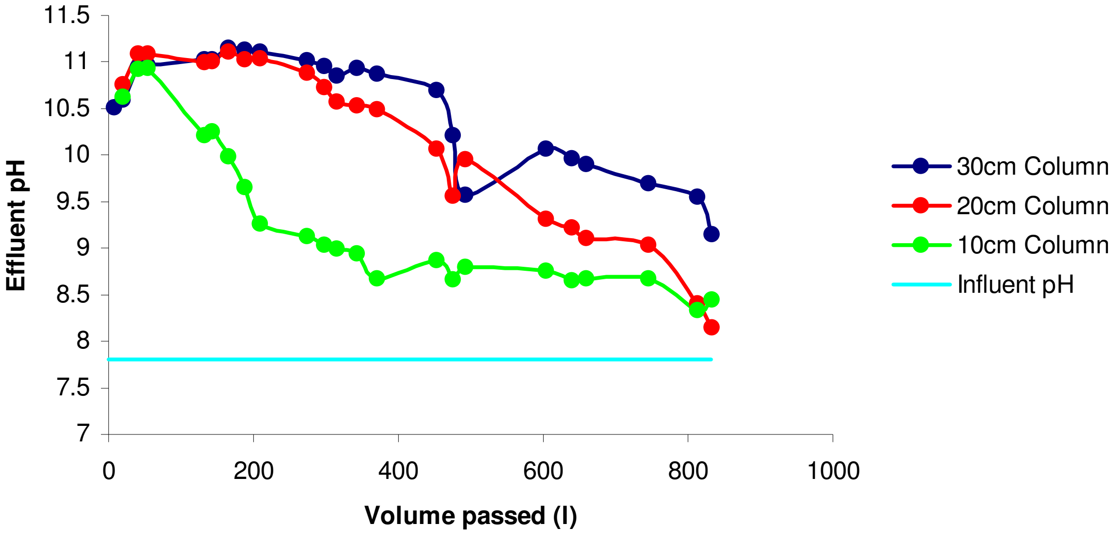


Figure 8.16 Effluent pH versus volume treated for column 3, the influent pH (7.9) is also shown.

After 54 litres have been treated the effluent pH of the 10cm length begins to drop below that of the other, longer, column lengths. From this point to the end of the test (833 litres treated) the pH drops from 10.93 to 8.44 as the effluent phosphorus concentration rises from 0.20mg/l to 6.58mg/l. The effluent phosphorus concentration of the 10cm column rose above that of the other two, to 0.47mg/l (compared to 0.21 and 0.19mg/l) after 165 litres were treated, at this point the effluent pH was 9.98 and the other two column lengths both had a pH of 11.10 a marked difference. At breakthrough for the 10cm length, 190 litres had been treated and the effluent pH was in the region of 9.66. After this point the effluent pH of the 10cm column length plateaus at around a pH of 8.7, still above the influent pH of 7.9.

The 20cm column length follows a similar pattern, the effluent phosphorus concentration was at 0.20mg/l after 659 litres had been treated, after 745 litres this had risen to 0.724mg/l and at the end of the experiment (833 litres) the effluent concentration was 1.30mg/l. Over the same period the pH dropped from 9.10 to 9.03 after 745 litres and finished at 8.14. At breakpoint for this column length 770 litres has been treated and at this point the pH was 8.8, lower than the pH for the 10cm column at breakthrough. The conditions at breakthrough for all columns and lengths are shown in Table 8.3.

The 30cm column length also follows the sample pattern of lower effluent pHs correlating with higher effluent phosphorus concentrations. The phosphorus concentration was at 0.28mg/l after 659 litres were treated, this rose to 0.66 after 745 litres and finished at 0.95mg/l. at these volumes treated the pH dropped from 9.90 to 9.70, finishing at 9.15. At breakpoint, after 833 litres had been treated the effluent pH was 9.147.

After the column had been rested for a week, the pH of the 10cm column length remained constant. The effluent pH of the 30cm column dropped from 10.693 to 10.213 and that of the 20cm column from 10.064 to 9.557 respectively, these are quite significant changes. The effluent phosphorus concentration remained consistently low throughout this period for the 30cm and 20cm lengths.

Now that all the raw data has been presented, the effluent phosphorus concentrations are plotted again the corresponding calcium concentrations, this is shown in Figure 8.21

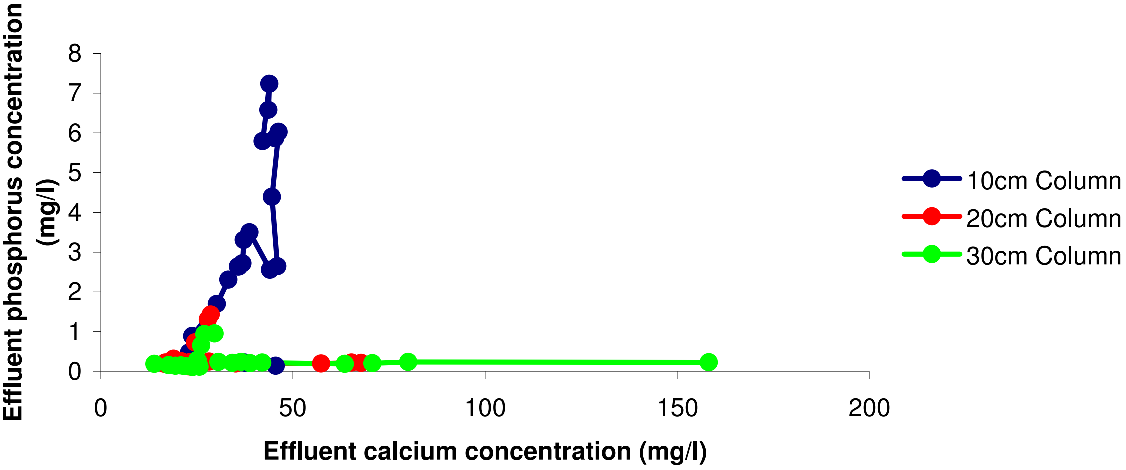


Figure 8.17 Relationship between effluent calcium and phosphorus concentrations for column 3

As with columns 1 and 2 there is a large range of calcium concentrations over which the effluent phosphorus concentrations are very low. Dealing first with the 10cm column the calcium concentration starts at just 42mg/l and then drops to 23mg/l. The calcium concentration then begins to rise again as the effluent phosphorous concentration also rises. This suggests that the reactivity of these pellets is much reduced as they are having a reduced impact on the effluent phosphorus, calcium and pH. The effluent calcium concentration becomes essentially a vertical line at a concentration of 43mg/l, this is just below the influent concentration and shows that here less calcium is being taken out of solution as less phosphorus is being removed. Both the 20cm and 30cm column lengths are exhibiting the start of the same pattern of behaviour as the 10cm column length with their data points laying on top those of the 10cm length.

The dip in phosphorus concentration and rise in calcium concentration due to taking the column offline and resting for the 10cm length can be seen, there is a sharp drop in phosphorus concentration, from 3.50 to 2.55mg/l, as the calcium concentration rises from 38.7 to 44.1 mg/l. To an extent this fits in with the findings of Drizo *et al.* (2002) who suggested that regeneration of the phosphorus removal capacity of an electric arc furnace slag occurred due to the bringing of calcium ions to the surface.

The relationship between effluent phosphorus concentration and effluent pH levels will now be shown in Figure 8.18

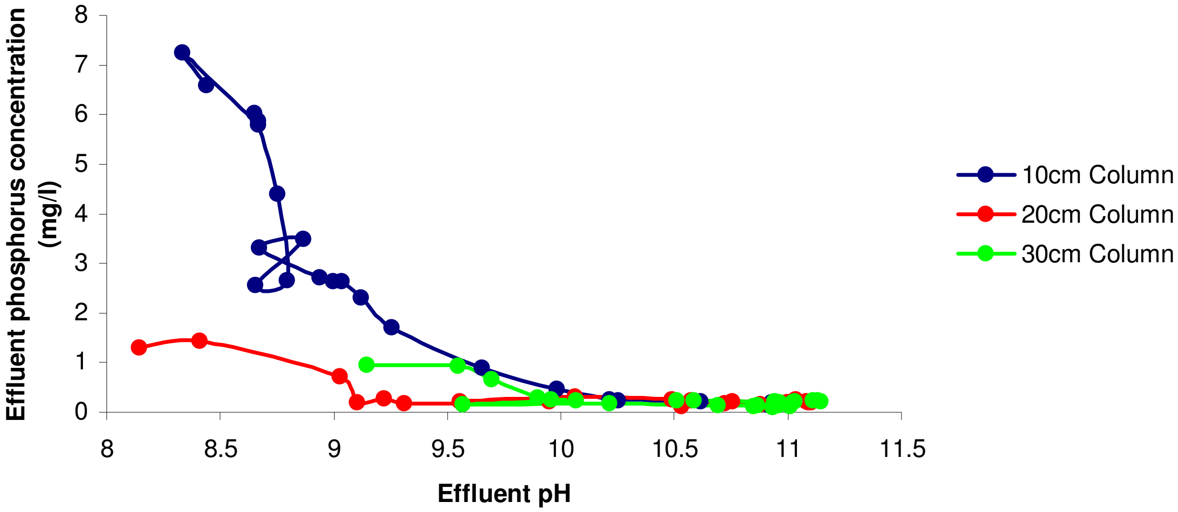
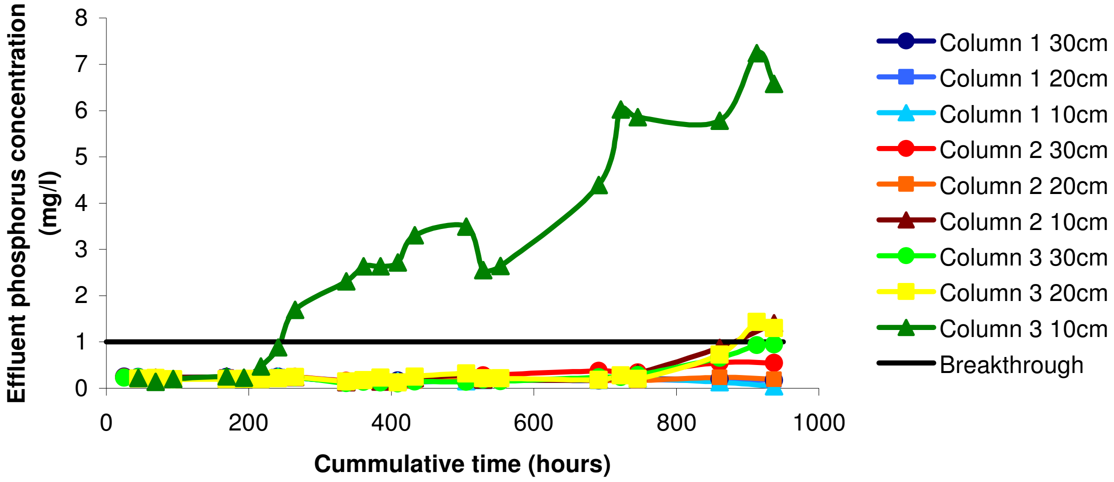


Figure 8.18 Relationship between effluent pH and phosphorus concentrations for column 3

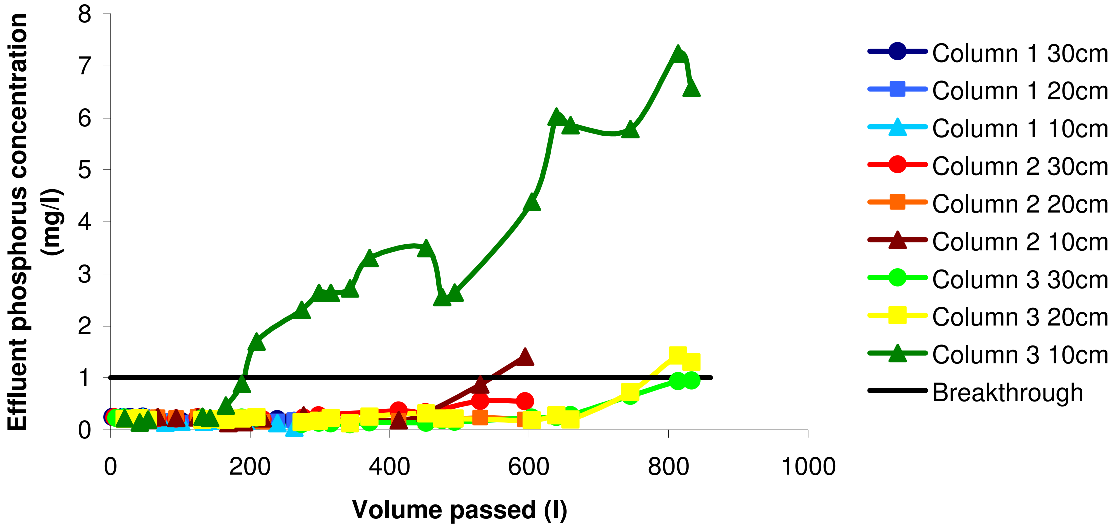
The effluent phosphorus concentration for the 10cm column length rose from 0.227 at a pH of 10.252 to 0.47mg/l at a pH of 9.983 and continues to rise to a concentration of 7.239mg/l as the pH drops to 8.335. The 20cm column shows a similar pattern, but the pH at which the phosphorus concentration begins to rise is 9.029, far lower than that for the 10cm column. As the pH drops from this value to 8.408 the effluent phosphorus concentration rises from 0.724 to 1.434mg/l. The 30cm column length also displays the same behaviour with phosphorus concentrations remaining in the region of 0.2mg/l until the pH dropped to 9.695 where the phosphorus concentration had risen to 0.654mg/l, the phosphorus concentration then rose to 0.949mg/l as the pH dropped to 9.147. Therefore for all column lengths there is a clear relationship between lower pHs and higher phosphorus concentrations.

8.4 Comparison of the three columns

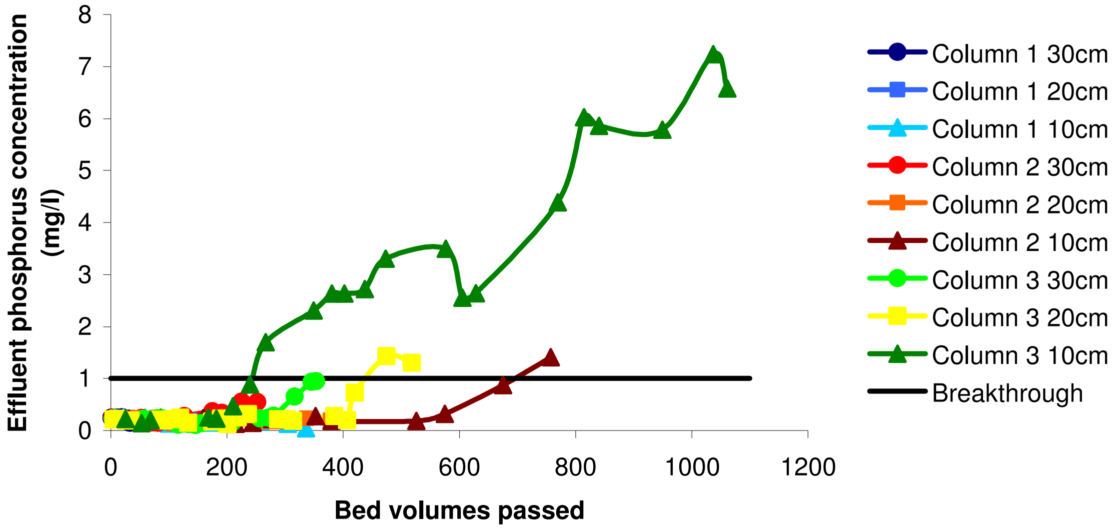
The results for all three columns and all nine column lengths are now directly compared in Figure 8.19. As before firstly the effluent phosphorus concentration will be plotted against test length in hours (a) and volume treated in litres (b) and bed volumes (c).



(a)



(b)



(c)

Figures 8.19 (a), (b) and (c) Effluent phosphorus concentration versus (a) cumulative time and water treated in (b) litres and (c) bed volumes for all three columns

The 10cm column lengths for columns 2 and 3 can be directly compared. Column 2 had a residence time of 6.6 minutes and treated 550 litres before breakthrough, column 3 had a residence time of 4.7 minutes and treated 190 litres before breakthrough. Therefore increasing the residence time and therefore filter size by a factor of 1.4 would result in the filter lifespan increasing 2.9 times. No strong conclusions or comparisons can be made for the column lengths that did not reach breakthrough.

These column results can be compared to the kinetic results from Section 7.2. These kinetic tests used 0.3g of 63-125µm pellets in 800ml, a pellet concentration of 0.375g/l. The initial phosphorus concentration was comparable at 11mg/l. Taking the 10cm length of column 3 as a first example, this length held 886g and in total treated 833 litres, thus can be viewed as a pellet concentration of 1.06g/l. The average retention time for this column length was 4.7 minutes and therefore will be compared to the 5 minute results for the kinetics tests. At the end of the column test, the 10cm length of column 3 had an effluent concentration of 6.579mg/l and had removed 7.55mg/g. After 5 minutes the kinetic tests had reduced the initial concentration to 8.343mg/l which resulted in a phosphorus loading of 7.09mg/g. These results are therefore not dramatically different. The 10cm column of column 2 removed 7.3mg/g with a final concentration 1.411mg/l and a residence time of 6.6 minutes. Interpolating between the 5 and 10 minutes results from the kinetic tests gives a phosphorus loading of 7.63mg/g at a concentration of 8.14mg/l. These two column lengths therefore achieved comparable phosphorus loadings to the kinetic studies with similar retention times. The other column length results have lower phosphorus loading values and are less comparable.

At the 1mg/l breakthrough concentration the Freundlich isotherm for the solids from Horden from Section 6.2 shows a loading of 5.81mg/g. The 10cm length of column 2 is the only value found above this showing that the loadings achieved are not above those that adsorption could achieve, however due to the elevated pHs which will retard anionic adsorption, the decrease in surface area through pelletisation, and the correlation of phosphorus concentration with effluent pH and calcium it seems that calcium phosphate precipitation is still the dominant removal mechanism.

The effluent calcium concentrations for all columns and column lengths are now compared in Figure 8.20.

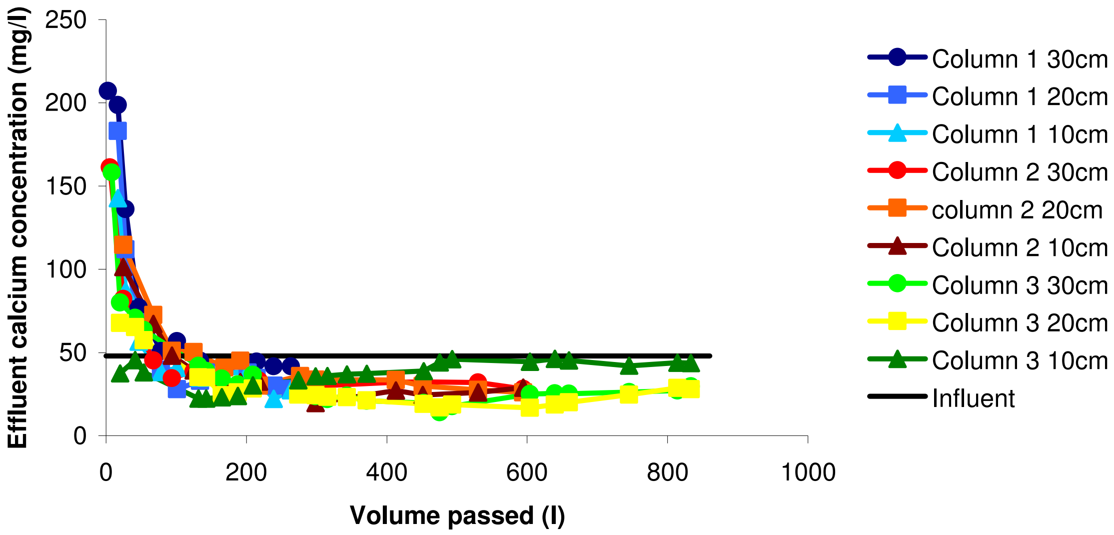


Figure 8.20 Effluent calcium concentration versus volume treated for all three columns, the influent calcium concentration is also shown (48.7mg/l).

All three columns have similar patterns of effluent calcium concentration, with relatively high initial concentrations quickly dropping below the influent concentration and remaining thus. The main point of difference is with column 3, particularly the 10cm column length where at the higher volumes passed the effluent calcium concentration rises towards the influent concentration as discussed in Section 8.3.2.

In Section 7.3.3 it was shown that the 63-125µm pellets were releasing between 47 and 50mg/g (mg of calcium per gram of pellets). In Section 7.3.4, pellets were found to release 114-146mg/g of calcium. The calcium released by pellets in these columns can be calculated from the following equation.

(Calcium in effluent) – (Influent Calcium) = (Calcium released by pellets) - (Calcium consumed by precipitation) Equation 8.1

The total calcium effluent is determined by integrating underneath the relevant data set in Figure 8.22. The influent calcium is determined by multiplying the influent calcium concentration (48.67mg/l) by the total volume treated. The calcium consumed by precipitation is calculated from knowing the mass of phosphorus removed and using the 1.67 Ca:P molar ratio for HAP precipitation. The calculation of these three values therefore allows the determination of the calcium released by the pellets. The results of this calculation for all nine column lengths are shown in Table 8.1 wherein 1:30 represents the 30cm length of column 1 and so on.

Table 8.1 Data for calculation of calcium released by pellets

Column Length	1:30	1:20	1:10	2:30	2:20	2:10	3:30	3:20	3:10
Total Ca effluent (g)	16.96	12.87	11.72	21.95	24.30	20.65	25.61	22.22	31.48
Influent Ca (g)	12.82	12.82	12.82	28.93	28.93	28.93	40.54	40.54	40.54
Difference (g)	4.13	0.05	-1.11	-6.98	-4.63	-8.28	-14.94	-18.32	-9.07
Ca for P precipitation (g)	6.25	6.26	6.26	13.95	14.10	13.88	19.60	19.51	14.42
Ca Released (g)	10.38	6.30	5.16	6.97	9.47	5.61	4.67	1.19	5.35
Ca released (mg/g)	3.90	3.55	5.82	2.62	5.34	6.32	1.76	0.67	6.04

Table 8.1 shows that the calcium released by these pellets ranges from 0.67-6.32mg/g. Compared to the range of values from Chapter 7 (47-50mg/g from Section 7.3.3 and 114-146 from Section 7.3.4) these values are very low. For 7 out of the 9 column lengths it was found that the total mass of calcium leaving the column was actually lower than the total mass of influent calcium. This net loss of calcium shows that the precipitation reactions are consuming more calcium than the pellets are releasing. The influent calcium concentration is therefore important to the performance of these columns and the pellets primary role is as a source of hydroxide ions.

The variation of effluent pH with volume of water treated for all column lengths is explored in Figure 8.21

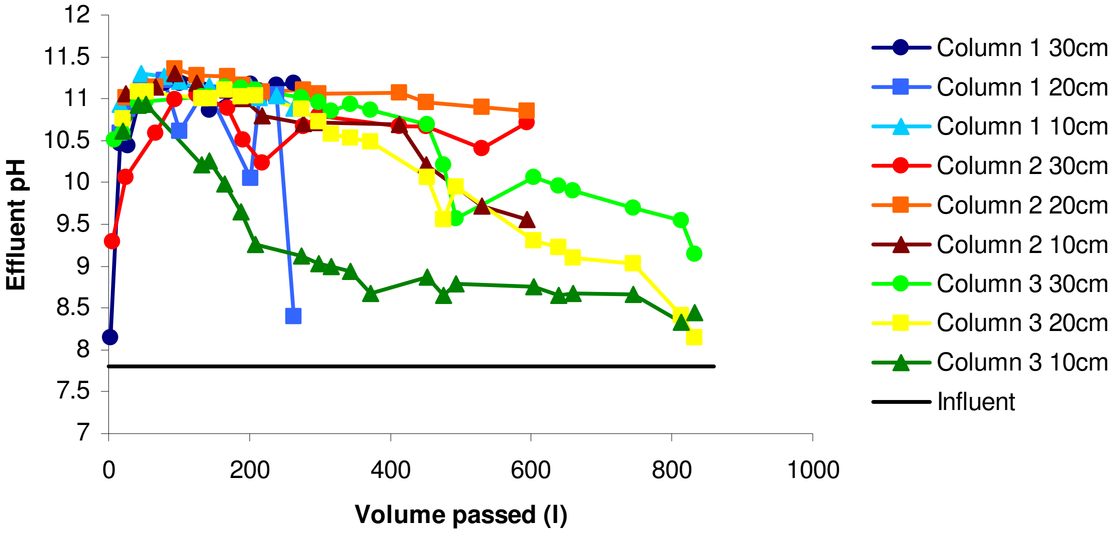


Figure 8.21 Effluent pH versus volume treated for all three columns, the influent pH (7.9) is also shown.

The majority of effluent pH values early on can be seen to be similar, the pH values for column lengths then drop below the others in the order that they reached breakpoint. Dobbie *et al.* (2009) carried out phosphorus removal pilot plant tests on pellets also made from the addition of cement to waste AMD, however effluent pHs were not recorded. Mayes *et al.* (2009) also based at Newcastle University carried out column tests using similar pellets to Dobbie *et al.* (2009) to remove zinc from mine water. They found an average effluent pH of 8.7, with the early stages of the test reaching a pH of 11.9. The results in this chapter found an average effluent pH value of 10.83 for column 1, 10.77 for column 2 and 10.01 for column 3, with an overall average of 10.54. There are many experimental differences between the experiments carried out in support of the current thesis and that of Mayes *et al.* (2009) such as pellet size but clearly these similar pellets are both elevating effluent pH. Mayes *et al.* (2009) suggest that the problem of high effluent pH could be avoided by washing of the pellets, changing the cement binder used, perhaps to a silicate based cement or by reducing the amount of cement used. These are all viable options but this thesis and other studies such as Berg *et al.* (2005) suggest that the calcium and hydroxide ions present in the cement are the essential ingredients. There may be a compromise between lower pHs and yet retention of a decent removal efficiency. Virotec have also reported this problem of elevated pHs with their

Bauxsol technology and have also suggested that a change in binder could overcome this problem.

The effluent phosphorus concentration for all column lengths is plotted against the relevant calcium concentrations in Figure 8.22

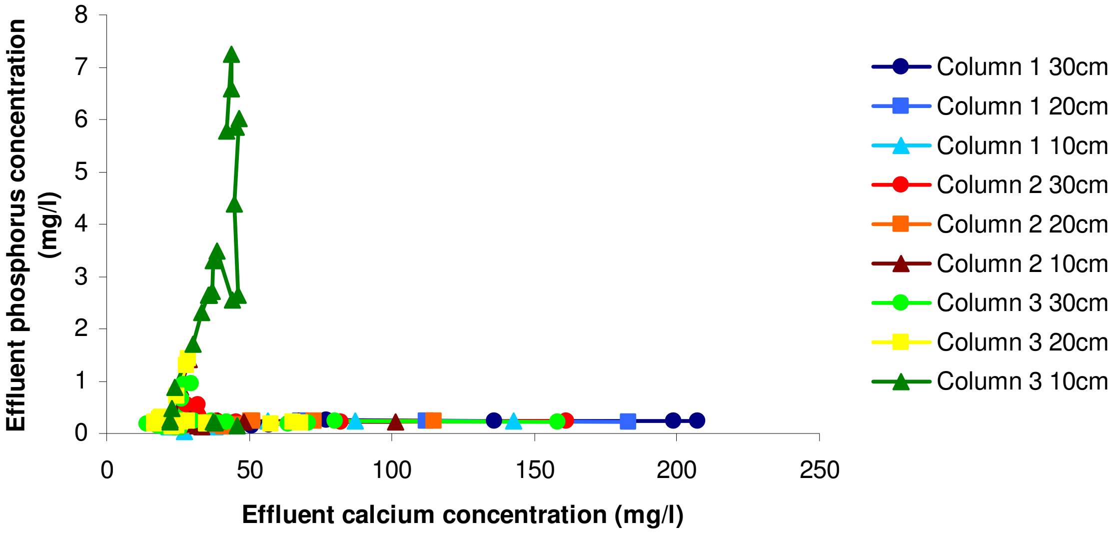


Figure 8.22 Effluent phosphorus concentration versus effluent calcium concentration for all nine column lengths.

Figure 8.22 shows that the relationship between calcium and phosphorus concentrations was found to be essentially universal for all nine column lengths. Phosphorus concentrations were consistently low over a large range of higher calcium concentrations and both the calcium and phosphorus concentrations were found to rise together. The effluent calcium concentrations at breakpoint were found to be relatively similar ranging from 23.8-29.7mg/l for all four column lengths that achieved breakthrough, the conditions at breakthrough are summarised in Table 8.3. The effluent phosphorus concentrations are compared to the effluent pH levels in Figure 8.23.

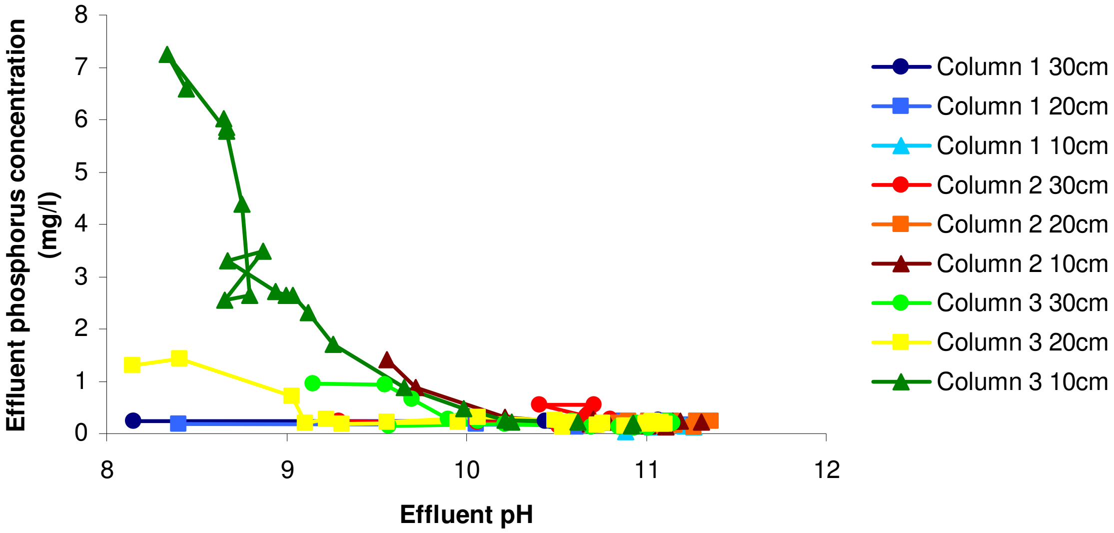


Figure 8.23 Effluent phosphorus concentration versus effluent pH for all nine column lengths.

There is a general trend between effluent pH and phosphorus concentration in that lower pHs are correlated with higher phosphorus concentrations. There are exceptions to this trend, with the 20cm and 30cm lengths of column 1 both reporting low pH values for low phosphorus concentrations. Although there is a general correlation between effluent pH and phosphorus there does not seem to be an absolute pH value at which the phosphorus concentrations begin to climb. These results do tie with the findings of Johansson and Gustafsson (2000) who found that a pH of above 9 was required for efficient calcium phosphate precipitation.

The data at points of interest for all column lengths are presented in Table 8.2 so as to allow quick comparison. 1:10 represents the 10cm length of column 1 and so on.

Table 8.2 Comparison of data at all points of interest for all three columns

Column	1:10	1:20	1:30	2:10	2:20	2:30	3:10	3:20	3:30
Flow rate (l/hr)	0.28	0.28	0.28	0.60	0.60	0.60	0.87	0.87	0.87
Contact time (minutes)	13.8	27.7	41.5	6.6	13.1	19.2	4.7	9.4	14.1
Volume treated (m^3)	263	263	263	544	544	544	833	833	833
Bed volumes treated	336	168	112	757	380	252	1061	518	354
P conc at end (mg/l)	0.04	0.18	0.17	1.41	0.18	0.55	6.58	1.30	0.95
P loading at end (mg/g)	3.28	1.64	1.09	7.3	3.69	2.43	7.55	5.10	3.42
P loading at end (kg/m^3)	3.70	1.85	1.23	8.24	4.17	2.74	8.52	5.76	3.86
% capacity at end (%)	5.5	2.7	1.8	12	6.2	4.1	15	8.5	5.7
Ca conc at end (mg/l)	27.24	28.07	41.69	28.77	25.87	28.01	43.69	27.88	29.66
High ph	11.30	11.22	11.19	11.31	11.36	11.04	10.93	11.10	11.14
Low ph	10.88	8.40*	8.15*	9.56	10.85	9.29	8.34	8.14	9.15
Avg pH	11.10	10.64	10.76	10.71	11.01	10.54	9.29	10.19	10.51

* indicates an apparent outlier

The important data for the four column lengths which reached the breakpoint are presented in Table 8.3

Table 8.3 Comparison of conditions at breakpoint

Column	Column 2 10cm	Column 3 30cm	Column 3 20cm	Column 3 10cm
Flow rate (l/hr)	0.60	0.87	0.87	0.87
Residence time (minutes)	6.6	14.1	9.4	4.7
Volume at breakpoint (l)	550	833	770	190
Bed volumes at breakpoint	700	352	490	242
Phosphorus loading at breakpoint (mg/g)	6.77	3.42	4.75	2.32
Phosphorus loading at breakpoint (kg/m^3)	7.68	3.86	5.36	2.62
Fractional capacity at breakpoint (%)	11	5.7	7.9	4.5
Calcium concentration at breakpoint (mg/l)	26.9	29.7	26.0	23.8
pH at breakpoint	9.67	9.15	8.81	9.65

The average calcium concentration at breakpoint was 26.6mg/l with a standard deviation of 2.4mg/l representing 9% of the average, this suggests calcium concentration to be an important factor. The average pH at breakpoint was 9.32, with a standard deviation of 0.42 representing 4.5% of the mean suggesting pH is also an important factor, this particularly resonates with the findings of as Johansson and Gustafsson (2000) who state that a pH of above 9 is required for efficient calcium phosphate precipitation. The importance of calcium concentrations and pH fit in with the conclusions reached in Chapter 7 of this thesis and also many other studies such Lu *et al.* (2009) and Aygei *et al.* (2002).

8.5 PHREEQCI

The software PHREEQCI was used to calculate saturation indices of precipitates and likely species in solution for a range of conditions related to the column tests presented in this chapter. The chosen concentrations and conditions were inputted into the program which then calculates the molality of species and the saturation indices of predicted precipitates.

Data was inputted for the concentrations of phosphorus, calcium, potassium and carbonate ions, the pH and temperature were also defined. The carbonate concentration was estimated from the influent calcium concentration of 48.67mg/l. If it is assumed that this was introduced as $CaCO_3$, of this, the carbonate ion represents 60% by weight. An influent carbonate (CO_3^{2-}) concentration of 73.0mg/l was therefore used. The potassium concentration was held at a constant 12.58mg/l for all analyses, this is the concentration resulting from the known addition of KH_2PO_4.

8.5.1 SI variation with pH

All tests upon pellets containing cement carried out in support of this thesis have shown that pH is an important factor in the removal of phosphorus through calcium phosphate precipitation. The importance of pH is also reported by many papers from the literature review such as Johansson and Gustafsson (2000), Oguz *et al.* (2003) and Chen *et al.* (2007). PHREEQCI was used to predict likely precipitates and to predict the variation of their saturation indices with pH. The program was operated with the influent concentrations of phosphorus 11.23mg/l, potassium 12.589mg/l, carbonate ion 72.93mg/l and temperature at 25°C. Three calcium concentrations were used so as to allow some appreciation of the importance of both pH and calcium. The three concentrations used were the influent concentration of 48.67mg/l a lower concentration of 20mg/l and a higher one of 100mg/l. The pHs values tested at were 6,7,8,9,10 and 11. PHREEQCI predicted three precipitates namely aragonite ($CaCO_3$) this is represented as AG in Figure 8.24, calcite ($CaCO_3$) represented as CT and hydroxyapatite ($Ca_5(PO_4)_3OH$) represented as HAP. The prediction of HAP as a likely precipitate backs up the conclusions of Chapter 7 of this thesis where strong evidence for this precipitate has been found. Many studies on the use of calcium containing materials to remove phosphorus reported in Chapter 3 such as Chen *et al.* (2007))and Kim *et al.* (2006) also predicted HAP as an end product.

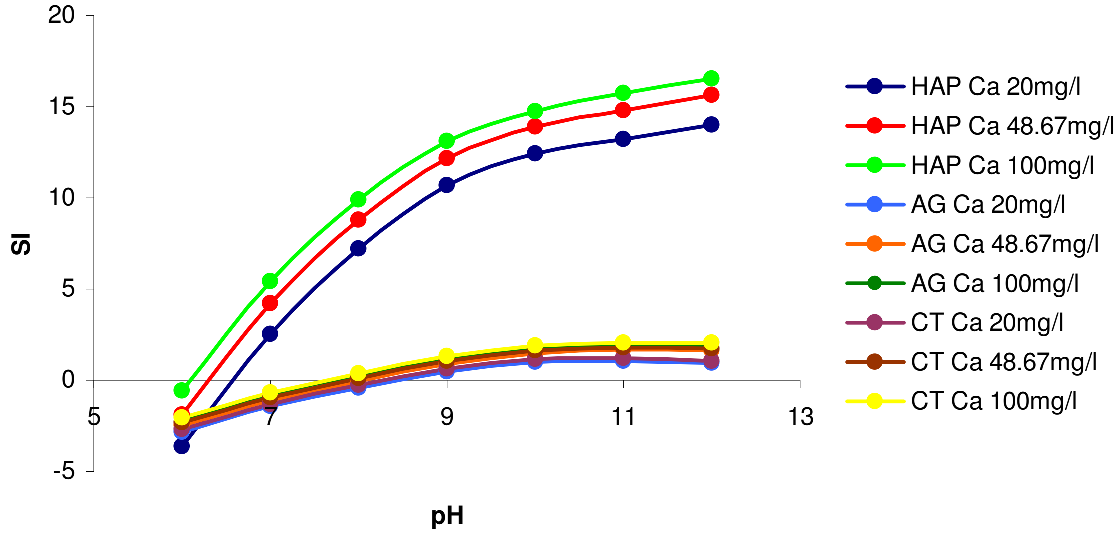


Figure 8.24 Variation of SI with pH for hydroxyapatite (HAP) aragonite (AG) and calcite (CT)

All three precipitates show a positive correlation between pH and SI. This correlation is particularly pronounced for HAP. At a pH of 6 the SI of HAP for all three calcium concentrations is negative, thus predicting no precipitation. The SI values then rise quickly until a pH of 9 whereafter the rate of increase in SI drops. The difference in SI for HAP due to change in pH can be seen to be much more dramatic than the change in SI due to the change in calcium concentration, therefore for the situations studied here, pH is the more important factor. The SIs of both aragonite and calcite remain low, becoming positive after a pH of 8.

8.5.2 SI variation with calcium concentration

The variation of the SIs of precipitates with calcium concentration is now more closely examined. Aside from the calcium concentration and pH all values were kept as in Section 8.5.1. The program was ran for three different pH values, the influent of 7.9, 9 and 11. For each of these, calcium concentrations of 10,20,40,60,80,100 and 120mg/l were used. The phosphorus concentration was set at 11.23mg/l and so the molar ratios between calcium and phosphorus were 0.69, 1.38, 2.76, 4.14, 5.52, 6.90 and 8.28, the stoichiometric ratio for HAP is 1.67. The temperature was set at 25^{o}C, the carbonate ion concentration at 72.93mg/l and the potassium concentration at 12.58mg/l. The results for this analysis are shown in Figure 8.25.

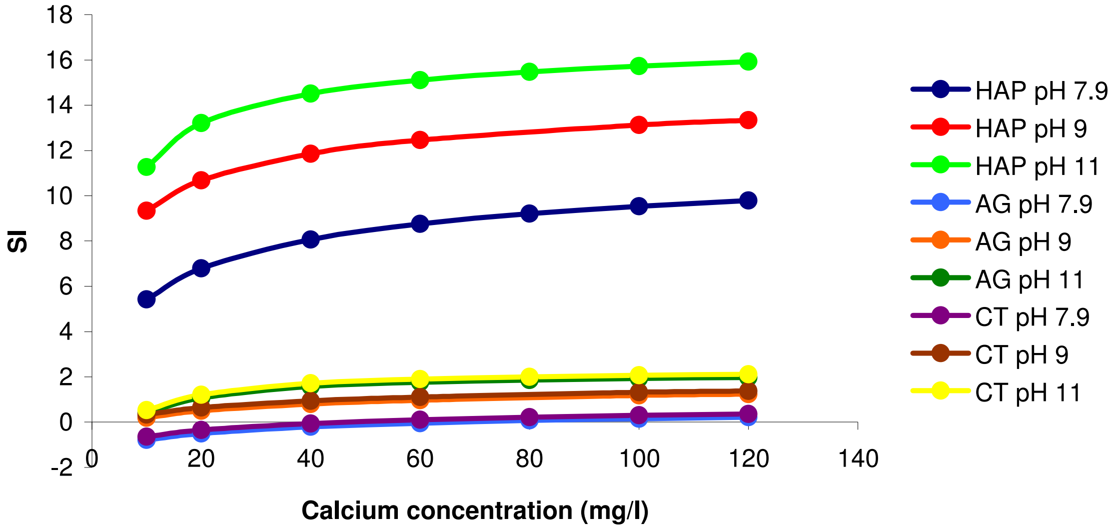


Figure 8.25 Variation of SI with calcium concentration for hydroxyapatite (HAP) aragonite (AG) and calcite (CT)

As expected from the results in Figure 8.24 there is a positive correlation between calcium concentration and SI for all three precipitates. After the 2nd data point for the HAP data streams (20mg/l) the stoichiometric ratio for HAP is passed. It can be seen that after this point the rate of change of SI drops. The change in SI for HAP due the change in calcium concentration is relatively small compared to the change due the different pHs used for each data set. This is supported by the results from Figure 8.24 and again suggests pH as the more important variable. The SIs for the two $CaCO_3$ precipitates again follows a similar pattern with a positive correlation over a small, low range of SIs.

8.5.3 SI variation with temperature

The variation of saturation indices with temperature was also determined. All tests were carried out at ambient laboratory conditions therefore it is important to investigate the potential impact of temperature over a range. Were this technology to be implemented at a WWTWs temperatures in the range of 0-30°C could be expected to be encountered and so temperatures in this range were inputted. Again three data streams were calculated at a pH of 7.9, 9 and 11. All other variables were fixed at their influent values. This data is plotted in Figure 8.26.

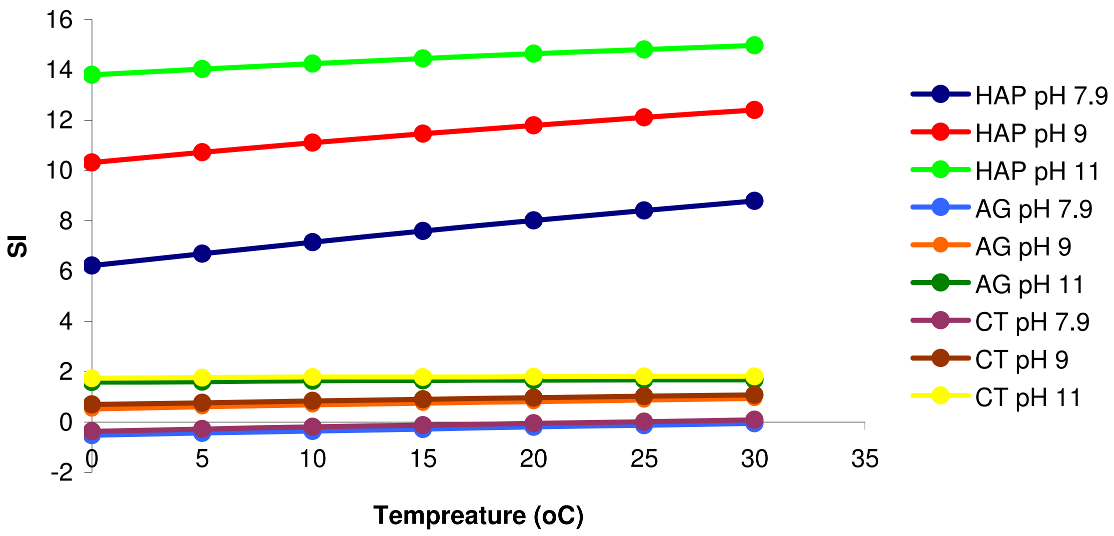


Figure 8.26 Variation of SI with temperature for hydroxyapatite (HAP) aragonite (AG) and calcite (CT)

HAP is shown to have a positive correlation between SI and temperature in Figure 8.26 and whilst the correlation is positive, the effect of temperature on the predicted SIs is relatively slight. The effect is slightly more pronounced at the lower pHs. The effect of temperature on the removal efficiency of this technology would therefore not be expected to be large. In terms of the predicted precipitation of the aragonite and calcite the effect of temperatures on the SIs can be seen to be minimal.

8.5.4 SI variation with carbonate concentration

The variation of the SIs with carbonate ion concentration were determined to see if PHREEQCI predicted any negative patterns as the calcium precipitated with the carbonate rather than with the phosphorus. The calcium in the first instance was maintained at the influent concentration of 48.67mg/l and just the carbonate ion concentration was varied from 40-100mg/l. For the second analysis the calcium concentrations ranging from 10-120mg/l were used and the carbonate concentration was calculated from these based on them originating from $CaCO_3$. Firstly the results for the variation of solely the carbonate ion are shown in

Figure 8.27. Data streams are presented for the influent pH of 7.9 and pH values of 9 and 11. All other variables were fixed at their influent values as before.

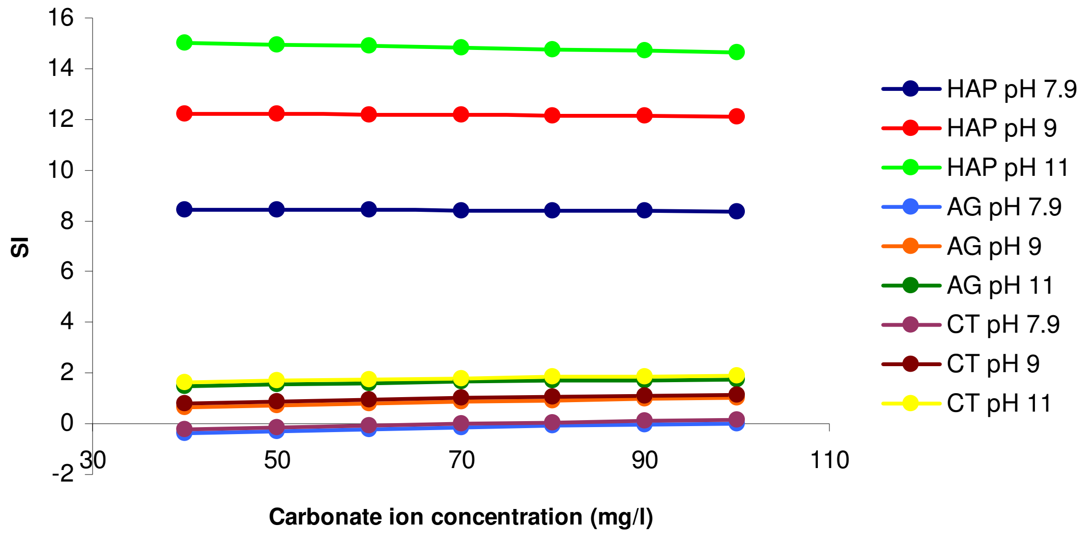


Figure 8.27. Variation of SI with carbonate ion concentration for hydroxyapatite (HAP) aragonite (AG) and calcite (CT)

There is a very slight negative correlation between carbonate ion concentration and SI for HAP. This relationship is very slight however and suggests that the carbonate levels studied should not dramatically affect the efficiency of this technology. As would be expected increased amounts of carbonate are predicted to increase the amounts of $CaCO_3$ precipitates, however this relationship is shown to be slight. Both the carbonate ion and calcium concentrations are now varied, the calcium concentrations ranging from 10-120mg/l, on a $CaCO_3$ basis, this resulted in carbonate ion concentrations of 15-180mg/l. Figure 8.28 shows the results of this analysis.

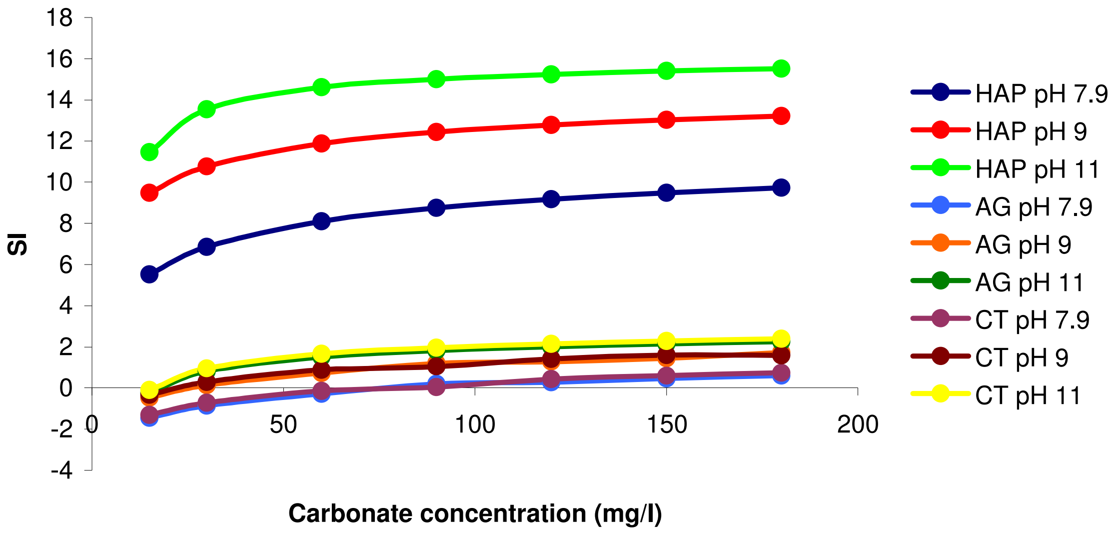


Figure 8.28 Variation of SI with carbonate ion concentration for hydroxyapatite (HAP) aragonite (AG) and calcite (CT)

When the carbonate ion and calcium concentrations are varied in line with each other a positive correlation with the SI of all three precipitates is found. The pattern and values found for HAP are very close to those shown in Figure 8.27 where just the calcium concentration was varied. Figure 8.31 also shows that in this case the SIs of the $CaCO_3$ precipitates are again predicted to increase with increasing concentrations of carbonate ions and calcium.

8.5.5 SI variation with phosphorus concentration

Analysis was carried out for phosphorus concentrations of 1,5,10,20,30,40 and 50mg/l. Three data streams were calculated, one at 20mg/l calcium concentration, one at 48.67mg/l and one at 100mg/l. The data stream with a 20 mg/l calcium concentration represents a range of Ca:P molar ratios of 0.31 to 15.5. The data with the influent calcium concentration of 48.67mg/l results in a range of molar ratios of 0.75 to 37.7 and the 100mg/l calcium concentration data 1.55 to 77.5. All calculations were carried out at a pH of 11, this is the highest found in tests and previous PHREEQCI calculations showed it to results in the highest SIs. Other variables were fixed as before.

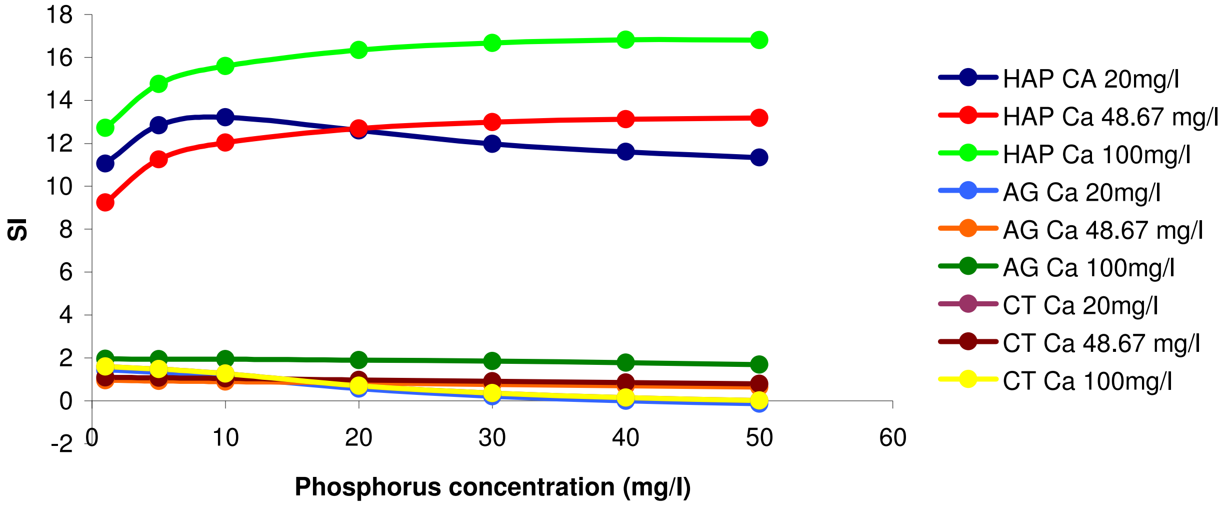


Figure 8.29 Variation of SI with phosphorus concentration for hydroxyapatite (HAP) aragonite (AG) and calcite (CT)

For the HAP data streams, the two with the higher calcium concentrations (48.67 and 100mg/l) show an early strongly positive correlation of SI with phosphorus concentration which then appears to reach a plateau. For the data stream with just 20mg/l calcium the same initial positive correlation is shown where after the SI values begin to drop. The SI drops as the Ca:P ration drops from 1.55 to 0.78, after this point, the SI values drop as do the Ca:P ratios. The $CaCO_3$ precipitates show a slight negative correlation between SI and phosphorus concentration.

8.5.6 Speciation

PHREEQCI was also used to predict what species are likely to be found in solution. pH has been shown to have the largest effect on the SI of HAP and so its effect on the species present was also determined. The species present at a pH of 9 and of 11 were determined, these roughly equating to the lower and upper pH limits found experimentally. All other variables were fixed at their influent values from the column tests. Figure 8.30 presents the predicted species present in terms of their molality (moles per kg of water) this is wide ranging and so the log of the molality is plotted upon the y-axis. Only predicted species containing calcium or phosphorus are shown.

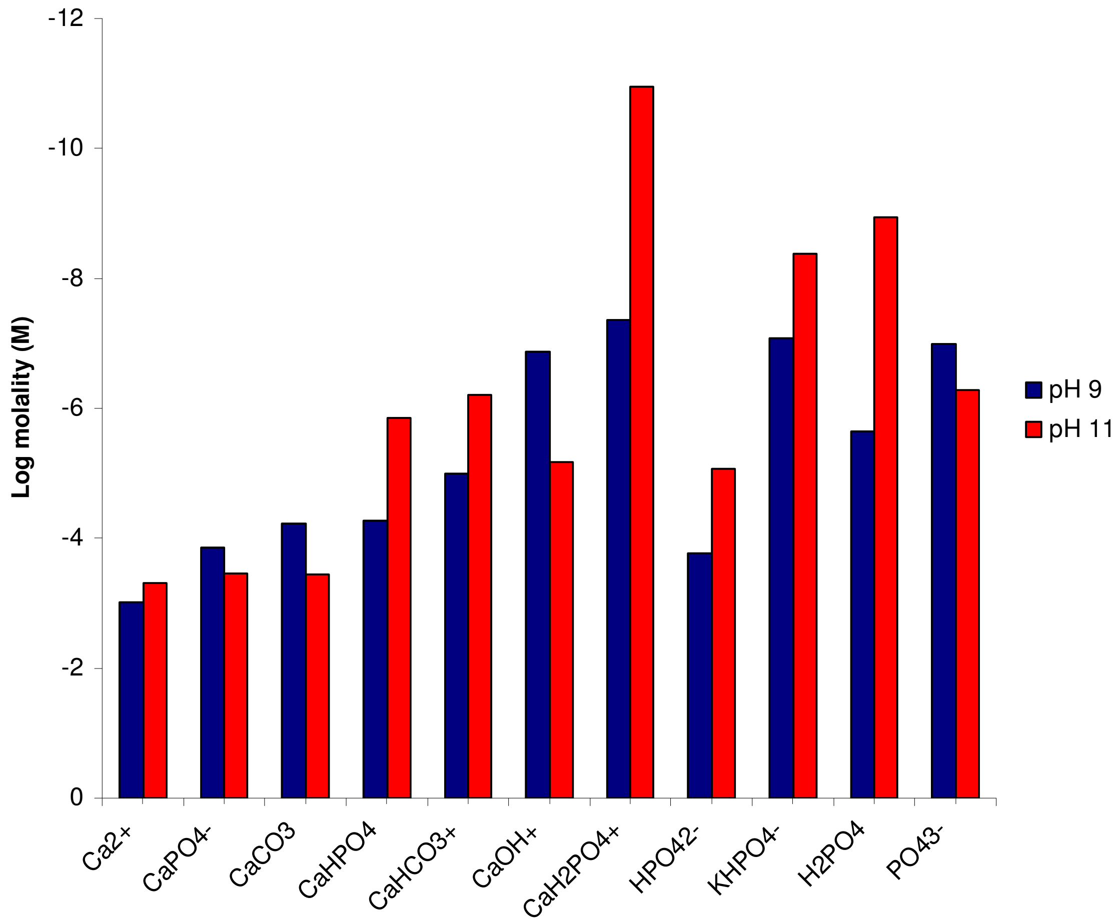


Figure 8.30 PHREEQCI predicted calcium and phosphorus species, presented as the log of their molalities.

Song *et al.* (2002) who carried out similar analysis using the same program found a general decrease in the "acidic" species such as CaH2PO$_4$ and H_2PO and an increase in the "basic" species $CaPO_4$ ¸CaOH and PO_4. The results for the analysis do not follow the same pattern as (Song *et al.* 2002), this difference can be attributed to the fact that Song *et al.* (2002) did not include the carbonate ion in their calculations.

8.6 Up scaling models

This section presents simplistic up scaling calculations and the calculations of two up scaling models, namely the Empty Bed Contact Time (EBCT) method and the Bed-Depth Service Time (BDST) method. The details behind these two methods are shown in Section 4.3.2.

Basic up scaling calculations can be carried out for the four bed lengths that reached breakpoint. Starting with the 30cm length of column 3, this had an area flow rate of 10.76l/hr/m^2. Using data for the Moreton WWTWs (Table 8.5) with a Dry Weather Flow (DWF) of 1086m^3/day, this would required an area of 408.5m^2 to maintain the same area flow rate. At the influent of 11.23mg/l and a 30cm bed depth this would last the same time as this column lasted until breakthrough i.e. 973 hours or 40.5 days. This filter would hold 138.4 tonnes of pellets. The results for the other column lengths are calculated in the same fashion and all are presented in Table 8.4.

Table 8.4 Basic up scaling data

Column	1:10	1:20	1:30	2:10
Area flow rate (l/hr/m^2)	10.8	10.8	10.8	76.4
Surface area (m^2)	408.5	408.5	408.5	592.4
Operational lifespan (hrs)	275	881	973	879
Pellet tonnage	46.1	92.3	138.4	66.9
Tonnes/hour	0.17	0.10	0.14	0.08

The most efficient column length is the 10cm length of column 2. The 66.9 tonnes of pellets would require 31.4 tonnes of dry Horden solids, this column would treat water for 36.6 days during which time the Horden plant generates 38.3 tonnes of waste on a dry basis (Hancock 2004), therefore there would be sufficient material to replace the pellets. However a relatively small WWTWs consuming the total output of a minewater treatment plant suggest that large scale implementation of this technology is not likely to be feasible.

Table 8.5 Data for the Moreton WWTWs (Coulton 2008)

DWF (m^3/day)	Population equivalent	Indicative Total phosphorus load (kg/day)	Average influent P concentration (mg/l)
1086	4157	10.4	9.6

8.6.1 Empty Bed Contact Time

Figure 8.31 shows the Empty Bed Contact Time (EBCT) plot for all three lengths of column 3 and the 10cm length of column 2. The EBCT in minutes is plotted upon the x-axis and the usage rate in terms of kg/m^3 upon the y-axis. The theory behind the EBCT plot is presented in Section 4.3.2.1.

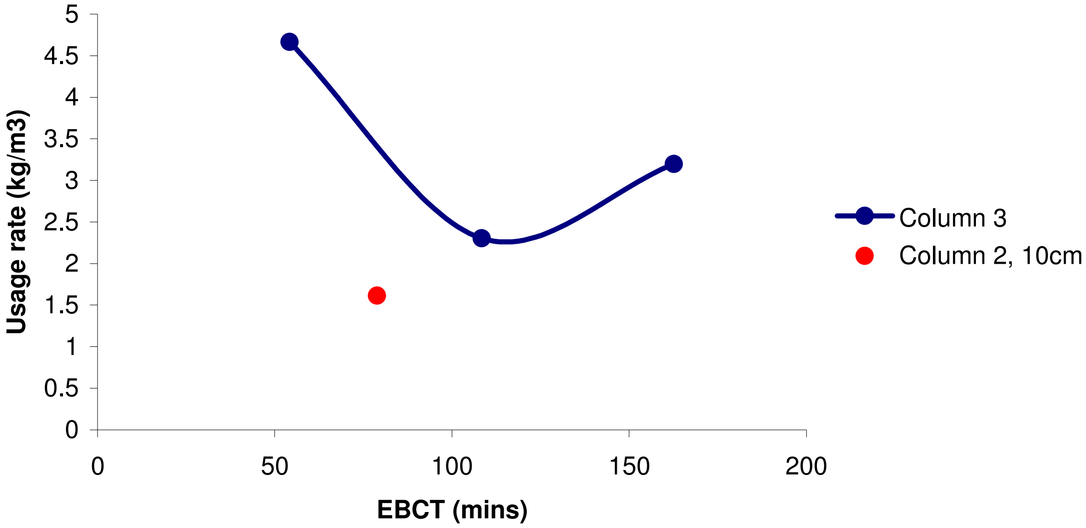


Figure 8.31 Empty Bed Contact Time plot for the four column lengths that reached breakpoint

For column 3, the EBCT method does not behave as expected. Classically as the EBCT increases, the usage rate drops and plateaus, as shown in Figure 4.6. This pattern is not seen here as the 30cm column length contained 33% more pellets than the 20cm column, yet only treated 8% more water and therefore in fact had a higher usage rate than the 20cm column. This ties in with the theory that any material above the mass transfer zone was not taking part in removal, yet was still having the hydroxide and calcium ions leached out. Thus when the mass transfer zone moved up to these pellets their ability to remove pellets was already reduced and breakthrough was quickly achieved. These results therefore suggest that large, tall filters holding a large amount of pellets may not be suitable for the use of this material.

The 10cm column length from column 2 has the lowest usage rate at 1.61kg/m^3 with an EBCT of 78.9 minutes, this compares to 4.67kg/m^3 at an EBCT of 54.2 minutes. Therefore an increase in EBCT, or filter size, of 1.45 times results in a 2.9 fold drop in the usage rate. To treat water at Moreton WWTW, with an EBCT of 78.9 minutes would require a filter size of 123.39m^3 to treat the daily flow averaged over 24 hours. This size filter would contain 139.30 tonnes of pellets. At the usage rate of 1.61kg/m^3 this would treat 224273 m^3 of water, equivalent to 206 days treatment at Moreton. This is equivalent to 0.67 tonnes per day, compared to 1.83 tonnes for the results shown in Table 8.4. This may be an over estimation of the true lifespan of the column, as any pellets uninvolved in removal may still be having their calcium and hydroxide ions washed out to an extent. Thus the choice of plant may be very important to maximise the potential of this material.

8.6.2 Bed Depth Service Time

Figure 8.31 shows the BDST plot for column 3. The three bed depths are plotted upon the x-axis and the time until breakpoint upon the y-axis. The full theory behind this plot is shown in Section 4.3.2.2

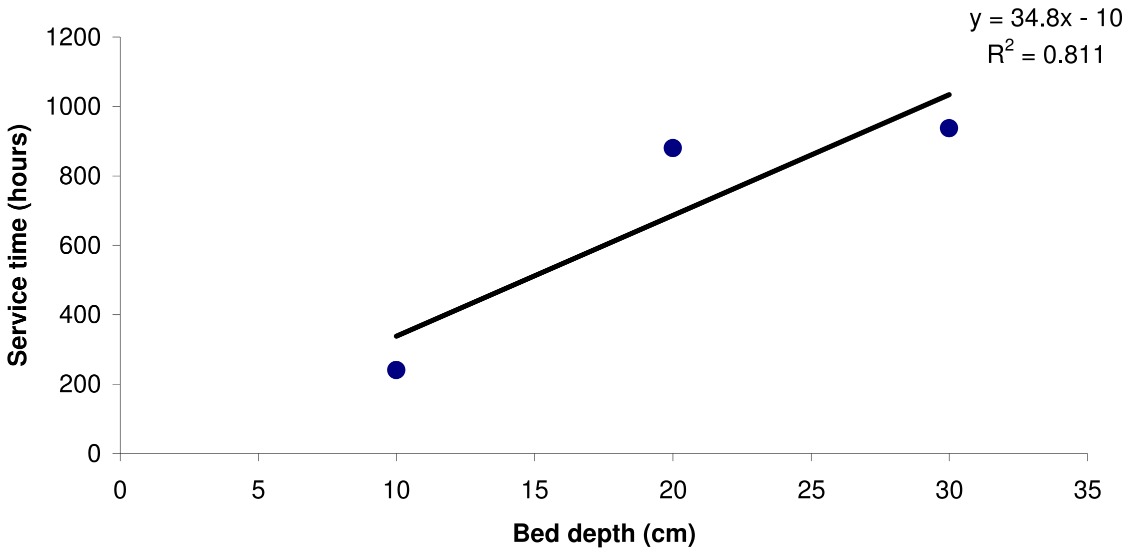


Figure 8.32 Bed Depth Service Time plot for column 3

The linear line of best fit does show a reasonable R^2 value but, as with the EBCT plot, the increase in bed depth from 20 to 30cm has resulted in a minor increase in service time of 880 to 937 hours. Figure 8.31 could be viewed as the service time reaching a plateau as the bed depth passes 20cm where after little benefit is gained from deeper columns. The pellets above the mass transfer zone having their hydroxide and calcium ions washed out before they get a chance to take part in removal. The benefit from increasing the bed depth from 10 to 20cm can be seen as the service time rises from 241 hours to 880 hours. The apparent plateauing of service time suggest that for the flow rate studied (0.87l/hour) this 20cm column length would appear to be the optimum.

Although it appears that the BDST theory may not be completely applicable to this data, the calculations are still carried out. The theory behind the BDST method is discussed in Section 4.3.2.2. The line of best fit from Figure 8.32 gives a slope of 34.8, from Section 4.3.2.2

$$Slope = \frac{N_o}{C_o u}$$

The adsorptive capacity, No (mass per unit volume) can then be calculated since the linear flow rate and initial concentration are both known, this results in a No value of 0.498 kg/m^3. This value is much lower than those loadings found experimentally in this chapter (1.23-8.52kg/m^3). The rate constant can then be calculated from the intercept, b

$$b = \frac{\ln\left(\frac{Co}{Cb} - 1\right)}{kC_o}$$

This results in a value of 20.74 (kg/m^3)/hr for the rate constant

And therefore the BDST equation for this column is

$$t = \frac{0.498}{Cou}\left[L - \frac{u}{20.74 * 0.498}\ln\left(\frac{Co}{Cb} - 1\right)\right]$$

By substituting t=0 into the above equation the Mass Transfer Zone Length was determined as 0.29m, this is essentially the complete length of the column, and again suggests that the BDST model may not be suitable for this material as the results indicate the progression of a much smaller mass transfer zone.

If the service time for a column is set as 30 days (720 hours) and the area flow rate is maintained the same at 110.76 l/hr/m^2 with the initial and breakthrough concentrations as before a bed depth of 20.85m is given. To treat the 1086 m^3 of daily flow from Table 8.4 which is equivalent to an average flow of 12.57l/sec, this divided by the area flow rate of 110.76 l/hr/m^2 (0.031 l/sec/m^2) results in a column area of 408.55m^2 is. Thus a circular column would have a diameter of 22.8 metres. These are huge dimensions and result in a column with a volume of 8518m^3 which would hold 9617 tonnes of pellets and according to this model treat just a months worth of water. These values suggest the BDST model may not be used for this setup.

The general lack of applicability of these two models shows the complex nature of the prediction of the lifespan of these columns. The material not directly involved in the removal of phosphorus appears to still have its reactivity reduced through the washing out of calcium and hydroxide ions and therefore there is not a linear relationship between bed depth and the service time of the column. Although there does appear to be a distinct mass transfer zone by the time it moves up, the reactivity of the pellets it moves into has been reduced and little further removal occurs.

8.7 Plant Options

The results suggest that a classic column type filter may not be suitable for the use of this material. The reactivity of this material appears to be reduced through the dissolution of the calcium and hydroxide ions and when the material is above the MTZ, this dissolution occurs without offering any benefit towards phosphorus removal. Therefore shallow beds may be the best design for this technology.

Another problem that a column type setup could encounter is the potential build up of organic matter upon the filter resulting in clogging. (Dobbie *et al.* 2009) who used similar pellets in a pilot plant at a WWTWs found that they had to weekly remove organic matter from their filter to avoid clogging. The calcium carbonate crust found in this thesis and also by (Mayes *et al.* 2009) could also cause clogging of a filter.

Heal *et al.* (2004) viewed the potential of AMD solids to be used in a wetland situation and Dobbie *et al.* (2009) directly tested this. A wetland could be a viable plant option for this technology. A wetland could have the benefit of minimal operator input as, depending on the size, there could be an interval of years between having to refresh the substrate. The retention times would likely be higher than those tested here and so larger pellets may be used to offer a slower release of calcium and hydroxide ions and thus increase the lifespan of the wetland. The problem of reducing the reactivity of the pellets not involved in removal would still be present however.

Cooper *et al.* (1996) suggest a size of 1m^2/PE (Population Equivalent) for BOD control using a wetland. A typical depth of 0.6m is also given, therefore, for the Moreton treatment works (see Table 8.4) A wetland 0.6m deep with a surface area of 4157m^2 would be required, giving a total volume of 2494m^3. This would result in an EBCT of 10.5 hours. This size filter would hold 2816 tonnes of pellets. Using the highest loading at breakpoint found from the column tests (6.77mg/g from column 2) this mass of pellets would be capable of removing

19064kg of total phosphorus. The Moreton works treats 1086 m^3/day, at 10mg/l phosphorus this is 10.86 kg to be removed each day for complete removal. This size wetland would therefore last 1755 days or 4.8 years before renewal was required. The accuracy of this estimation is complicated. A higher phosphorus loading may be expected to be achievable due to the much higher contact time however the apparent reduction in reactivity of pellet not involved in removal found by this thesis could shorten the expected lifespan. Where WWTWs have wetlands already installed for tertiary treatment replacement of the substrate with this material to facilitate phosphorus removal could easily be achieved.

8.7.1 Other areas of implementation

This technology may have applications other than at WWTWs. Heal *et al.* (2004) viewed AMD solids as being applicable to controlling agricultural runoff as did Sibrell (2007). As mentioned in Chapter 2 diffuse pollution can be a large problem in respect to freshwater quality. There are also point sources related to agricultural industry where this technology could be implemented. Adler and Sibrell (2003) looked at the use of treated AMD flocs as both a soil and manure amendment, there to control the leaching of phosphorus.

8.9 Comparisons to other technologies

The results from the test presented in this chapter have been compared to those of Dobbie *et al.* (2009) who studied similar materials to those used in this thesis and also to the Bauxsol material from Virotec.

8.9.1 Dobbie *et al.*

Dobbie *et al.* (2009) used similar pellets to those used in the experimental side of this thesis at WWTWs, two tests were carried out, one involved solely the use of AMD-cement pellets and so this one is focused on. After 1000 hours of vertical flow operation 502g of total phosphorus was found to have been removed, equivalent to 0.49g/kg which compares to the highest loading from the current study of 7.55mg/g. The pellets used were spherical with diameters between 6.4-9.5mm and retention times of between 7 and 26 minutes were used. Phosphorus removal was found to increase as the contact time was increased, this fits in with the results presented in the current thesis. Dobbie *et al.* (2009) encountered problems during their experiment with organic growths blocking the filter and also biofilm growth inhibiting the contact of water with the pellets.

8.9.2 Virotec - Bauxsol

In 2005 The Water Research Council (WRC) carried out a long term (column test lasting six months to asses the phosphorus removal capability of Bauxsol pellets (Lowrie and Dee 2005). These tests used 2-8mm pellets in two circular columns 0.2m in diameter and 6m long. The average phosphorus influent concentration was 7.4mg/l with an average effluent of 1.7mg/l. The average contact time was 6 hours and this was altered to maintain the effluent concentration below 2mg/l. The phosphorus loading achieved was 5kg/tonne, this is 3.65 kg/m^3 with the stated bulk density of 730 kg/m^3. It is stated that in other tests loadings up to 14kg/tonne has been achieved.

The results for the column tests studied for the current thesis compare favourably to those found by Lowrie and Dee. For the lower breakthrough concentration of 1mg/l up to 6.8 kg/tonne has been achieved at breakthrough, with a contact time of 6.6 minutes. This highest value of 6.8kg/tonne is equivalent to 7.68kg/m^3. Wood *et al.* (2007) gives a costing of £23-27 per kg of phosphorus removed for Bauxsol at small to medium WWTWs. The maximum phosphorus loading found from these column tests at breakthrough was 6.77kg/tonne, at this loading rate 0.148 tonnes of material is required for remove 1kg of phosphorus, therefore, to equate to the £23-27 per kg costing for Bauxsol a price range of £155 to £182 per tonne of pellets is given. This price will have to cover all transport and production costs and the 300kg of cement required per tonne of pellets. Wood *et al.* (2007) state that for conventional chemical dosing at small to medium

WWTWs the cost per kilogramme of phosphorus removed ranges from £15-£93 (average £46) where heavy metal consents are not imposed and £23-146 (average £72) where they are. These average values equate to £311 and £486 per tonne of pellets produced for the material studied in this thesis.

8.10 Chapter summary

This chapter detailed the results of three identical column tests operated with a range of flow rates, these flow rates were varied to investigate the effect of residence time on phosphorus removal and column longevity. Each 30cm tall column had a sampling port every 10cm and so was effectively split into three. The complete length of the column with the shortest retention time (14.1 minutes for the whole column) failed and so did the bottom 10cm of the column with the mid range retention time (19.7 minutes for the whole 30cm). These are therefore the only lengths from which strong conclusions may drawn. Taking all columns to exhaustion would have been ideal and would have enabled stronger conclusions to be made however due to laboratory time constraints this was not possible. The bed volumes until breakthrough for those four columns lengths were, for the column with the shortest retention time, 30cm 352, 20cm 531 and 10cm 242 bed volumes, at breakthrough the phosphorus loadings achieved were 30cm 3.42mg/g 20cm 4.75mg/g and 10cm 2.32 mg/g. The 10cm length of the column with the median retention time treated 701 bed volumes and achieved 6.77mg/g at breakthrough. It can be seen that these columns treated relatively few bed volumes before breakthrough and the loadings achieved were far below the maximum loadings found in the batch tests. The results from the column with the shortest retention time showed that the pellets above the mass transfer zone appear to be having their reactivity leached out by the passing water. As the entirety of only one column failed however, this pattern perhaps need further investigation. Due to the relatively high influent calcium concentration the pellets main role was to raise the pH of the passing water to a level conducive to calcium phosphate precipitation. There was a clear relationship between increasing phosphorus effluent concentrations and a decrease in both calcium and pH of the effluent. The effluent concentration could be seen to begin rising once the effluent pH dropped to around 10 and once the effluent calcium dropped to around 25mg/l. PHEEQCI modelling of the influent conditions also showed pH to have the largest effect on the supersaturation level of hydroxyapatite.

9 Conclusions and recommendations

This chapter presents the key conclusions and recommendations that the current study has lead to. Firstly the aims and objectives that were presented in Chapter 1 are shown again below to allow direct discussion of how well these were met**.**

Aims

The work presented in this thesis aims to asses the phosphorus adsorptive capacities of waste iron oxyhydroxides, pelletise one of these materials using cement, asses and maximise the phosphorus removal capability of these pellets and determine the dominant phosphorus removal mechanism. Finally to gain an appreciation of the suitability of these pellets for real world use continuous column tests are performed.

Objectives

- Produce adsorption isotherms for phosphorus removal by waste iron oxides and compare these to those for other waste materials and commercial sorbents
- Develop a method of pelletisation for waste AMD sludge using cement
- Asses the phosphorus removal capability of the produced pellets and optimise their removal capability.
- Determine the phosphorus removal mechanism by these pellets
- Determine the performance of these pellets in continuous column tests and therefore asses their suitability for use at WWTWs

How and to what degree each chapter contributed to the fulfilment of these objectives is discussed below.

9.1 Chapter 6 – adsorption study

This chapter presented adsorption data and adsorption isotherms for four materials: treated AMD solids from the Horden minewater treatment plant, an iron based filter cake from a water treatment works, the commercial sorbent Rowaphos and a second source of treated AMD solids from the Dawdon treatment plant. Kinetic tests were carried out on the solids from Horden which found that equilibrium in these cases was reached within an hour. The solids from Horden was the only material to have kinetic tests but the increase in test length from 1 to 16 hours was felt to be sufficient to ensure equilibrium was being achieved. The one area of slight concern here is the variation in solids and phosphorus concentrations between the kinetic and batch tests but again the large increase in test length allows confidence that equilibrium was reached. The adsorption isotherms for these materials were calculated from the results of the 16 hour batch tests, the Freundlich isotherm providing a superior fit to the data than the Langmuir for all materials. No other isotherms were calculated, these being two most commonly used and the Freundlich providing an excellent fit. The adsorption results for all four materials are summarised in Table 9.1.

Table 9.1 Summary of adsorption results

Material	Freundlich Isotherm	Phosphorus loading range (mg/g)	Equilibrium concentration range (mg/l)
Horden	$\frac{x}{m} = 5.81C^{0.2813}$	2.23-27.85	0.26-214.45
Filter cake	$\frac{x}{m} = 10.75C^{0.3056}$	9.80-65.30	0.88-373.43
Rowaphos	$\frac{x}{m} = 7.97C^{0.2411}$	3.34-32.89	0.31-282.33
Dawdon	$\frac{x}{m} = 9.36C^{0.3165}$	4.09-12.04	0.16-3.46

The calculation of these isotherms allowed direct comparison to the results of other studies on similar materials. This showed the AMD solids and Rowaphos to have phosphorous capacities fairly typical of similar materials and the filter cake to have a relatively good capacity. The results for the solids from Horden provided a base level to compare to and improve on in the pellet study investigated in the subsequent chapters.

9.2 Chapter 7 - batch pellet study

Chapter 7 presented the results of tests predominantly on pellets produced from the addition of cement to the sludge from the Horden minewater treatment plant. The sludge from Horden was chosen as the basis of the pellets due to large scale problem of AMD waste and the availability of this particular sludge to the author. The pelletisation method of casting blocks and crushing these to produce pellets was chosen due to its simplicity and repeatability. Cement was chosen as a binder due to its availability, cost, ease of use and its use in similar studies such as Sibrell (2007) and Dobbie *et al.* (2009) . A fixed amount of cement was used in each test (30% by weight) this was based on the amount used by Sibrell (2007) and produced solid, resistant pellets. The effect of the variation of cement was not investigated neither was the use of other binders, this is further explored in the recommendations section below. Chapter 7 was split into four sections, the first investigated the effect of pellet size on removal, the second investigated the kinetics of removal and started investigate the relationship between the calcium released by the pellet and the phosphorus removed. The third section looked at the effect that the length of test had on removal and investigated the relationship between calcium and phosphorus in solution in detail. The fourth section investigated the apparent redundant nature of the Horden solids in removal by pellets through tests on pellets devoid of these solids. The main conclusions from each of these sections will now be looked at in detail.

Pellets ranging in size from 2.8-4mm down to 45-63µm were tested and a relationship between a reduction in pellet size and phosphorus removal was shown and a rise in final pH was also correlated with a decrease in pellet size and an increase in phosphorus removal. These results are summarised in Table 9.2.

Table 9.2 summary of the effect of pellet size on phosphorus removal

Pellet size (mm)	Final concentration range	Phosphorus loadings achieved (mg/g)	Final pH range
2.8-4	48.62-417.66	2.28-12.47	6.7-7.9
1-2	43.40-362.19	3.32-23.56	6.9-8.0
1.18-2	6.06-76.03	2.79-3.95	9.4-11.5
0.85-1	0.11-69.51	1.10-3.31	9.6-11.6
0.212-0.300	5.98	8.40	11.3-11.7
0.063-0.125	5.29-75.43	14.64-37.02	9.6-10.6
0.045-0.063	0.08-53.64	11.13-45.74	9.9-10.5

The sub 0.125mm pellets were found to be removing more phosphorus than the unpelletised solids from Horden. If adsorption was the dominant removal mechanism this would be unexpected as the pellets had much reduced surface areas and the elevated pHs which would restrict anionic adsorption. These results initiated the theory that calcium phosphate precipitation was becoming the more important removal mechanism which was further investigated throughout Chapter 7. The reduction in pellet size would increase the surface area of the pellets, facilitating the dissolution of calcium and hydroxide ions thus creating conditions ideal for calcium phosphate precipitation.

Section 7.2 investigated the kinetics of removal by pellets. The first test lasted an hour and was carried out on 45-63µm and 63-125µm pellets as with Section 7.1 these two pellet sizes performed closely. The rate of removal for all tests was initially high and quickly dropped. For the 63-125µm pellets the time period 0-1 minutes had a removal rate of 1.78mg/l/min and the period 40-60mins had effectively a rate of zero.

The second kinetics test lasted 16 hours and the solutions were analysed for both calcium and phosphorus to investigate the relationship between these. A high rate of removal was found from 0-30 minutes and then until 5 hours the removal rate was relatively low, between 5 and 8 hours the removal rate increased again. This pattern was attributed to the early removal being dominated by adsorption and the later removal to precipitation. The pH of the solution rose consistently throughout the test and this would have tipped the balance towards precipitation becoming the dominant removal mechanism. The progression of the calcium concentration was found to increase initially and then drop off throughout the rest of the test and this was thought to be as a result of rapid release of calcium by the pellets followed by a reduction in calcium concentration as the calcium phosphate precipitates were formed.

Section 7.3 investigated the effect that test length had on phosphorus removal. The first experiment had test lengths of 1,2 and 3 weeks, much higher phosphorus loadings were found for these tests in comparison to the 16 hour tests, a summary of results is shown in Table 9.3. These results are far higher than those from the 16 hour tests and this coupled with the high final pH values found showed that adsorption could no longer be the major removal mechanism. The tests on the unpelletised solids from Horden only lasted 16 hours and so it could be said that these tests could be showing a long term adsorption removal mechanism however at these elevated pHs anionic adsorption will be limited.

Table 9.3 – Summary of effect of pellet test

Test	Phosphorus loadings (mg/g)	Final concentrations (mg/l)	Final pHs
1 Week	47.96-59.45	0.11-1.38	11.16-11.33
2 Weeks	53.95-59.86	0.12-0.36	11.03-11.51
3 Weeks	53.97-59.93	0.09-0.17	10.80-11.23
1 Day	34.18-44.59	47.67-128.13	7.90-10.20
3 Days	45.74-59.79	18.77-90.14	9.18-10.82
7 Days	52.41-69.31	2.09-66.35	9.49-11.00

The progression of both phosphorus and calcium concentrations was investigated for tests lengths of 1,3 and 7 days. The pattern of removal was found to by typical of crystal growth with an initially high rate of removal dropping a slower, long term removal rate. The phosphorus and pH results are presented in Table 9.3. A relationship between a decrease in both phosphorus and calcium concentrations was found and this coupled with the high final pH values was taken as strong evidence that calcium phosphate precipitation was the major removal mechanism. SEM-EDX was used to analysed the surface chemistry of the used pellets, this found an average calcium – phosphorus molar ratio of 1.62, very close to the 1.67 ratio of the expected end product hydroxyapatite. This result, coupled with the previous results was taken as confirmation that calcium phosphate precipitation, particularly hydroxyapatite was dominating phosphorus removal. Further work that could have been carried out to further confirm this could have included analytical techniques such as XRD.

The set of tests which maintained the initial phosphorus concentration but varied the solids concentration found comparable loadings to those of Section 7.3.3 after 7 days but the progression of phosphorus removal up to 7 days was found to be different. Again phosphorus removal was tied in with a reduction in calcium concentration and elevated pHs but no reason was found in the variation in removal rates from 1-3 days. The mg/g of calcium released in these tests was also found to be three fold of that released in the tests in Section 7.3.3 again no solid explanation was found for this.

The increased phosphorus loadings at elevated pHs and the relationship between phosphorus and calcium suggested that adsorption by the solids from Horden were making a negligible contribution to phosphorus removal by the pellets. Tests were therefore performed to highlight this. The first replaced the solids from Horden with crushed sand, these tests found slightly lower phosphorus loadings, but this was tied in with lower levels of calcium release, thought to be as a result of the interaction between the calcium and the silica from the sand. The second test used a crushed sample of concrete and both the phosphorus and calcium behaviour for these tests were very similar to those of the pellets containing the solids from Horden. Perhaps the most telling chart of the current study is Figure 7.94 which is reproduced below as Figure 9.1. This shows that a consistent relationship between changes in calcium and phosphorus was found for the tests from Sections 7.3.3, 7.3.4, 7.4.1 and 7.4.2. That is for both tests containing and devoid of the solids from Horden .

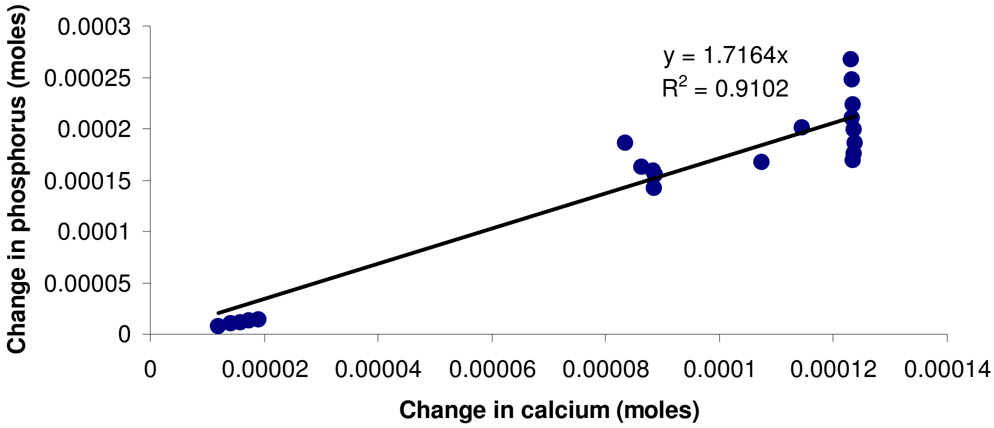


Figure 9.1 Variation in calcium and phosphorus for four separate tests.

9.3 Chapter 8 – continuous column tests

Chapter 8.reported on three column tests. These were performed to allow an appreciation of how these pellets would perform in a real world situation. Each column was split into three 10cm sections to allow the monitoring of the progression of the mass transfer zone. Therefore in total there were nine column lengths and of these four reached the chosen breakthrough concentration of 1mg/l. The whole length of the column with the shorted retention time was found to fail and so this is the only column from which strong conclusions can be made. Ideally all three columns would have been taken to failure and exhaustion but this was not possible due to laboratory time constraints. Whilst there are numerous data points for the column which failed, this is still technically only one column and therefore only one set of data. For further confidence in the results, repetition of this column or the other columns failing would have been ideal. The results for the failed column showed that in a column situation the removal mechanism was relatively short lived, the bottom 10cm treated 352 bed volumes before failure, the bottom 20cm 531 and the whole 30cm 242. The increasing effluent phosphorus concentrations were closely linked to decreasing calcium concentrations and pH values. The results suggested that whilst the majority of removal was occurring within the bottom sections of the column, the treated water was washing out the reactivity of the pellets above the mass transfer zone so as the mass transfer zone moved up, the column quickly failed. This can be seen as the 30cm column treated fewer bed volumes than the 20cm suggesting an ideal shallow bed depth. The influent water was made through the spiking of tap water with phosphorus, the tap water contained sufficient calcium to precipitate all of the phosphorus and so the primary role of the columns was found to be to raise the pH of the passing water to precipitate calcium phosphates.

9.4 Recommendations

When used in cemented pellets it was shown that the AMD solids have a negligible contribution to phosphorus removal. The redundant nature of the AMD solids does mean that this study did not find a commercial application for waste AMD solids. The dominance of calcium phosphate precipitation however shows the potential of the use of concrete and cement based waste for phosphorus removal. To the author’s knowledge this has been little researched in the past particularly in the form of structured column tests. There is therefore a potential for this large source of waste to be given a positive use. The use of cement based waste would however likely encounter the same problems found in the current thesis such as the effluent high pHs.

The high pH values caused by the cemented pellets would likely be a hindrance to their practical implementation. The avoidance of this could be investigated through the variation of the amount of cement used in the pellets or by the use of different binders. The problem with this of course, is the calcium and in particular the high pHs caused by the cement binder are essential to the effective phosphorus removal but there may be a compromise between pH and removal efficiency. An alternative could be to wash the pellets before use to remove some of the hydroxide ions. Again however this will reduce the effectiveness of the pellets.

The use of AMD solids and cemented pellets to remove phosphorus would have the potential to give the waste a commercial value but would not consume the waste, its final destination would still be landfill. There have been promising studies into the use of phosphorus saturated AMD solids as a phosphorus source for agriculture. The same studies have not been carried out for phosphorus saturated cemented pellets and this would be an important factor in the practical use of the pellets. The cement content of the pellets would also introduce a liming effect which is often desirable.

This study did not carry out any tests with real or synthetic waste water. The interaction of this with both the raw materials and the pellets would be interesting area of study and crucial if these materials were ever to be employed at a WWTWs.

The column tests showed that the material above the mass transfer zone was having its reactivity reduced before it became involved in removal. The complete length of only one column reached breakpoint however and further column tests taken to breakthrough and exhaustion would allow this theory to be confirmed. The same is true of the regeneration phenomenon following the resting of the column which was witnessed to some extent, but with only one example, could not be confirmed.

The finding that the iron based filter cake was a strong phosphorus adsorbent is an area that could benefit from some further work as unpelletised this material had good capacity and as a waste that the water industry creates, the ability to reuse the waste within the same industry is attractive.

10. References

Adler, P., Sibrell, P. 2003 Sequestration of Phosphorus by Acid Mine Drainage Floc *Journal of Environmental Quality* 32(3), pp 1122-1129

Agyei, N., Strydom, C.A., Potgieter, J.H. 2002 The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends *Cement and Concrete Research* 32(12), pp1889-1897

Anderson, P.R., Benjamin, M.M. 1985 Effects of silicon on the crystallisation and adsorption properties of ferric oxides *Environmental Science and Technology* 19(11), pp1048-1053

Arias, C. A., Del Bubba, M., Brix, H. 2001 Phosphorus removal by sands for use as media in subsurface flow constructed reed beds *Water Research* 35(5), pp1159-1168

Bastin, O., Janssens, F., Dufey, J., Peeters, A. 1999 Phosphorus removal by a synthetic iron oxide–gypsum compound *Ecological Engineering* 12(3-4), pp 339-351

Berg, U. Donnert, D., Ehbrecht, A., Bumiller, W., Kusche, I., Weidler, P.G., Nϋesch, R. 2005 Active filtration for the elimination and recovery of phosphorus from waste water *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 1-3, pp141-148

Boujelben, N., Bouzid, J., Elouear, Z., Feki, M., Jamoussi, F., Montiel, A. 2008 Phosphorus removal from aqueous solution using iron coated natural and engineered sorbents *Journal of Hazardous Materials* 151(1), pp 103-110

Brown, M. Barley, B. Wood, H. 2002 *Minewater Treatment Technology, Application and Policy* London; IWA Publishing

C. Pratt, C., Shilton, A., Haverkamp, R.G., Pratt, S. 2009 Assessment of physical techniques to regenerate active slag filters removing phosphorus from wastewater *Water Research* 43, pp277-282

C.W. Lee, C.W., Kwon, H.B., Jeon, H.P., Koopman, B 2009 A new recycling material for removing phosphorus from water *Journal of Cleaner Production* 17(7), pp683-687

Can, M.Y., Yildiz, E. 2006 Phosphate removal from water by fly ash: Factorial experimental design *Journal of Hazardous Materials*1235(1-3), pp 165-170

Chen, J., Kong, H., Wu, D., Chen, X., Zhang, D., Sun, Z. 2007 Phosphate immobilization from aqueous solution by fly ashes in relation to their composition *Journal of Hazardous Materials* 139(2), pp 293-300

Chen, J., Kong, H., Wu, D., Hu, Z., Wang, Z., Wang, Y 2006 Removal of phosphate from aqueous solution by zeolite synthesized from fly ash *Journal of Colloid and Interface Science* 300(2), pp 491-497

Chitrakar, R., Tezuka, S., Sonoda, A., Sakane, K., Ooi, K., Hirotsu, T. 2006 Phosphate adsorption on synthetic goethite and akaganeite *Journal of Colloid and Interface Science* 298(2), pp 602-608

Coal Authority *Dawdon and Horden: Regional Water Resource Protection Scheme* Available at http://coal.decc.gov.uk/en/coal/cms/environment/schemes/horden_dawdon/horden_dawdon.aspx [Accessed 26/06/2001]

Coal Authority *What is Ochre?* Available at http://www.coal.gov.uk/environmental/whatisochre.cfm?jHighlights=ochre [Acessed 30/04/2011]

Colombo, C., Barrón, C., Torrent, J. 1994 Phosphate adsorption and desorption in relation to morphology and crystal properties of synthetic hematites *Geochimica et Cosmochimica Acta* 58(4), pp 1261-1269

Cooper, P.F., Job, G.D., Green, M.B., Shutes, R.B.E. 1996 *Reed Beds and Constructed Wetlands for Wastewater Treatment* Swindon: WRC

Cordell, D., Drangert, J., White, S. 2009 The story of phosphorus: Global food security and food for thought *Global Environmental Change* 19, pp292-305

Corell, D.L. 1996 The Role of Phosphorus in the Eutrophication of Receiving Waters: A Review *Journal of Environmental Quality* 27(2), pp 261-266

Cornell, R. M. Schwertmann, U. 2003 *The iron oxides : structure, properties, reactions, occurrences, and uses* 2nd ed. Weinheim; WILEY-VCH

Coulton, R 2008 Personal Communication

Crittenden, B., Thomas, W.J., 1998 *Adsorption Technology and Design* Oxford: Butterworth-Heinemann

Cucarella, V., Zaleski, T., Mazurek, R., Renman, G. 2008 Effect of reactive substrates used for the removal of phosphorus from wastewater on the fertility of acid soils *Bioresource Technology* 99(10), 4308-4314

D Lowrie, D., Dee, A. 2005 Independent evaluation of Virofilter technology for enhanced phosphate removal WRC

D-D The Aquarium Solution *Rowaphos Enters the Olympics* Available at http://www.theaquariumsolution.com/rowaphos-enters-oympics [Accessed 01/05/2011]

D-D The Aquarium Solution *Rowaphos Tips for Use* Available at http://www.theaquariumsolution.com/rowaphos-tips-use [Accessed 01/05/2011]

D-D The Aquarium Solution *Use of Rowaphos on a Grand Scale* Available at http://www.theaquariumsolution.com/use-rowaphos-grand-scale [Accessed 01/05/2011]

de-Bashan, L.E., Bashan, Y. 2004 Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003) *Water Research* 38(19) 4222-4246

DEFRA 2008 *Consultation on options for controls on phosphates in domestic laundry cleaning products in England* London: Department for Environment, Food and Rural Affairs

Dobbie, K.E., Heal, K.V., Smith, K.A. 2005 Assessing the performance of phosphorus-saturated ochre as a fertilizer and its environmental acceptability *Soil Use and Management* 21(2), pp231-239

Dobbie, K.E., Heal, K.V., Aumônier, J., Smith, K.A., Johnston, A., Younger, P.L. 2009 Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater *Chemosphere* 75(6), pp795-800

Donnert, D., Berg, U., Weidler, P.G., Nüesch, R., Song, Y., Salecker, M., Kusche, I., Bumiller, W., Friedrich, F. 2002 Phosphorus removal and recovery from waste water by crystallisation

Drizo, A., Comeau, Y., Forget, C., Chapuis, R.P. 2002 Phosphorus Saturation Potential: A Parameter for Estimating the Longevity of Constructed Wetland Systems *Environmental Science and Technology* 36, pp 4642-4648

Drizo, A., Forget, C., P. Chapuis, R. P., Comeau, Y. 2006 Phosphorus removal by electric arc furnace steel slag and serpentinite *Water Research* 40(8), pp1547-1554

Emsley, J. Hall, D. *1976 The chemistry of phosphorus : environmental, organic, inorganic, biochemical and spectroscopic aspects* London : Harper & Row

Environment Agency 2011 (2) *Water Quality* Available at http://www.environment-agency.gov.uk/research/planning/34383.aspx [Accessed 30/04/2011]

Environment Agency 2011 *Phosphorus – total.* Available at http://www.environment-agency.gov.uk/business/topics/pollution/39111.aspx [Accessed 30/04/2011]

Fytianos, K., Voudrias, E., Raikos, N. 1998 Modelling of phosphorus removal from aqueous and wastewater samples using ferric iron *Environmental Pollution* 101(1), pp 123-130

Geelhoed, J.S., Hiemstra, T., Riemsdijk, W.H.V. 1997 Phosphate and sulfate adsorption on goethite single anion and competitive adsorption *Geochimica et Cosmochimica Acta* 61(12), pp 2389-2396

Geelhoed, J.S., Hiemstra, T., Riemsdijk, W.H.V. 1998 Competitive interaction between p and citrate on goethite *Environmental Science and Technology* 32(14), pp 2119-2123

Genz, A., Kornmüller, A., Jekel, M. 2004 Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and
Giesen,A. 1999 Crystallisation Process Enables Environmental Friendly Phosphate Removal at Low Costs *Environmental Technology* 20(7), pp 769-775

Gong, G. Ye, S., Tian, Y., Wang, Q., Ni, J., Chen, Y. 2009 Preparation of a new sorbent with hydrated lime and blast furnace slag for phosphorus removal from aqueous solution *Journal of Hazardous Materials* 166(2-3), pp 714-719
granulated ferric hydroxide *Water Research* 38(16), pp 3523-3530

Grubb, D.G., Guimaraes, M.S., Valencia, R. 2000 Phosphate immobilization using an acidic type F fly ash *Journal of Hazardous Materials* 76(2-3), pp 217-236

Han, J.S., Min, S., Kim, Y. 2005 Removal of phosphorus using AMD-treated lignocellulosic material *Forest Products Society* 55(11), pp48-53

Hancock, Sophie 2004 *Quantifying Ochre Arisings: Output from the UK Coal Authority's Mine Water Treatment Sites* 9th International Mine Water Congress

Heal, K., Younger, P.L., Smith, K., Glendinning, S., Quinn, P., Dobbie, K. 2003 Novel use of ochre from mine water treatment plants to reduce point and diffuse phosphorus pollution *Land contamination and Reclamation* 11(2), pp145-152

Heal, K.V., Smith, K.A., Younger, P.L., McHaffie. H., Batty, L.C. 2004 Removing phosphorus from sewage effluent and agricultural runoff using recovered ochre In: Valsami-Jones, E. ed. *Phosphorus in environmental technologies: Principles and applications*

Heal, K.V., Dobbie, K.E., Bozika, E., McHaffie, H., Simpson, A.E., and Smith, K.A. 2005 Enhancing phosphorus removal in constructed wetlands with ochre from mine drainage treatment *Water Science and Technology* 51(9), pp275-282

Hilton, J., O'Hare, M. Bowes, M.J., Jones, I.J. 2006 How green is my river? A new paradigm of eutrophication in rivers *Science of the Total Environment* 1-3, pp66-83

HM Revenue and Customs 2011 *A General Guide to Landfill Tax* Available at http://customs.hmrc.gov.uk/channelsPortalWebApp/channelsPortalWebApp.port al?_nfpb=true&_pageLabel=pageExcise_ShowContent&propertyType=document&id=HMCE_CL_000509#P143_15433 [Accessed 14/06/2011]

Huerta-Diaz, M.A., Tovar-Sánchez, A., Filippelli, G., Latimer, J., Sañudo-Wilhelmy, S.A. 2005 A combined CDB-MAGIC method for the determination of phosphorus associated with sedimentary iron oxyhydroxides *Applied Geochemistry* 20(11), pp2108-2115

Jang, H., Kang, S., 2002 Phosphorus removal using cow bone in hydroxyapatite Crystallization *Water Research* 36(5), pp1324-1330

Jarvie. H.P., Neal.C, Withers, P.J.A. 2006 Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? management *The science of the total environment* 360, pp246-253

Jeanmaire N, Evans T. 2001 Technicoeconomic feasibility of recovery from municipal wastewaters *Environmental Technology* 22(11), pp1355-1361

Jekel, M., Genz, A. *Studies on phosphorus removal from fresh water and sea water by commercial sorbents* Technical University Berlin

Johansson, L. 1999 Blast furnace slag as phosphorus sorbents} column studies *Science of The Total Environment* 229, pp89-97

Johansson, L., Gustafsson, J. P., 2000 Phosphate removal using blast furnace slags and opoka-mechanisms *Water Research* 34(1), pp 259-265

Johnston, A.E., Richards, I.R. 2003 Effectiveness of different precipitated phosphates as phosphorus sources for plants *Soil Use and Management* 19(1), pp 45-49

Kang, S., Choo, K., Lim, K. 2003 Use of Iron Oxide Particles as Adsorbents to Enhance Phosphorus Removal from Secondary Wastewater Effluent *Seperation Science and Technology* 38(15), pp3853-3874

Khomskii, E.V. 1969 *Crystallization from Solutions* New York: Consultants Bureau

Kim, E. Lee, D, Hwang,. H., Yim, S 2006 Recovery of phosphates from wastewater using converter slag: Kinetics analysis of a completely mixed phosphorus crystallization process *Chemosphere* 63(2), pp192-201

Korkusuz, E.A., Beklioğlu, M., Demirer, G.N. 2007 Use of blast furnace granulated slag as a substrate in vertical flow reed beds: Field application *Bioresource Technology* 98(11), pp 2089-2101

Kostura, B., Kulveitová, H., Leško, J. 2005 Blast furnace slags as sorbents of phosphate from water solutions *Water Research* 39(9), pp1795-1802

Kotz, J.C., Treichel, P., Harman, P.A. 2003 *Chemistry and chemical reactivity* USA: Thomson

Kwon, H., Lee, C,. Jun, B,. Yun, J., Weon, S., Koopman, B. Recycling waste oyster shells for eutrophication control *Resources, Conservation and* Recycling 41(1), pp75-82

Langmuir, D 1997 *Aqueous Environmental Geochemistry* New Jersey: Prentice-Hall Inc

Li, L., Stanforth, R. 2000 Distinguishing Adsorption and Surface Precipitation of Phosphate on Goethite (α-FeOOH) *Journal of Colloid and Interface Science* 230(1), pp 12-21

Lu, S.G., Bai, S.Q., Zhu, L., Shan, H.D. 2009 Removal mechanism of phosphate from aqueous solution by fly ash *Journal of Hazardous Materials* 161(1), pp 95-101

Lydersen, A.L. 1983 *Mass Transfer in Engineering Practice* New Jersey: John Wiley & Sons Ltd

Mainstone, C.P., Parr, W. 2002 Phosphorus in rivers - ecology and management *The science of the total environment* 282-283, pp 25-47

Mayes, W.M., Potter, H.A.B., Jarvis, A.P. 2009 Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide *Journal of Hazardous Materials* 162, pp512-520

Metcalf and Eddy 2003 *Wastewater Engineering Treatment and Reuse* New York: McGraw-Hill

Moore, D.S. 1995 *The Basic Practice of Statistics* New York: W.H. Freeman

Moriyama, K., Kojima, T., Minawa, Y., Matsumoto, S., Nakamachi, K. 2001 Development of artificial seed crystal for crystallization of calcium phosphate *Environmental Technology* 22(11), pp1245-1252

Morse, G.K., Brett, S.W., Guy, J.A., Lester, J.N. Review: Phosphorus removal and recovery technologies *The Science of the Total Environment* 212, pp69-81

Neville, A.M. 1995 *Properties of Concrete* 4th ed Harlow: Longman Group

Ofwat 2005 *Water Framework Directive – Economic Analysis of Water Industry Costs Final Report*

Oguz, E. 2005 Sorption of phosphate from solid/liquid interface by fly ash *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 262(1-3), 113-117

Oguz, E., Gürses, A., Canpolat, N. 2003 Removal of phosphate from wastewaters *Cement and Concrete Research* 33(8), pp 1109-1112

Park, J., Byun, H., Choi, W., Kang. W. 2008 Cement paste column for simultaneous removal of fluoride, phosphate, and nitrate in acidic wastewater *chemosphere* 70(8), pp 1429-1437

Park, W.H., Polprasert. C. 2008 Roles of oyster shells in an integrated constructed wetland system designed for P removal *Ecological Engineering* 1(4), pp 50-56

Persson, P., Nilsson, N., Sjöberg, S. Structure and bonding of orthophosphate ions at the iron oxide-aqueous interface *Journal of Colloid and Interface Science* 177(1), pp 263-275

Piekema, P. Giesen, A. Phosphate recovery by the crystallisation process: experience and developments. Available at http://www.nhm.ac.uk/research-curation/research/projects/phosphate-recovery/Nordwijkerhout/Piekema.pdf [Acessed 30/04/2011]

Rietra, R.P.J.J., Hiemstra, T., Riemsdijk, W.H.V. 1999 The relationship between molecular structure and ion adsorption on variable charge minerals *Geochimica et Cosmochimica Acta* 63(19-20), pp3009-3015

Rietra, R.P.J.J., Hiemstra, T., Riemsdijk, W.H.V. 2001 Interaction between calcium and phosphate adsorption on goethite *Environmental Science and Technology* 35(16), pp3369-3374

Rouquerol, F., Rouquerol, J., Sing, K. 1999 *Adsorption by Powders & Porous Solids* London: Academic Press

Sakadevan, K., Bavor, H.J. Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems *Water Research* 32(2), pp 393-399

Sakadevan, K., Bavor, H. J. 1998 Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems *Water Research* 32(2), pp 393-399

Schipper, W.J., Klapwijk, A., Potjer. B., Rulkens, W.H., Temmink, B.G., Kiestra, F.D.G., Lijmbach, A.C.M. 2004 Phosphate Recycling in the Phosphorus Industry *Phosphorus Research Bulletin* 15, pp47-51

Seida, Y., Nakano, Y. 2002 Removal of phosphate by layered double hydroxides containing iron *Water Research* 36(5), pp1306-1312

Shilton, A.N., Elmetri, I., Drizo, A., Pratt,.. Haverkamp, R.G., Bilby, S.C. 2006 Phosphorus removal by an ‘active’ slag filter–a decade of full scale experience *Water Research* 40(1), pp113-118

Sibrell, P. 2007 Method of Removing Phosphorus from Wastewater US Patent 7,294,275 B1

Sibrell, P.L., Montgomery, G.A., Ritenour, K.L., Tucker, T.W. 2009 Removal of phosphorus from agricultural wastewaters using adsorption media prepared from acid mine drainage sludge *Water Research* 43(8), pp 2240-2250

Simmons, J.A. 2010 Phosphorus Removal by Sediment in Streams Contaminated with Acid Mine Drainage *Water, Air and Soil Pollution* 209(1-4), pp123-132

Smith, V.H., Tilman, G.D., Nekola, J.C. 1999 Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems *Environmental Pollution* 100, pp179-196

Smol, J. P 2008 *Pollution of lakes and rivers a paleoenvironmental perspective* Oxford: Blackwell Publishing

Song, Y., Hahn, H.H., Hoffmann, E. 2002 Effects of solution conditions on the precipitation of phosphate for recovery A thermodynamic evaluation *Chemosphere* 48, pp1029-1034

Soroka, I. 1979 *Portland cement and concrete* London: Macmillan

Stroud, K.A., Booth, D. 2001 *Engineering Mathematics* 5th ed Basingstoke: Palgrave Macmillian

Stumm, W. 1987 *Aquatic Surface Chemistry Chemical Processes at the Particle-Water Interface* USA: John Wiley and sons Inc

Stumm, W. 1992 *Chemistry of the Solid-Water Interface* USA: John Wiley and sons Inc

Sundstrom, D.W., Klei, H.E. 1979 *Wastewater Treatment* New Jersey: Prentice-Hall Inc

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y. 2005 Recovery of phosphorous from swine wastewater through crystallization *Bioresource Technology* 96(14), pp1544-1550

Swift, L. 1997 *Mathematics and statistics for business, management and finance* Basingstoke: Macmillan

Tate, C.M., Broshears, R.E., McKnight, D.M. phosphate dynamics in an acidic mountain stream: interactions involving algal uptake, sorption by iron oxide, and photoreduction *Limnology and Oceanography* 40(5), pp938-946

Torrent, J., Barron, V. Schwertmann, U. 1990 Phosphate adsorption and desorption by goethites differing in crystal morphology *Soil Society of America*

Torrent, J., Schwertmann, U., Barron, V. 1992 Fast and slow phosphate sorption by goethite-rich natural materials *Clays and Clay Minerals* 40(1), pp 14-21

Treybal, R.E. 1968 *Mass-Transfer Operations* 2nd ed. New York: McGraw-Hill

Ugurlu, A., Salman, B. 1998 Phosphorus removal by fly ash *Environment International* 24(8), pp911-918

Virotec 2006 Case study: shandon lagoon,south Carolina, USA. Available at http://www.virotec.com/pdf/shandonlagoon_cs_05dec06.pdf [Accessed 30/04/2011]

Virotec 2006a Virofilter water treatment – an innovative system to treat acidic water & remove heavy metals Available at http://www.virotec.com/pdf/virofilter_tds_8dec06.pdf [Acessed 30/04/2011]

Vohla, C., Koiv, M., Bavor, J.H., Chazarenc, F., Mander, U. 2011 Filter materials for phosphorus removal from wastewater in treatment wetlands—A review *Ecological Engineering* 37, pp70-89

Wang, S., Wu, H. 2006 Environmental-benign utilisation of fly ash as low-cost adsorbents *Journal of Hazardous Materials* 136(3), pp482-501

Water Framework Directive 2000 Directive 2000/60/EC

Wei, X., Viadero, R.C., Bhojappa, S. 2008 Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants *Water Research* 42(13) 3275-3284

Wood, E., Fergusson, L., Lowe, M., Leigh, S., 2007 The Application of ViroFilter Technology at Yorkshire Water *European Water & Wastewater Management Conference*

Xiong, J., He, Z., Mahmood, Q., Liu, D., Yang, X., Islam, E. 2008 Phosphate removal from solution using steel slag through magnetic separation *Journal of Hazardous Materials* 152(1), pp211-215

Xu, K., Deng, T., Liu, J., Peng, W. 2010 Study on the phosphate removal from aqueous solution using modified fly ash *Fuel* 89(12), pp 3668-3674

Xue, Y., Hou, H., Zhu, S. 2009 Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag *Journal of Hazardous Materials* 162(2-3), pp973-980

Yamada, H., Kayama, M., Saito, K., Hara, M. 1986 A fundamental research on phosphate removal by using slag *Water Research* 20(5), pp547-557

Yan Yu, Y., Wu, R., Clark, M. 2010 Phosphate removal by hydrothermally modified fumed silica and pulverized oyster shell *Journal of Colloid and Interface Science* 2(15), pp 538-543

Younger. P.L., Wolkesdorfer, C. ERMITE consortium. 2004 Mining Impacts on the Fresh Water Environment: Technical and Managerial Guidelines for Catchment Scale Management *Mine Water and the Environment* 23(1)

Zeng, L., Li, X., Liu,, J. 2004 Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings *Water Research* 38(5), pp 1318-1326

Zhong, B., Stanforth, R., Wu, S., Chen, J.P., 2007 Proton interaction during phosphate adsorption onto goethite *Journal of Colloid and Interface Science* 308(1), pp 40-48

11. Appendices (CD-ROM)

Chapter 6

Data from Sections 6.1, 6.2, 6.3, 6.4 and 6.5

Chapter 7

Data from Section 7.1, 7.2, 7.3 and 7.4

Chapter 8

Data from Sections 8.1, 8.2, 8.3 and 8.4

PHREEQCI output files

Output files for Figure 7.77 and Section 8.5