

Cranfield University

**School of Applied Science
Department of Sustainable Systems
Centre for Water Science**

MSc by research

2007

David J L Thomas

Maximising Struvite Recovery from Real Wastewater Sources

Supervisor: Professor Simon A. Parsons

April 2007

**This thesis is submitted in partial fulfillment of the requirements for the Degree of
Master of Science.**

**©Cranfield University, 2007. All rights reserved. No part of this publication may be
reproduced without the written permission of copyright holder**

ProQuest Number: 10832125

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10832125

Published by ProQuest LLC (2019). Copyright of the Dissertation is held by Cranfield University.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

Abstract

Formation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) in reactors is proposed to limit struvite problems in sewage treatment works (STW) and offer a method of phosphorus recovery and recycling. Four sites of interest were identified by Severn Trent Water Ltd: Derby, Wanlip, Stoke Bardolph STW and Coleshill sludge destruction plant for their potential to produce struvite. Initial tests on sludge liquors collected from the four sites showed that >80% of initial orthophosphate could be removed when the $\text{Mg}:\text{PO}_4$ ratios was adjusted to >2:1 for Wanlip, Stoke Bardolph STW and Coleshill at pH 9.

Two reactor types, a fluidised bed reactor (FBR) and a stirred tank reactor, were trialled in Phase 1 testing with Wanlip STW liquors. The FBR was able to achieve a >90% orthophosphate removal with Mg additions of 3.5 to 5 mmol but produced a suspended solid content of $\sim 300 \text{ mg L}^{-1}$. To overcome the problem of 'fines' a metallic mesh accumulation device was fitted to the reactor. The mesh system was able to reduce the suspended solids within the liquors $< 50 \text{ mg L}^{-1}$ when the reaction time was increased from two to three hours. The stirred tank reactor was able to remove on average 55% of the phosphate content of the liquors with a magnesium addition of 5mmol.

In Phase 2 testing both types of reactor were run side-by-side in a continuous operation. In the three experiments carried out the initial orthophosphate concentration was adjusted to 95 mg L^{-1} (1mmol). The stirred tank reactor was able to consistently remove $\sim 65\%$ of the influent orthophosphate concentration in the 3 experiments at a $\text{Mg}:\text{PO}_4$ ratio of 3.5:1. The FBR removal steadily improved from 25% to 65% over the 3 experiments. The metallic mesh system was further trialled here and successfully captured 4.1g of struvite. A cationic polymer, polyDADMAC, was also tested for the capture of fines with less success than in previous reports. The precipitate from each reactor was analysed with SEM-EDS and XRD. The FBR produced relatively pure struvite and stirred tank a struvite and amorphous material mixture.

Acknowledgements

To my family for all their support; Prof. Simon Parsons for his infinite patience; Dan Murray for keeping me amused on campus; Tom Bond for leading me astray; Jitka Macadam for proofreading previous work; John Churchly at Severn Trent Water for answering all my questions; all of the people at Wanlip STW who helped with sample collection, and Severn Trent Water Ltd for providing the funding.

Table of Contents

Abstract.....	III
Acknowledgements	IV
Table of Contents	V
1. Introduction.....	1
1.1 Background.....	1
1.2 Project development.....	4
1.3 Aims and Objectives	4
2 Literature review	6
2.1 Introduction.....	6
2.2 The chemistry of struvite	10
2.2.1 Effect of pH on the formation of struvite.....	10
2.2.2 Supersaturation and its effect on the formation of struvite	14
2.2.3 The effects of other ions on the formation of struvite.....	17
2.2.4 Effect of temperature on the formation of struvite.....	18
2.2.5 Struvite as a fertiliser	19
2.2.6 Summary	20
2.3 Types of reactor for the recovery of struvite.....	21
2.3.1 Stirred Reactors.....	22
2.3.2 Fluidised Bed Reactor (FBR).....	24
2.4 Optimisation of reactor conditions for the controlled formation of struvite	27
2.4.1 Concentration of constituents.....	27
2.4.2 pH alteration; how, why and to what effect	29
2.4.3 The role of seed and accumulation materials	30
2.4.4 Design of reactor for phosphorus recovery	32
2.4.5 Hydraulic retention time	35
2.5 Summary	35

2.6 Appendix Tables	36
2.7 References	42
3 Experimental	55
3.1 Collection and characterisation of centrate liquors	55
3.2 Jar Tester precipitation.....	56
3.3 Phase 1 fluidised bed reactor design and operation	58
3.4 <i>Accumulation system design and configuration</i>	59
3.5 Phase 1 stirred tank reactor	60
3.6 Side-by-side operation of a FBR and stirred tank reactor	61
4 Results	64
4.1 Physiochemical results	64
4.2 Jar tester precipitation tests	68
4.3 Phase 1: FBR results	75
4.4 Phase 1 stirred tank results.....	82
4.5 Phase 2: Side-by-side comparison results	84
5 Discussion	92
5.1 Implications of this study to the wastewater industry	92
6 Conclusions.....	97
7 Further work	99
8 References	100
Appendix 1	105
Appendix 2	111
Appendix 3	116
Appendix 4	121
Appendix 5	123
Appendix 6	131

List of figures

<u>Chapter 1</u>	Page
Figure 1.1: The factors that influence and need to be understood for controlling the precipitation of struvite from sludge liquors.....	3
 <u>Chapter 2</u>	
Figure 2.1: An example of the BNR process (A2O BNR process which is used at the Treviso STW, Italy).....	7
Figure 2.2: Cell uptakes and discharges during anaerobic and aerobic stages of BNR.....	8
Figure 2.3: Changes in protonation of phosphate with change in pH of environment.....	13
Figure 2.4: Simple mechanically stirred tank reactor, though stirring can be provided by air as well.....	23
Figure 2.5: Simplified Phosnix FBR at Shimane, Japan	25
Figure 2.6: Geesterambacht Crystalactor [®] design.....	33
Figure 2.7: Slough stirred tank reactor design.....	34
 <u>Chapter 3</u>	
Figure 3.1: Image of jar tester setup for precipitation tests.....	53
Figure 3.2: Schematic and picture showing the setup of the crystallisation reactor for struvite precipitation.....	54
Figure 3.3: Image and schematic of the accumulation mesh used to collect struvite from	56

the crystallisation reactor and it's positioning within the reactor.....

Figure 3.4: Set up for side by side analysis of each type of reactor..... 57

Figure 3.5: Image and schematic showing stirred tank reactor and clarifier..... 58

Chapter 4

Figure 4.1: The impact on orthophosphate removal % with an increase in Mg:PO₄ ratio.... 66

Figure 4.2: The impact of Mg:PO₄ increase on the d_{0.5} particle size of precipitate..... 67

Figure 4.3: Analysis by SEM on the effect of changes in Mg:PO₄ ratio (same as Ca:Mg) on crystal morphology for the Coleshill centrate sample (8.06.06)..... 69

Figure 4.4: XRD analysis of Mg:PO₄ ratios of 1.1:1 and 3.1:1 precipitates..... 70

Figure 4.5: Suspended solids collected from the FBR effluent in experiments 1-4..... 73

Figure 4.6: The suspended solids and solids collected on the mesh for experiments 5-12... 75

Figure 4.8: The struvite scaling rate of the metallic mesh system ($\text{g m}^{-2} \text{h}^{-1}$) in experiments 9-12..... 76

Figure 4.7: Image and EDS analysis of precipitate collected from metallic mesh after experiment 9..... 77

Figure 4.8: The change in orthophosphate concentration over time..... 79

Figure 4.9: Images of precipitate sticking to the reactor sides and air diffuser (experiment 19)..... 83

Figure 4.11: XRD trace of the solids collected from experiment 20, metallic mesh. Highlighted lines on spectra show database comparison for struvite.....	84
Figure 4.12: XRD trace of the solids collected from the stirred tank in experiment 19 with the addition of polyDADMAC. Lines show database comparison for struvite.....	85
Figure 4.13: SEM and EDS analysis showing crystal morphology and elemental analysis of solids captured on the mesh accumulation device.....	86
Figure 4.14: SEM and EDS analysis showing crystal morphology and elemental analysis of solids collected from the stirred tank reactor (experiment 1).....	86

List of tables

Chapter 1

Page

Table 1.1: Requirements for nutrient release into watercourses as set out by 'The Urban Waste Water Treatment Directive (91/271)'	1
---	---

Chapter 2

Table 2.1: Change in phosphate, ammonia and magnesium concentrations through the Slough STW (Jaffer <i>et al</i> 2001).....	12
Table 2.2: Full scale struvite precipitation reactors.....	37
Table 2.3: Pilot plants operated onsite.....	38
Table 2.4: Pilot plants operated onsite.....	39
Table 2.5: Laboratory scale struvite Reactors.....	40
Table 2.6: HAP reactors.....	41

Chapter 3

Table 3.1: Methods used to characterise liquor samples.....	57
---	----

Chapter 4

Table 4.1: Concentrations of selected determinants taken from four sites.....	67
Table 4.2: Reports by other authors on the concentrations of PO ₄ , Mg, NH ₄ and Ca recorded at Wanlip STW and Coleshill sludge destruction plant.....	68

Table 4.3: Derby STW centrate liquor PO ₄ removal as a function of Mg:PO ₄ and the change in pH over the course of experiment. Sample number 1.....	70
Table 4.4: Stoke Bardolph STW centrate liquor PO ₄ removal as a function of Mg:PO ₄ and the change in pH over the course of experiment. Sample number 2.....	70
Table 4.5: Coleshill STW centrate liquor PO ₄ removal as a function of Mg:PO ₄ and the change in pH over the course of experiment.....	70
Table 4.6: Wanlip STW centrate liquor PO ₄ removal as a function of Mg:PO ₄ and the change in pH over the course of experiment. Sample number 4.....	70
Table 4.7: Summary of experiment conditions tested with the FBR and the overall orthophosphate removal percentage.....	77
Table 4.8: Summary of reaction conditions, initial liquor characteristics and the final orthophosphate removal %.....	83
Table 4.9: Outline of the operation conditions for each reactor.....	85
Table 4.10: The results collected for the experiments ran with the reactors.....	87

1.0 Introduction

1.1 Background

In 1988 the EEC enacted 'The Urban Waste Water Treatment Directive, 91/271' (UWWTD, 1991) which established nutrient discharge limits to watercourses for the wastewater industry (see Table 1.1). These discharge limits have required secondary processes in wastewater treatment to be updated, as older practises were unable to achieve the limits imposed in the legislation (Battistoni *et al.*, 2002a).

Figure 0-3

Determinant	Population Equivalent (P.E)	Concentration (mg L⁻¹)	Minimum Reduction (%)
Total	10,000-100,000	2	80
Phosphorus	>100,000	1	80
Total Nitrogen	10,000-100,000	15	70-80
	>100,000	10	70-80

Two methods are commonly employed by the wastewater industry in the UK for the removal of phosphorus from wastewater: chemical and biological. Severn Trent Water Ltd at present operates 50 (as of April 2007) sites using chemical methods for P removal and just two biological nutrient removal (BNR) plants for P, Derby and Tewksbury. Both processes of P removal are well understood though both have identified draw backs associated with their operation i.e. chemical P removal produces large quantities of sludge that needs disposal and the biological removal of P has had reports of efficiency problems (Stratful *et al.*, 1999).

Struvite, magnesium ammonium phosphate, offers a solution to these problems of P removal by being an easy to produce and handle product, which can later be recycled as a commercial 'green' fertiliser (Ueno and Fujii, 2001). Struvite is formed by the combination of magnesium, ammonia and orthophosphate in equal molar ratios, with its formation mainly

dependent on the environmental pH and concentration of constituent ions (see Figure 1.1) (Kofina and Koutsoukos, 2005).

Scaling caused by deposits of struvite have been the cause of reported operational problems at Coleshill Sludge Destruction plant (Doyle *et al.*, 2002) and Slough sewage treatment works (STW) (Williams, 1999). Over the last 15 years there has been a move towards deliberately precipitating struvite in dedicated reactors operating on side streams at STW (Abe *et al.*, 1995; Ueno and Fujii, 2001; Jaffer *et al.*, 2002; and Battistoni *et al.*, 2006b). Different locations have been trialled for the placement of recovery plants; with post dewatering processes the most popular option for recovery operations.

The move towards a controlled precipitation of struvite is not limited to curtailing scaling problems and the removal of P but is also due to reports of the effectiveness of struvite as a fertiliser (Potjer, 2001). Struvite was shown by Richards and Johnston (2001) to be as an effective fertiliser as current commercial fertilisers. The cost of operating a struvite recovery plant depends on the physiochemical characteristics of the wastewater to be used. Operational cost analysis by Jaffer *et al.* (2002) showed the major cost to be addition of NaOH for the pH adjustment when the influent Mg:PO₄ ratio is close to 1:1, whereas Turker and Celen, (2007) reported 55-60% of cost to be from addition of Mg as MgCl₂ when significant quantities of Mg are required to achieve the required operation Mg:PO₄ ratio.

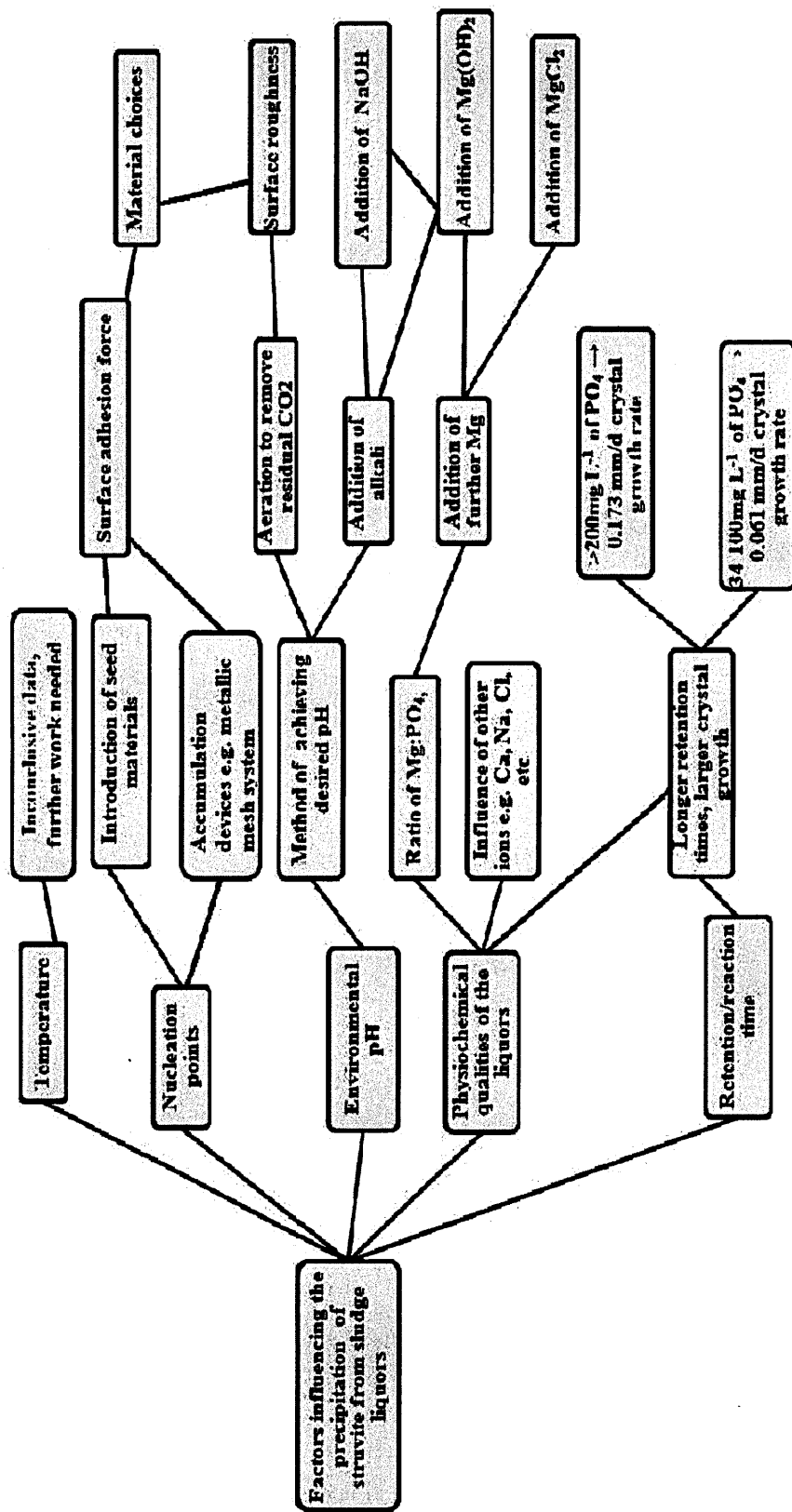


Figure 0-4.1: The factors that influence and need to be understood for controlling the precipitation of struvite from sludge liquors

1.2 Project development

Struvite scaling has previously been identified in UK STW (Doyle *et al.*, 2002). Scale formation in sludge liquor return lines have led to the adoption of often expensive scale prevention procedures, for example Severn Trent Water Ltd use *Antiplax*, a commercial chemical additive for the prevention of scale formation and can cost from \$100,000 annually for maintenance (Benisch *et al.*, 2000). This is added to the centrifuge supernatant collecting well at a number of STW to combat scale problems in later pipework. Severn Trent Water having previously sponsored a number of research projects looking at the formation and control of struvite scale (Wall *et al.*, 1999; Doyle *et al.*, 2002; Le Corre *et al.*, 2006c) and are now interested in struvite recovery. Four sites of interest were identified initially by Severn Trent for investigation as to their suitability for a struvite precipitation reactor and in this thesis we have compared the merits of the two reactor types currently available for the precipitation of struvite: fluidised bed reactor (FBR) and stirred tank reactor

1.3 Aims and Objectives

The aim of this project was to evaluate the potential for P recovery as struvite from STW sludge liquors using a FBR and stirred tank reactors. Particularly attention will be paid to orthophosphate removal, crystal quality and particle size. It is hoped that the results from this project will lead to the commissioning of a full scale struvite reactor.

The objectives for the project were;

- Identify a STW centrifuge supernatant (centrate) with suitable physiochemical characteristics for struvite precipitation and determine suitable magnesium doses for successful struvite precipitation.
- Evaluate the chosen STW centrate with a fluidised bed reactor (FBR) and stirred tank type reactor in a batch type mode.

Introduction

- Test a FBR with a metallic mesh accumulation device for collection of precipitate.
- Design and commissioning a stirred tank reactor.
- Assess the performance of the FBR and stirred tank reactors in side-by-side and continuous operation.

2 Literature review

2.1 Introduction

Many sewage treatment works (STW) incorporate a biological nutrient removal (BNR) process whereby bacteria are used to remove phosphorus and nitrogen from sewage. This leads to an increase in the concentration of phosphorus and ammonia in the sludge produced after stabilisation in a digester. The implementation of the EC 'The Urban Waste Water Treatment Directive, 91/271' (UWWTD, 1991) has instructed the STW sector 'to phase out any dumping or discharge of sewage sludge into surface waters'. The Directive states release limits on determinants of water quality i.e. biological oxygen demand (BOD), suspended solids and nutrient concentrations of nitrogen and phosphorus. Nitrogen and phosphorus are particularly important due to the link between elevated levels of these nutrients in waterways and eutrophication of sensitive water areas (Sharpley, 1994).

The main sources of phosphorus in UK wastewater come from human activity, detergents, and livestock (*Morse et al.*, (1993)). There exist two main methods for the removal of phosphorus from wastewater, chemical and biological. For a complete review of methods for the removal of phosphorus from wastewaters see De Bashan and Bashan (2004). Chemical addition of metal salts to wastewater is a well understood process whereby phosphate is removed by the formation of insoluble metal salts. Typically alum, ferric chloride/sulphate or lime is added to the wastewater in a 1:1 ratio in order to overcome competing side reactions (Neethling and Benisch, 2005). Addition of metal salts to sequester phosphate produces large amounts of sludge that needs handling and disposal. The disposal of the extra sludge produced due to metal salt addition adds a significant cost to the overall operation costs of a STW and is particularly undesirable for this reason (Edge, 1999).

BNR has over recent years become a popular method for the removal of nitrogen and phosphorus in one unit at activated sludge type STW. Other methods do exist for the removal of phosphorus such as trickling filters where the BOD of the wastewater is not high enough to

sustain a BNR (Strickland *et al*, 1999). BNR works by sewage passing through three individual reaction zones, anaerobic, anoxic and aerobic with part of the flow being recycled back to the anoxic zone (see Figure 2.1).

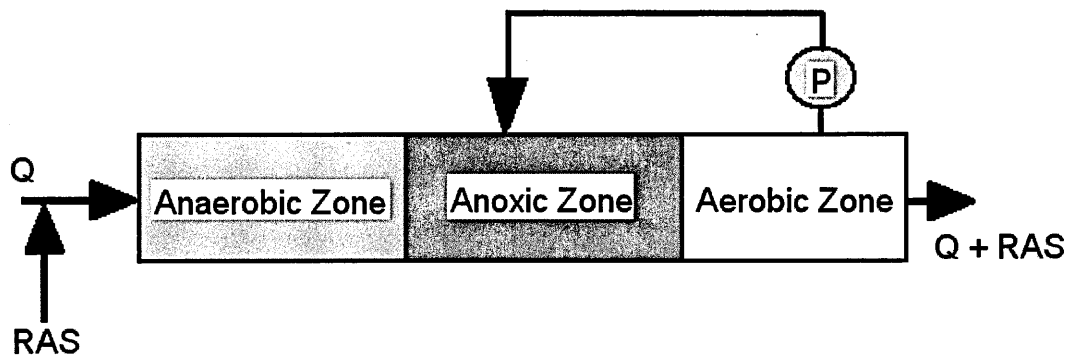


Figure 0-1.1: An example of the BNR process (A₂O BNR process which is used at the Treviso STW, Italy)

Heterotrophic bacteria, termed polyphosphate accumulating organisms (PAO), are used to convert and concentrate phosphorus to poly-phosphate within the BNR plant (Figure 2.2) (Jeyanayagam, 2005). What makes PAO different to other bacteria is their ability to concentrate roughly three times more phosphate within their biomass than other types of bacteria. During the anaerobic stage the PAO take up and store volatile fatty acids (VFA) as poly-b-hydroxybutyrate (PHB) for example. The energy required for the uptake of the VFA is provided by the cleaving of the poly-phosphate chains; subsequently phosphate is released into the surrounding water. In the aerobic stage phosphorus released during the anaerobic stage and additional phosphorus is taken up PBO with the energy required being provided by the VFA was stored during the anaerobic stage. When the phosphorus loaded cells are removed in the waste and surplus activated sludge (SAS) a reduction in the phosphorus content of upto 85% is achievable (Williams, 1999).

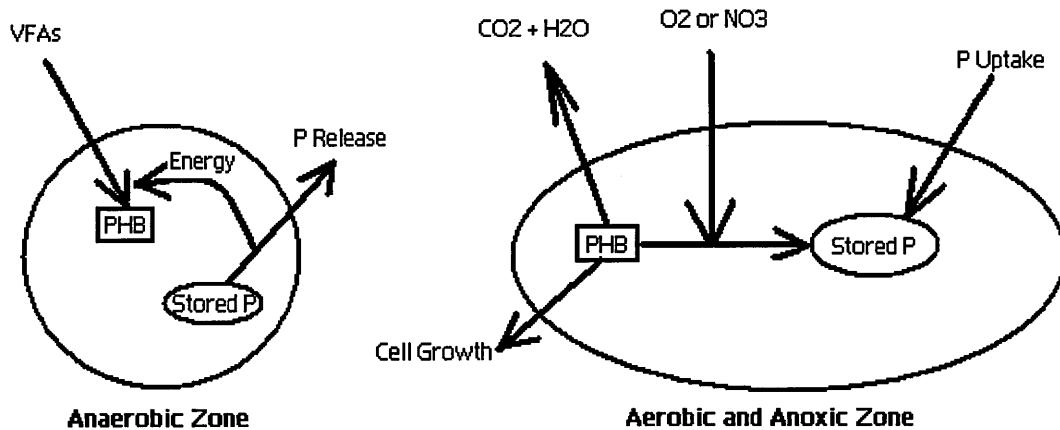


Figure 2.2: Cell uptakes and discharges during anaerobic and aerobic stages of BNR

The sludge that is removed from the BNR is typically higher in phosphorus than that coming from an activated sludge plant. Hwang and Choi (1998) reported a total phosphorus content of 335mg L^{-1} for a BNR plant's sludge compared to 143mg L^{-1} for an activated sludge plant's sludge.

Anaerobic digestion is usually used to stabilise the sludge produced from the BNR plant. During anaerobic digestion, magnesium and phosphorus are released back into the surrounding waters due to cell lysis (Battistoni *et al*, 2005). The release of phosphate during anaerobic digestion can be fixed by calcium and magnesium. Magnesium combines with the soluble phosphate and ammonia to form magnesium ammonium phosphate, struvite. Jarden and Popel (1994) estimated that 20% of the total phosphorus in the digester could be fixed as struvite.

The first occurrence of struvite within a STW was reported by Rawn in 1939, who reported the discovery of struvite in the digested sludge supernatant lines (Rawn, 1939). The first problems associated with struvite scaling within a STW were reported in 1963 at the Los Angeles Hyperion treatment works (Borgerding, 1972). Borgerding (1972) reported the

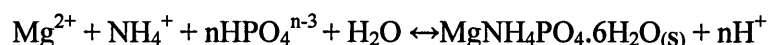
discovery of a white scale on the separation screens at the treatment works. A solution was thought to have been found whereby the influent was diluted and initial reports suggested that this method had solved the scaling problem. Five years later the pipe work had become so clogged with scale that the entire pipe work needed removal and maintenance.

To solve this problem, STW with a struvite scaling problem need to either employ a costly pipe maintenance program whereby pipes are removed for maintenance work (Williams, 1999) or in extreme circumstances complete replacement of pipework (Benisch *et al.*, 2000). Benisch *et al.* (2000) estimated the cost to operations at \$100,000 annually for maintenance at a 25 million galleon daily plant. An alternative to a pipe maintenance program is the addition of chemicals to the post BNR liquor streams to stop scale formation. The addition of EDTA to streams leaving the BNR was reported as being the best solution by Doyle *et al.* (2002) though it should be noted the addition of EDTA has a well understood and severe impact on the environment due to its efficient chelating ability. Struvite accumulation needn't be a costly problem to STW though as struvite has been shown to be an effective slow release fertilizer (Bridger, 1961).

Approaches for the removal of phosphorus as struvite are the focus of this review due to indications that struvite may have a role as a commercial fertiliser. A number of different methods have been developed to facilitate phosphate removal from STW. A host of reactor designs have been implemented on a pilot and full scale in an approach to recover phosphate from the liquors leaving the digester and dewatering centrifuge, as previous investigations have shown these to have the largest potential for struvite recovery (Lowenthal *et al.*, 1994). Two crystalline products have been investigated for the recovery of phosphate i.e. struvite and apatite. The chemistry of struvite and its recovery is covered mainly here but the process of apatite recovery is very similar to that of struvite recovery and so is also covered.

2.2 The chemistry of struvite

Struvite is an orthorhombic mineral that is formed by the combination of magnesium, phosphate and ammonia in equal molar quantities as shown in the following equation (Abbona and Boistelle, 1985):



Struvite is also found in nature where it has been identified in guano (Cullen, 1988) as well as in kidney stones produced due to bacterial infections within the kidneys (Coe *et al.*, 2005).

2.2.1 Effect of pH on the formation of struvite

Two distinct process stages have been observed in the formation of struvite (Ohlinger *et al.*, 1999). The first stage of struvite formation is nucleation of the constituent ions of struvite. The second stage is the growth of crystals until equilibrium is achieved or growth will continue in systems that are maintained with fresh ions indefinitely e.g. wastewater streams (Ohlinger *et al.*, 1999). Introduction of seeds into the liquor can bypass the nucleation stage of formation. Seeds can be suspended solids present within the liquor or deliberately introduced seed material e.g. quartz sand (Battistoni *et al.*, 2005) and struvite crystals (Ueno and Fujii, 2001). It has also been seen that surface roughness of pipework and walls can act as nucleation points for the formation of struvite (Neethling and Benisch, 2000).

The nucleation of struvite is managed by pH, supersaturation, temperature and interaction with other ions. Nucleation occurs when the combined concentrations of Mg^{2+} , NH_4^+ , and PO_4^{3-} exceed the struvite solubility limit (K_{sp}). K_{sp} of struvite is defined as:

$$K_{sp} = [Mg^{2+}] [NH_4^+] [PO_4^{3-}]$$

Where $[x]$ refers to concentration of constituent.

One limitation of this equation is that it ignores the effect of pH. The concentrations of these ions within wastewater liquors are pH dependent. It follows that the solubility of struvite is also pH dependent. As the pH of the liquor is raised so the solubility of struvite decreases. With a calculated K_{sp} a conditional solubility product (K_{so}) can be calculated. The K_{so} of struvite is defined as:

$$K_{so} = \frac{K_{sp} MgNH_4PO_4}{\alpha_{Mg} \alpha_N \alpha_P}$$

where α is the fraction of magnesium, nitrogen and phosphorus available for the formation of struvite.

The K_{so} when calculated takes into account the effect of pH on the formation of struvite, a K_{so} value can only be used for the calculation of the solubility product at a specific pH. The solubility of struvite decreases within the pH range (6.0-8.0) typically found within wastewater liquors, though it should be noted that the solubility begins to rise at pH values <9 (Snoeyink and Jenkins, 1980). If the environmental pH drops below 6 then the solubility of struvite rises, though the dissolution reaction is very slow (Ohlinger *et al.*, 1999).

Induction times of struvite formation have been reported to be greatly effected by the pH of the liquor. Booram (1975) showed a pH of 7 was the minimum for struvite formation with computer calculations, though at such low pH's the induction time was measured in days by Momberg and Ollermann (1992). Such long formation times are obviously unsuitable for a recovery operation, though are a problem for STW in scaling. Momberg and Ollermann

(1992) went on to show that at pH 8.5 the precipitation was reduced to under an hour and at pH 9 the formation of struvite was observed in less than 5mins. Nelson *et al.* (2003) were able to demonstrate a minimum solubility pH of struvite formation in swine lagoon liquors of 8.9-9.25 without dependence on the Mg:P ratio. Of note from Nelson *et al.* (2003) was a rise in the rate of reaction, a near tripling of the rate constant from 3.7 h^{-1} to 12.4 h^{-1} with a rise in the pH from 8.4 to 9. Work by Wang *et al.* (2005) demonstrated that when the pH of the solution was raised above 10 an amorphous precipitate was produced with particularly high impurity.

The pH within wastewater liquors is generally higher after anaerobic digestion, where most struvite scaling problems occur in pipework etc (Neethling and Benisch, 2004). Table 2.1 shows how the pH and concentrations of struvite constituents changes through Slough STW (Jaffer *et al.*, 2001)

Table 2.1: Change in phosphate, ammonia and magnesium concentrations through the Slough STW (Jaffer *et al.*, 2001)

Determinant	BNR effluent (average of 4 lanes)	Blended SAS	Digested Sludge	Centrifuge liquor
pH	7	7	7.3	7.6
$\text{PO}_4^{3-} \text{ (mg L}^{-1}\text{)}$	4	65	153	95
$\text{NH}_4^+ \text{ (mg L}^{-1}\text{)}$	2	90	1166	615
$\text{Mg}^{2+} \text{ (mg L}^{-1}\text{)}$	9	97	153	44

Not only does the pH rise after digestion but also the concentrations of struvite constituents, though there is some loss of nutrients in the centrifuge sludge cake. Sen and Randal (1988) attributed the rise in ammonia to the degradation of proteins and the rise in magnesium and phosphate concentrations to cell lysis during the digestion processes.

The pH of the liquor also plays an important role in the speciation of phosphate and ammonia. The change in speciation of phosphate as the pH changes is particularly dramatic. Figure 2.3 shows the changes in the speciation of phosphate at different pH values based on the measured pK_a values of the different protonated forms of phosphate.

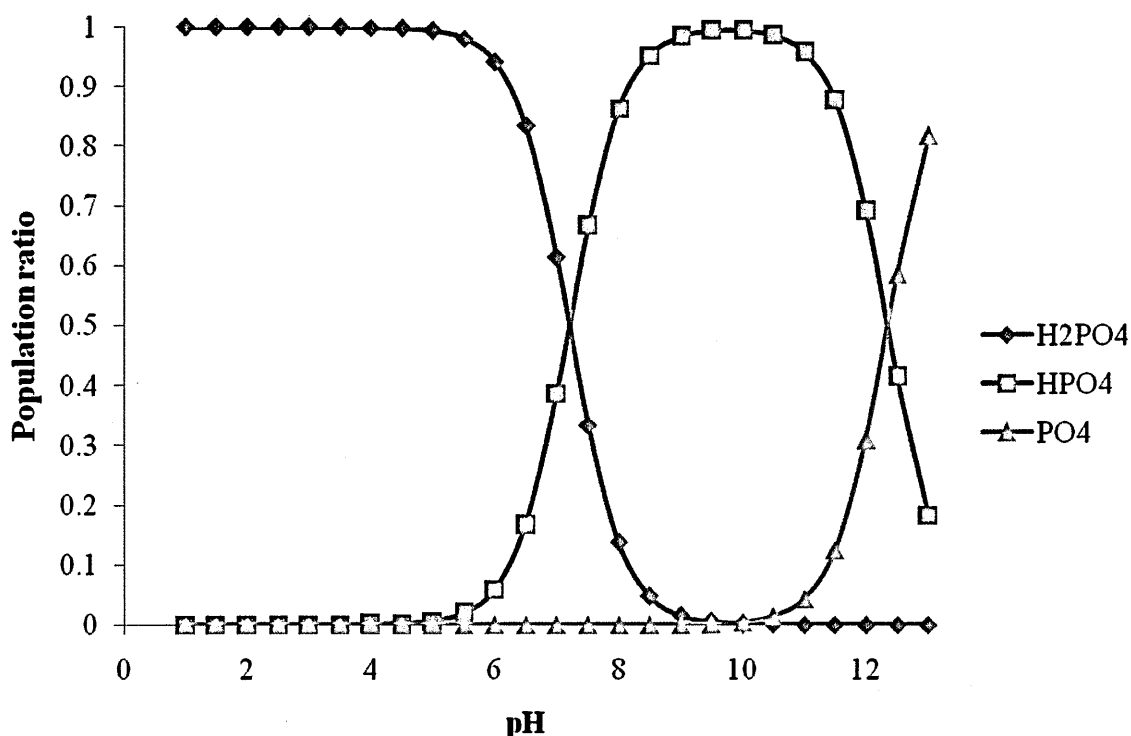


Figure 2.3: Changes in protonation of phosphate with change in pH of environment

It can be seen at a pH value of 7.4, typical for a digested liquor stream, there are equal amounts of $H_2PO_4^-$ and HPO_4^{2-} . As the pH rises above 7.5 then HPO_4^{2-} becomes the dominant species within the liquor. This data is important to recovery operations as all are run between pH values of 8-9 where HPO_4^{2-} is the major ion.

The speciation of ammonia is also dependent on pH. The equilibrium constant, K_a , has been reported as 5.7×10^{-10} , and as can be seen in the following equation is dependent on the pH of the solution (Suschka and Poplawski, 2004);

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = 5.7 \times 10^{-10}$$

Miles and Ellis (2001) showed with MINTEQA2 calculations that ammonia would start to be evolved at pH 9, with the rate of evolution increasing exponentially. Recent work though by Hafner *et al.* (2006) with ammonia volatilization within anaerobic digesters has shown this model to be out by as much as 45-200% at pH values of >8.8 due to the activity coefficients being equal to unity. Ali and Schneider (2006) found that up to 27% of ammonia was being lost from their reactant feed tanks due to ammonia gas formation. This would suggest that setting the pH of a recovery operation to under 9 would lessen ammonia loss but due to ammonia being in excess (<200mg L⁻¹) in all sites (Ueno and Fujii, 2001; Jaffer *et al.*, 2001; Battistoni *et al.*, 2005) the loss of ammonia to the atmosphere would have little impact on its availability for struvite formation.

2.2.2 Supersaturation and its effect on the formation of struvite

Crystal growth of struvite will continue until equilibrium is established or will continue indefinitely if there is a constant supply of constituent ions (Ohlinger *et al.*, 1999). The concentration of constituent ions is thus extremely important for the continued growth of struvite crystals.

Supersaturation of a solution can be defined as an “unstable system which has a greater concentration of material in solution than would exist at equilibrium” (Atkins, 2000). If a solution is supersaturated with respect to Mg, NH₄, and PO₄ then struvite precipitation can occur (Ohlinger *et al.*, 1998). The motivating factor for the formation of struvite in solutions supersaturated with these nutrients is the difference between the chemical potentials, $\Delta\mu$. This is calculated as the difference between the chemical potential of the salt in a supersaturated solution, μ_s , and that of the equilibrium potential, μ_∞ (Kofina and Koutsoukos, 2004).

$$\Delta\mu = \mu_{\infty} - \mu_s = [\mu_{\infty}^0 + kT \ln (a_{\text{mg}}^{2+} \cdot a_{\text{NH}_4}^+ \cdot a_{\text{PO}_4}^{3-})_{\infty}^{1/3}] - [\mu_s^0 + kT \ln (a_{\text{mg}}^{2+} \cdot a_{\text{NH}_4}^+ \cdot a_{\text{PO}_4}^{3-})_s^{1/3}]$$

Where k is the Boltzmann constant, T is the absolute temperature. If the chemical states of both standard states are considered to be equal the following equation holds:

$$\Delta\mu = kT \ln \frac{(a_{\text{Mg}^{2+}} \cdot a_{\text{NH}_4^+} \cdot a_{\text{PO}_4^{3-}})_s^{1/3}}{(a_{\text{Mg}^{2+}} \cdot a_{\text{NH}_4^+} \cdot a_{\text{PO}_4^{3-}})_{\infty}^{1/3}} = \frac{kT}{3} \ln \Omega$$

Where Ω can be defined as the divergence of the system from equilibrium (saturated) and is the motivating force for the formation of struvite. For $\Omega = 1$, the system is at equilibrium, for $\Omega > 1$ the system is supersaturated and precipitation can occur (Kofina and Koutsoukos, 2004). A relative supersaturation can be defined as

$$\sigma = \Omega^{1/3} - 1$$

The effect of the activities of different species within the system on the availability of constituent ions has been calculated with MINTEQA2 and MINEQL+ by a number of authors. Buchanan *et al.* (1994) and Ohlinger *et al.* (1998) took into account only four complexes of magnesium, three involving phosphate and one of ammonium but took different stability constants for each complex. The work of Buchanan *et al.* (1994) found that struvite's minimum solubility was at pH 9 and that struvite could precipitate between pH values of 7-9. Work by Bouropoulos and Koutsoukos (2000) took three more complexes involving magnesium into account with their calculations in an attempt to make the picture of struvite formation clearer. Bouropoulos and Koutsoukos (2000) found that no matter what level of supersaturation were trialled at pH 8.50, struvite was the only precipitate formed. It was also found in this work that induction time and supersaturation shared an inverse proportionality relationship.

Kofina and Koutsoukos (2004) in an attempt to better understand the formation of struvite included more complexes of magnesium and phosphate to their MINEQL+ calculations, 34 complexes compared to the seven used by Ohlinger *et al.* (1998). Included within the complexes examined was the effect of carbonate ions on struvite formation. The addition of carbonate ions into the calculations simulates the conditions within STW closer than previously done, where an alkalinity of 200mg L⁻¹ is typical (Jaffer *et al.*, 2001). In two different types of experiments, constant supersaturation (achieved by automated addition) and constant pH, it was found the threshold for homogeneous/heterogeneous nucleation was $\Omega = 3.18$ for constant pH and $\Omega = 4.45$ for constant supersaturation. Rates of precipitation were seen to have a parabolic dependence on supersaturation. It was also seen that sulphate, present as an electrolyte, had a delaying effect on the nucleation step for formation, which could have an effect on the recovery of struvite from STW liquors as sulphate is normally present at ~100mg L⁻¹ (Metcalf and Eddy, 2003)

Levels of supersaturation of $\Omega > 2$ have been linked to the production of struvite crystal fines. Fine crystals are small, unwanted crystals within a struvite recovery process (Battistoni *et al.*, 2006). Shi *et al.* (2006) reported that for liquors where the solution was overly supersaturated with struvite components it lead to the production of fines. Fines are particularly unwanted due to the difficulty with harvesting and the possibility of them being returned to the STW process where the possibility of scaling could occur (Battistoni *et al.*, 2001). The production of fines has been linked to the precipitation of struvite stripping available magnesium and limiting any further growth due to lack of magnesium (Abe, 1995). Abe (1995) was able to link the production of fines to a high phosphate concentration within the influent.

To overcome the production of fines, authors have found that by setting the reactor pH to ≥ 8.50 the reaction enters a metastable region (Hirasawa, 1996; Battistoni *et al.*, 2005; Ali and Schneider, 2005). The metastable is defined as the area between thermodynamic and kinetic equilibrium (Battistoni *et al.*, 2006). This condition is brought about by an appropriate operative pH and determined supersaturation levels from computer simulation programs (Ali

and Schneider, 2006). The metastable zone for a system is still considered to be supersaturated but crystallization occurs from surface diffusion which allows the growth of bigger crystals (Ali and Schneider, 2006). Nucleation within the metastable region is limited. Within this region it has been reported that precipitation cannot occur without the presence of seed materials e.g. quartz sand for the nucleation of struvite (Hirasawa, 1996). The metastable region is exploited to great effect at the Treviso struvite recovery plant (covered in greater detail later on in this review). Reactor conditions are not limited to struvite recovery but are also a feature of many industrial reactors operating with supersaturation conditions (Thaller *et al.*, 1981; McPherson, 1988)

2.2.3 The effects of other ions on the formation of struvite

The presence of calcium ions has been shown to affect the rate of formation and also the quality of struvite crystals produced. Le Corre *et al.* (2005); Wild *et al.* (1996); Momberg (1999) showed that by varying the Mg:Ca ratio the formation and quality of struvite crystals produced varied vastly. At ratios of 1:1 and above Le Corre *et al.* (2005) found that no crystalline material was produced in the reaction only amorphous sludge. Kofina and Koutsoukos (2005) showed that a competitive precipitation of calcium phosphate and struvite occurred with an increase of the concentration of calcium ions. In this study a critical supersaturation ratio of 50:1 was found to favour the struvite precipitation phase over that of calcium phosphate.

Apart from calcium effects of other ions present within wastewater streams have an effect on the formation of struvite. As already noted, Kofina and Koutsoukos (2005) noted that sulphate ions, present as electrolyte, increased the induction time of struvite formation. Kabdasli *et al.* (2004) reported a change in the induction time of struvite formation from 179sec for a sulphate concentration of 12.5 mmol to 265sec for a sulphate concentration of 25 mmol in solutions containing 2.45 mmol of $\text{NH}_4\text{H}_2\text{PO}_4$ and MgCl_2 . Of interest is the result that when the sulphate concentration was raised to 75 mmol there was an increase in the induction time to 46mins.

The effect of sodium and chloride were also measured by Kabdasli *et al.* (2004). Though the data isn't easy to understand due to unstable fluctuations in the concentrations present within the system it can be seen that sodium and chloride have a detrimental effect on the formation of struvite. An increase in the concentration of both sodium and chloride from 5mmol to 55mmol increased the induction time from 2min to 20min.

2.2.4 Effect of temperature on the formation of struvite

The effect of increasing temperature on reactions in general is an increase of the rate of reaction (Atkins, 2000). Temperature has also been shown to effect the crystallisation of struvite by Abbona *et al.* (1982), with a maximum of 50° C reported for the formation of struvite. A temperature limit of 30°C was shown by Choi and Eum (2002) with swine waste water, containing 220mg L⁻¹ of soluble phosphate at pH>8 to be the highest temperature for struvite precipitation. Celen and Turker (2001) showed that a temperature change of 25-40°C did not affect the removal of ammonia as struvite and it was only a change in magnesium source that had an effect on the amount of ammonia removed in the experiments. Jeong and Kim (2001) showed that a temperature of 45°C did not affect the production of struvite crystals in a composting process. Choi *et al.* (1997) saw that the production of struvite below 15°C was distinctly inhibited in a nightsoil system at pH 7.94 which contained between 480-780mg L⁻¹ of available phosphate. The effect of temperature on struvite precipitation seems to be inconclusive with different authors finding contradictory results. The data from the literature is very varied but for a recovery process where the temperature would very rarely rise above 20° C these results would have very little impact

Temperature has also been seen to have an effect on the solubility of struvite. Within the temperature range 10-50°C Aage *et al.* (1997) found that the thermodynamic solubility product was significantly affected by temperature rises due to the activity coefficients being dependent on temperature;

$$L_a = K_{sp} \cdot \gamma_{Mg^{2+}} \cdot \gamma_{NH_4^+} \cdot \gamma_{PO_4^{3-}}$$

where γ is the activity coefficient for each nutrient within the liquor and L_a is the thermodynamic solubility product.

The solubility product was seen to increase and reached a maximum of 37.3×10^{14} . At a temperature of 65°C there was a great drop in the L_a of struvite to an average of 17.5×10^{14} . Crystallographic investigation of the structure of struvite produced at 67°C showed an absence of the typical struvite structure. This information is particularly useful for any method for the drying of struvite and shows that only low temperatures may be used to dry recovered product e.g. air drying.

2.2.5 Struvite as a fertiliser

It has been often discussed that struvite could be used as a fertiliser for domestic and agricultural use (Potjer, 2001). Early reports appeared in the literature indicating the use of struvite as a slow release fertiliser due to its low solubility in water (Bridger *et al.*, 1961). The slow release property of struvite is particularly attractive to agriculture as nutrients are discharged throughout the growing cycle (Munch and Barr, 2001). With this gradual release of nutrients to soil it means that a smaller number of applications to crops are required which lessens the chances of damage to crops due to over application (Schuiling and Andrade, 1998).

More recently the fertiliser value of struvite was directly compared to monocalcium phosphate (MCP) by Richards and Johnston (2001). The study found that struvite was as good a fertiliser as MCP. The authors also extolled the virtues of struvite as a commercially attractive product due to its environmentally friendly production.

One weakness of struvite as a fertiliser is the lack of potassium (Gaterall *et al.*, 2000). Potassium is a requirement for effective growth of crops and the lack of potassium would mean further addition of potassium for struvite to be a complete fertiliser. Field trials of struvite blended with other nutrients were undertaken with struvite recovered from Slough STW (Jaffer *et al.*, 2001 and Johnson *et al.*, 2004). Struvite recovered was washed with water to remove organic and other solids and dried at 24°C. Blending of struvite for addition of other nutrients was done with rape seed meal, kali vinasse (plant used for the production of yeast, produced from the addition of ammonium sulphate to Vinasse), and hydrolysed feather meal. All blending agents provided a clear increase in leaf and plant diameter of petunias. Operations were seen to be commercially cost effective if not profitable.

Commercial sales of struvite to industry and the public have been taking place for the past eight years by Unitika Ltd, Japan (Ueno and Fujii, 2001). Full scale plants within Japan have been developed using the Phosnix process (see later for full description). The struvite that is produced is blended with other fertilisers to augment its effectiveness. The fertiliser is promoted on the name “Green MAP II” with focus on its environmental credentials i.e. produced from recycled waste of STW. The final product is sold for €250/ton, with transport costs borne by the purchaser.

2.2.6 Summary

Four conditions have been shown to affect the formation potential of struvite within STW i.e. pH, supersaturation, temperature, and the presence of other ions. Arguably the condition that plays the greatest role in the precipitation of struvite is the liquor pH. The pH controls the rate of formation and the speciation of struvite constituents which affects the engineering of a recovery operation. Supersaturation within the liquor also plays a significant role in struvite formation. Supersaturation controls the formation potential of struvite and has been investigated with computer calculations as well as experimental observations. Temperature of the liquors plays a role in the formation of struvite, though the data within the literature is

slightly confusing with different maximums reported for the precipitation of struvite and little information on minimum temperatures for struvite formation. The formation of struvite has been shown to be effected greatly by the presence of other ions within the liquor with calcium and sulphate being shown to have the greatest effect on the formation and quality of recovered crystals.

Struvite has been shown to be an effective fertiliser, especially when blended with a source of potassium. The use of recovered struvite as a fertiliser has already been shown to be commercially viable in Japan, with emphasis being placed on its 'green' qualities on the packaging.

2.3 Types of reactor for the recovery of struvite

There are at present four full scale operations for the recovery of phosphorus in the form of struvite from sewage liquors, although a number of other methods have been demonstrated for removal of phosphorus without recovery e.g. wetlands. Within the scope of this review only the two chemical methods which have received most attention will be examined. For a full review of other methods of phosphorus removal refer to Stratful *et al.* (1999) and Bashan and de Bashan (2004)

As two products exist for the recovery of phosphorus from sludge liquors, the concentrations of magnesium and calcium within the stream dictate the final product (Van Dijk and Wilms, 1991).

There are three elements that are typically altered within the reactor to aid precipitation of the desired product;

(i) Chemical constituents are altered simply by the addition of chemicals that are considered to be the limiting factors in the formation of the product. This is done to achieve supersaturation or metastable conditions within the reactor

(ii) The influent pH is altered commonly by the addition of base or the use of aeration to strip carbon dioxide so that the nucleation step can be made faster.

(iii) Addition of seed material allows for the growth of struvite crystals on the surface of seed materials which in turn allows for the growth of larger particles, which facilitates easier collection from the reactor.

2.3.1 Stirred Reactors

The simplest of the reactor designs available is the stirred reactor (see Figure 2). The stirring is generally carried out by mechanical paddle that operates at a constant speed, recirculation of reactant through the reactor (Ali and Schneider, 2006) or by the aeration of the solution with air (Jaffer *et al.*, 2001). These processes allow for there to be even distribution of chemicals throughout the system thus stopping any limitations on chemicals at crystal growth sites (Ali and Schneider, 2006). The nature of crystal growth requires that there is a constant source of chemicals for continued growth (Ohlinger *et al.*, 1999).

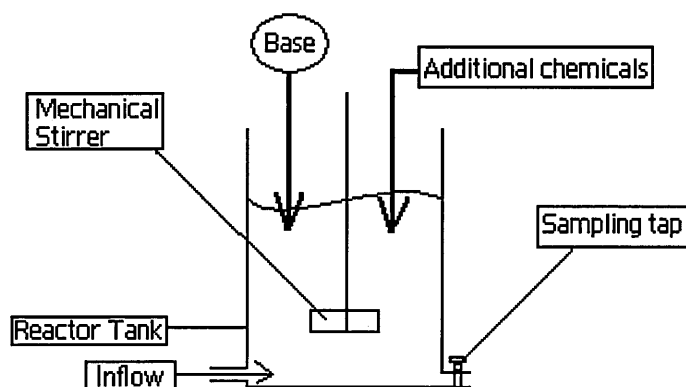


Figure 2.4: Simple mechanically stirred tank reactor, though stirring can be provided by air as well

Stirred reactors often require the addition of base to the solution to allow the elevation of pH (Mamais, 1994). A number of chemical methods have been tested to assess the effectiveness, product quality and economical cost of each method. The most common method for elevation of pH is with base with the addition of sodium hydroxide or magnesium hydroxide and is covered in greater detail in the following section.

Large scale stirred reactors for the production of struvite are not widely reported in the literature. Burns *et al.* (2001) used a 140,000 litre tank for the production of struvite from animal waste material with addition of 2000L of magnesium chloride, a 90% removal of phosphate was achieved. The recovered product was used as a fertiliser on nearby fields though unfortunately no results were given on the effect to these crops.

A 13,000L struvite reactor was trialled by Jaffer *et al.* (2001) at Slough STW with mixing achieved by aeration. With a relatively short residence time of one hour within the reactor, addition of magnesium chloride and sodium hydroxide for pH elevation a phosphate removal of 64% was achieved. Along with good phosphate removal large quantities of struvite were produced which were subsequently trialled successfully as a fertiliser when blended with a potassium source (Johnson *et al.*, 2004).

The effect of seeding a stirred reactor has been reported by Mangin *et al.* (2004). The authors found that seeding the 21L reactor with sand had no effect on changing the precipitation of struvite from homogeneous primary nucleation to heterogeneous primary nucleation. The reactor produced a large quantity of fines which was linked to the over supersaturation of the solution. This lack of nucleation was seen by Le Corre *et al.* (2006) in AFM studies on different types of seed material. It was seen in these studies by Le Corre *et al.* (2006) that sand had the second lowest affinity to stick to struvite. Mangin *et al.* (2004) trialled struvite as a seed material in further experiments. Struvite was shown to be ineffective also as a seed material for the stirred tank reactor due the production of a large amount of fines. Mangin *et al.* (2004) reported that even with dilution of the influent that there was still the over production of fines within the reactor.

2.3.2 Fluidised Bed Reactor (FBR)

In the fluidised bed reactor (FBR) the liquor passes upwards through a bed, generally made up of small particulate matter e.g. sand, at sufficient enough velocity to fluidise the media (see figure 3). This process is used in all full scale phosphate recovery processes i.e. Geesterambacht, Treviso and Shimane. At Treviso (Battistoni *et al.*, 2000) and Geesterambacht (Van Dijk and Wilms, 1991) the bed is quartz sand and at Shimane (Phosnix process) (Ueno and Fujii, 2001) the process uses recycled struvite 'fines'. The fluidisation process increases the surface area of the particulate matter as all faces of the solid are now accessible as reaction sites (Metcalf and Eddy, 2001). By using a high enough air inflow the solid material is able to overcome any aerodynamic drag and gravity to become suspended within the liquid. The fluidisation of the particles is used to achieve a greater level of mixing within the reactor and thus achieve a uniform mixing of reactants. A greater mixing of reactants will increase the nucleation rate and lower the chances of local supersaturation levels within the liquor which can lead to the over production of fines (Ohlinger *et al.*, 1999).

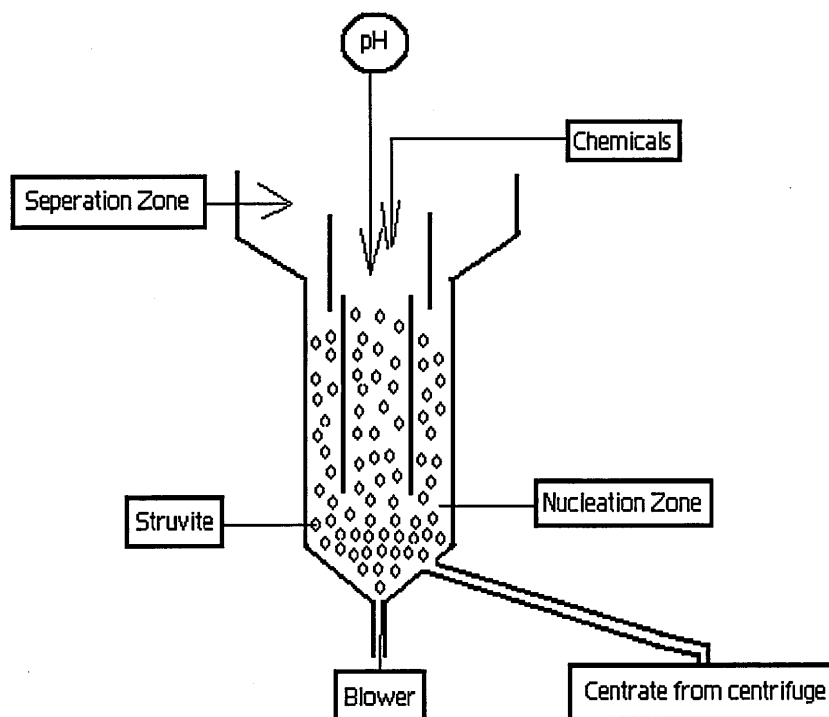


Figure 2.5: Simplified Phosnix FBR at Shimane, Japan

Fluidising the solution has been reported that it causes the fracturing of weaker particles thus producing more nucleation sites (Mersmann, 2001). The fluidisation of the bed also stops agglomeration of the seed materials thereby maximising the surface area of seed material (Van Dijk and Wilms, 1991). Van Dijk and Wilms (1991) reported the additional benefit of this system was that the pellets are relatively water free and did not require any further processing to remove water.

The FBR process for recovery of phosphate is generally divided into two separate phases, the air stripping phase and the reaction phase (Ueno and Fujii, 2001 and Battistoni *et al.*, 2005). The air stripping phase of the process is used to increase the pH of the solution by removal of carbon dioxide from the liquor. The air stripping phase can have a significant effect on the rate of precipitation where Battistoni reported the reaction period can be reduced from 8 days to 100mins (Battistoni *et al.*, 1998). Air stripping allows for the phosphate recovery process to proceed with a reduction in the amount of base needed in order to raise the pH of the

influent. It was shown by Battistoni *et al.* (1998) that air stripping allowed for a higher conversion and same product type as with a natural ageing process, though it should be noted that Treviso has a relatively low phosphate removal rate ~60% compared to Shimane <90%. This low result for Treviso could be attributed to the low phosphate influent concentration i.e. 42mg L⁻¹ for Treviso compared to 120mg L⁻¹ for Shimane, this low concentration has been seen within my work to have a significant impact on overall phosphate removal.

The reactor phase of FBR plants are mostly seeded so as to allow the greatest recovery rates of phosphorus (see later section on seeds and appendix tables for details on seed materials used). Seeding is undertaken so as to allow a nucleation site for struvite precipitation. A number of mathematical models for the precipitation of hydroxyl apatite (HAP) onto the solid surfaces have been put forward which can be applied to the process of struvite recovery. The first model put forward by DeRooij *et al.*, (1984) was produced under strict experimental conditions with the pH of the solution allowed to change from 5 to 8. This thermodynamic model measured the Gibbs free energy of the solution as related to the energy change from the supersaturated solution to a saturated solid phase where the product was growing. This showed that the growth of product on the seed material was pH specific.

A second model was developed from the work of DeRooij *et al.* (1984) by Kaneko and Nakajima (1988) where they described the growth of HAP under metastable conditions. Metastable conditions are defined as concentrations of constituents that are just below supersaturation, where precipitation can occur but not as rapidly as supersaturation conditions. This model proved to be very accurate and has been built upon by Battistoni *et al.* (2000) where the precipitation efficiency on seed materials could be related to the saturation of the solution. Further work by Battistoni *et al.* (2002) was able to link pH with saturation on the precipitation with seed materials. This further model proposed allows predictions on the precipitation efficiency of a FBR with a given concentration of constituents at a set pH e.g. at pH 8.5 a precipitation efficiency of 70% can be achieved with a contact time of 0.2h. Though this isn't the full story, the conversion of phosphorus to struvite is higher than the nucleation efficiency on the seed material; this implies the production of fines. To avoid the production of fines a higher contact time within the reactor is needed. To achieve a higher contact time

within a reactor recirculation of the fluid is needed though recirculation can be avoided by the introduction of a larger bed.

2.4 Optimisation of reactor conditions for the controlled formation of struvite

2.4.1 Concentration of constituents

The concentration of constituents in the liquor must exceed the solubility product of struvite for crystal growth to begin (Taylor *et al.*, 1963 and Ohlinger *et al.*, 1998). Constituent concentrations are thus related to the solubility of struvite and that supersaturation of these constituents needs to be achieved for effective precipitation.

For supersaturation to be achieved most reactors require dosing of magnesium, except for Treviso, Italy (Battistoni *et al.*, 2005) which has a higher magnesium influent concentration i.e. 45mg L^{-1} which is due to its location near sea water. Amounts of magnesium added to the influent are varied for two reasons. The first is the ratio of magnesium to phosphate within the influent. Some reactors raise the magnesium concentration to achieve a 1:1 ratio with phosphate e.g. Shimane and Osaka, or others raise it above a 1:1 ratio. Burns *et al.* (2001) showed that magnesium to phosphorus ratio of 1.6(Mg):1(PO_4) is ideal as not all magnesium will be available for precipitation due to the formation of other complexes within the solution (Buchanan *et al.*, 1994). The other reason which is not expressly suggested within the literature is to maybe counteract the influence of calcium ions within the influent. As already stated the calcium to magnesium ratio cannot be greater than 1:1 due to the influence of calcium species on struvite precipitation i.e. poor crystalline amorphous product Le Corre *et al.* (2005). Generally calcium is in excess of phosphate within liquors so a ratio of greater than 1:1 Mg:Ca should be set within a recovery operation to stop the detrimental effects of calcium on struvite precipitation.

Two forms of magnesium are typically used for the addition of magnesium. Magnesium chloride is the preferred choice within the literature e.g. Jaffer *et al.* (2001), Lee *et al.* (2004), though magnesium hydroxide has also been trialled e.g. Munch and Barr (2000); Ueno and Fujii (2001); Miles and Ellis (2001). Magnesium hydroxide is an attractive choice for reactors as it will raise the pH of the solution, which would lower the cost of raising the pH with the addition of base but pH cannot be altered independently of magnesium addition. Ueno and Fujii (2001) use sodium hydroxide to alter the pH to offer finer control. There is a downside to magnesium hydroxide addition and that is its low solubility which has been linked to the clogging of pipes and having a detrimental effect on crystal quality of recovered product (Miles and Ellis, 2001). Due to these reasons the use of magnesium chloride is more popular. Magnesium chloride is cheaper than magnesium hydroxide and is readily soluble in water. One other source of magnesium has been trialled within a pilot plant and that is the use of magnesium sulphate. Both magnesium chloride and sulphate are near equal in price (Fisher chemicals, UK) and Yoshino *et al.* (2003) (Table 4.3) found that using magnesium sulphate did not lead to any detrimental effects in the operation like those associated with magnesium hydroxide. With this information the use of magnesium chloride would be favoured though the further trialling of magnesium sulphate should be considered.

Chemical speciation within the liquor has been shown to depend on pH (Ohlinger *et al.*, 1998). As has been previously shown (see section; chemistry of struvite) phosphate and ammonia exist in different forms at different pH values. The solubility of struvite was linked by Ohlinger *et al.* (1998) to the speciation of these components. The author was able to show that the presence of magnesium phosphates within the solution lowered the solubility of struvite by the removal of these vital components, with their presence prevailing at pH 8.5. The lowest point of struvite solubility had been shown to be at pH 9. A rise above pH 9 saw the stripping of ammonia from the liquor and an increase of phosphate concentration (Booker *et al.*, 1999), which has been linked to the over production of fines due to the stripping of magnesium from the liquors. Though it should be noted a number of higher minimum solubility's have been published in the literature at pH 10 or higher (Ohlinger *et al.*, 1998, Booram *et al.*, 1975; Momberg, 1992). Katuura *et al.* (1998) showed that the removal of phosphate from the solution increased as the pH of the solution increased from 8-9 but after a pH of 9 no more phosphate was removed from the solution. Understanding the speciation of

struvite components and the solubility is thus vital to a decision on the pH in the reactor. For a reactor which has a short HRT (hydraulic retention time) then the ideal pH would be 9, for longer HRT's then a pH of 8.5 would be more suitable.

2.4.2 pH alteration; how, why and to what effect

Arguably the most important condition within a reactor is the pH of the liquor. pH choice plays a extensive role in the speciation of reactants, speed of reaction, nature of product and overall reactor design.

By far the easiest method to alter pH is with the addition of base such as sodium hydroxide e.g. Shimane and Osaka. The addition of base is an expensive process and methods to avoid this procedure have been well researched. Treviso and Geesterambacht both employ an air stripping unit for the removal of carbon dioxide from the liquor. Carbon dioxide within the liquor reversibly forms carbonic acid (H_2CO_3) thereby lowering the pH. The removal of this CO_2 by injection of air into the liquor raises the pH without the addition of base (Battistoni *et al.*, 1997). This method while very attractive requires a substantial unit for the removal of CO_2 from the liquor which makes it an expensive investment. Ohlinger *et al.* (1999) were able to show that vigorous stirring of solutions was able to raise the pH from 8-8.5 though this took a mixing speed of 500rpm and economics of such a reactor should be taken into account.

The speed of formation of struvite has been shown to be controlled by the liquors pH and for a commercial recovery operation this is very important. Momberg (1994) was able to show that by increasing the pH to 9 then nucleation could be achieved within a few minutes. One problem with such high pH is the production of fines. Fines have been a problem for a number of authors e.g. Mangin (2004) and Le Corre *et al.* (2006). Due to the production of fines at high pH's Battistoni *et al.* (2005) were able to show that by setting the pH to 8.5 the precipitation of struvite could be changed from a homogeneous to heterogeneous process

with the use of a seed material. Depending on the conditions required within the reactor, that is a seeded or non-seeded reactor, the selection of the pH will be dependent.

2.4.3 The role of seed and accumulation materials

Seed and accumulation materials are used within reactors to aid the growth of crystals. The formation of fines within reactors is a well reported problem as has already been indicated (see Section 2). To overcome the formation of fines within reactors, the use of seed materials and accumulation devices has been reported greatly. The use of seed material is generally carried out in the meta-stable zone of struvite supersaturation. This is generally achieved by setting the pH >8.6 in the reactor. Within this area of thermodynamic instability, nucleation of struvite may only happen on the surface of seed material, so eliminating the formation of fines.

A system of self seeding is employed at Shimane, Japan (Ueno and Fujii, 2001) (Table 2.2). The Shimane recovery plant has three reactors for the recovery of struvite, two 500 m³ d⁻¹ reactors and one 150 m³ d⁻¹ reactor. Fine struvite crystals are grown within the reactor column at a pH of 8.2-8.8. Approximately every ten days fine crystals are discharged from the bottom of the FBR and collected. Fine struvite crystals are reintroduced to the nucleation zone of the reactor for continued growth. Larger struvite pellets are collected separately from the FBR and are dewatered. This method is very successful with 500kg of struvite being produced per day and a 90% reduction of phosphorus from the influent. To achieve these results though a high hydraulic retention time (HRT) of 10 days is employed which is quite high when compared to other reactors e.g. Suzuki (2005) 3.6h, Jaffer *et al.* (2001) 64min and Munch and Barr (2001) 1h, but then Shimane has one of the highest phosphate removals.

Sand is relatively cheap material that has been used as a seed material. Sand has been used in the recovery of calcium phosphate at both Geesterambacht and Treviso HAP trial (Table 2.2 and 2.6 respectively). At Treviso the use of sand as a seed material for the production of

struvite has achieved excellent results. Treviso uses a combination of air stripping to provide the bulk of the pH rise and the addition of small amounts of sodium hydroxide to aid the air stripper. In a demonstrative experiment 650m³ of influent was able to produce 280Kg of struvite. It should be noted that Treviso has a very low phosphorus concentration in the influent but even so recovery rates of 60-75% of phosphorus as crystalline material are achieved.

A system of self seeding of struvite is employed in a pilot plant by Ishikawa *et al.* (2004). This method uses a second smaller reactor connected to the main reactor. Within the smaller reactor 'fine' struvite crystals are allowed to grow to 0.1mm in diameter. These crystals are then reintroduced to the main reactor where growth is continued and grain sizes of between 0.25-0.4mm are achieved. This method is very successful with a 97% reduction of soluble phosphorus from the influent. To achieve these results though a high hydraulic retention time (HRT) of 3-4 days is employed which is quite high when compared to other reactors.

Shimamura (2003) (Table 4.4) operated a similar pilot plant to Ishikawa but with the objective of being able to control the crystal particle size with a shorter HRT. Conditions within the reactor were set so that crystals entering the main reactor were of a defined size. By defining the size of the seed materials entering the authors were able to control the product crystal size. Shimamura (2003) went on to show that the phosphorus recovery rate was related to the influent phosphorus concentration and the surface area of the struvite seed material, they were also able to show that as the influent phosphorus concentration rose so the production of 'fines' rose as well. This relationship suggests a method of being able to overcome the production of fines within reactors which can plague phosphorus recovery methods i.e. find a suitable phosphate influent concentration and alter with dilution to maximise particle size. Wang *et al.* (2006) was able to show that the low specific gravity of struvite and its ease of being fluidised made it an excellent seed material. The authors were also able to conclude that due to its higher surface area to weight ratio it was a better seed material than sand or granite.

Accumulation devices work in a different manner to seed materials. Suzuki *et al.* (2005 table 4.3) used a 1mm diameter mesh to facilitate the accumulation of struvite. The mesh was submerged within the top half of the reactor and struvite cross bridged on the surface. Different materials were trialled with metals i.e. steel, copper and aluminium all working well. It was found by the authors that a mesh made of rubber was particularly unsuitable for struvite recovery. The mesh was submerged for 30 days for the experiments with the struvite being harvested by the light brushing of the mesh. A 50% reduction in effluent phosphate though is rather low and cause for note. This method of recovery is very attractive due to the simple nature of the reactor setup; the cheapness of the material also helps make this an area for further investigation.

2.4.4 Design of reactor for phosphorus recovery

There currently exist five full scale phosphorus recovery operations, three in Japan and two in Europe. All five of the operations share a very similar design philosophy with the only differences being in seed material used and the way the desired pH is achieved.

The Shimane plant reactor has two internal compartments for the reaction and the settling of struvite. The inner section of the reactor is the nucleation zone and the outer section of the reactor is the separation zone (see Figure 2.5). The separation zone allows the settling of struvite crystals with collection happening about every ten days by discharge from the bottom of the reactor. The smaller struvite crystals, fines, are returned to the reactor to provide new seed material for the reactor to continue operating.

With the Crystalactor[®] at Geesterambacht, a similar reactor design is seen but instead of recycled struvite acting as a seed material for the growth of product, quartz sand is used to grow HAP on (see Fig 4). The influent is pumped in an upward direction at high velocity (30-50m/h) to enable a complete fluidisation. Pellets of HAP-sand grow and as their mass increases there isn't enough pressure to keep them fluidised and so they settle at the bottom

of the reactor. Treviso's reactor also has the same design as the Crystalactor[®] with pellets grown on sand and removed in the same manner.

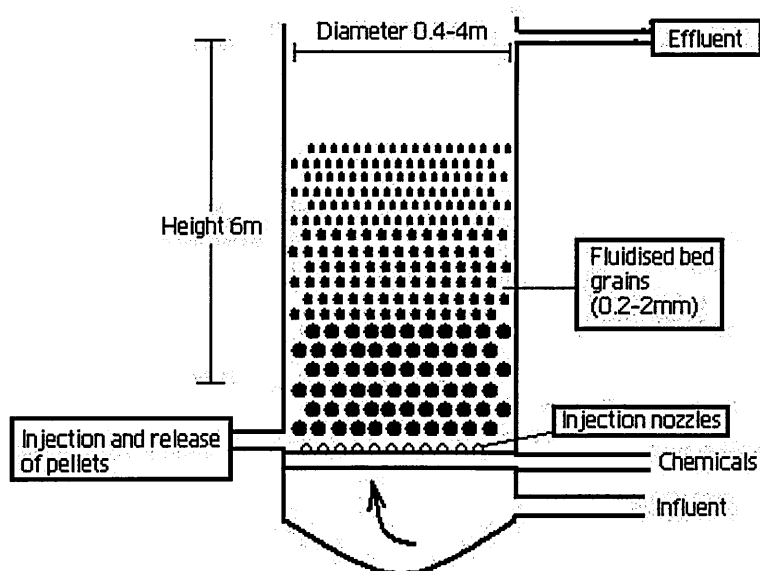


Fig 2.6 Geesterambacht Crystalactor[®] design

The design philosophy for an FBR reactor in the literature is quite standardised. There exist two main options which are varied in all the operations, how to achieve operation pH and collection of product. Aeration has been demonstrated as a good method for the raising of the pH and has been successfully demonstrated at Treviso and Geesterambacht. The addition of base though is far easier method and doesn't require the installation and operation of a further unit, with NaOH being a relatively cheap chemical to purchase, though amounts required would vary depending on the alkalinity of the liquors. The other choice when designing a recovery operation is the method of recovering the product. Settling within the reactor is considered the easiest method available and is achieved by the use of seed materials at Shimane, Treviso and Geesterambacht. Two other options are available though for the recovery of the final product, accumulation device and coagulating polymers. Accumulation devices such as steel mesh as reported by Suzuki *et al.* (2005) and Le Corre *et al.* (2006) have

both shown great results for the collection of struvite and initial results from this project have confirmed these results. One problem with this method though is how to transfer it to a full scale operation. Unfortunately it is difficult to set a machine to clean the mesh and so it would need to be done by hand, adding costs to the operation. The use of polymers to coagulate the crystals was shown by Le Corre *et al.* (2006) to be an effective means for the collection of the product in synthetic liquors. This method for the collection of product is to be investigated further within this project.

Though FBR reactors seem to be the most popular type stirred reactors have been trialled at two sites and along with many bench scale tests. Stirred reactors have their own problems but one big advantage in that they are relatively simple to operate. The reactor design of Slough was designed with the same principles as that of the Phosnix process i.e. two zones within the reactor, one for nucleation and another for settling (see Fig 5)

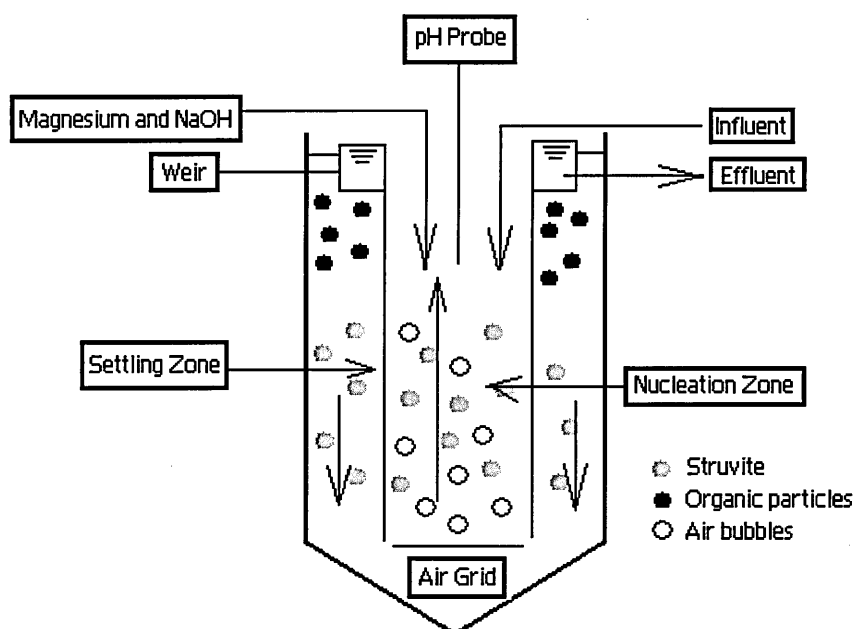


Fig 2.11 Slough stirred tank reactor design

2.4.5 Hydraulic retention time

The HRT of a reactor is of particular importance to the design. HRT is a measure of the average residence of a soluble compound within a reactor (Sinnott, 2005). The longer the HRT the larger the reactor needs to be. In theory the longer the HRT the larger the crystal size and phosphate removal should be. To achieve larger crystal sizes a high HRT (10 days) is coupled with a recycling unit in the Phosnix process. Mamais *et al.* (1994, Table 2.5) found that a HRT of 14 days was most suitable and achieved a 91% removal of phosphate, though there is very little information on product size or quality.

Other authors have found that shorter HRT's have yielded good results. Suzuki *et al.* (2005) found that a HRT of 22h was suitable for the accumulation reactor and Jaffer *et al.* (2001) was able to precipitate good sized crystals with a very short HRT of 64mins within a stirred reactor. Short HRT's are more attractive due to the lower costs and ways of achieving this should be investigated further

Munch and Barr (2001) though showed by varying the HRT between 1-8h there was no effect on the product size or removal rate. By linking other's work it might mean that HRT does not have that great effect on the crystal size or removal rates. Crystal size and phosphorus removal could then be a function of the operating pH. For the reactors with the longest HRT a link can be made to the pH being >8.7 . This idea is not expressly presented in the literature and could be an area of further research.

2.4.6 Summary

Optimisation of the recovery process can be undertaken in a number of different ways. By changing the concentration of the constituents within the liquor supersaturation of the solution can be achieved although this has a detrimental effect on the size and quality of particles. Conditions within what is known as the meta-stable region have been seen to reduce

the production of fines when seed material is used. Further addition of magnesium is generally required due to low concentration and the achievement of a 1:1 ratio with magnesium. Magnesium may be added in a number of ways though the most common and least problematic is with the addition of MgCl_2 . In this thesis a range of $\text{Mg}:\text{PO}_4$ ratios will be tested so as to be able to make a choice of the best ratio for struvite precipitation.

Changing the pH of the solution allows you to decrease the nucleation time of struvite, making it more commercially viable. Again there are a number of methods available to raise the pH. The addition of NaOH is the most common chemically due to its high availability and in the current work is the method of pH adjustment. Stripping of carbon dioxide from liquors is the other favoured method for raising the pH of the solution and is done by the injection of air to the liquor. Though initially expensive to set up it generally requires the addition of smaller amounts of chemicals to achieve the desired pH. The pH level within recovery processes varies from 8.2-9 depending on the strategy of the recovery process. Within the current work a pH of 9 was selected to allow for rapid struvite nucleation, in awareness that this can cause the precipitation of fines.

All five of the major phosphate recovery operations employ the use of seed materials within the reactors. Addition of seed material provides nucleation sites for the growth of struvite. Choice of seed material depends on the system in question with air stripping favouring the use of sand and chemical base addition the use of struvite as a seed material. Steel mesh has been seen to provide an excellent accumulation material for the capture of struvite and is an area of further research interest. The current work will focus on testing both types of reactor i.e. the FBR and stirred tank, to allow a direct comparison between each type. Methods for accumulating struvite crystals will be investigated to overcome the production of fines.

2.5 Appendix Tables

Table 2.2: Operational phosphorus reactors

Reference	Process	Method	Influent	Seed	Dimensions	Flow rates	pH adjustment	Influent constituent conc. (mg/L ⁻¹)	Chemicals added to aid precipitation	Phosphate removal	Product type and structure	Further information
'Shimane, Japan' Ueno (2001)	FBR, Phosnix Process	Continuous	Filtrate from mechanical dewatering process	Reused MAP from previous recoveries to seed the reactor	Capacity 1500m ³ d-1. Reactor 5.5m by 2.5m	46m ³ /h of filtrate enters reactor. HRT= 10days	8.2 - 8.8	Mg: 11.2	NaOH used to control pH and Mg(OH) ₂ as a source of Mg	Works currently removes 90% of soluble P that enters the reactors	~500kg of MAP produced each day, large crystals produced, between 0.5-1mm	Continuous flow through with MAP being siphoned off and crushed
								PO ₄ : 120				
'Geestmerambacht, Holland' Crystallactor Piekma, P.G. (2002)	FBR Bio-Chemical, 'Crystallactor'	Continuous	Secondary effluent	Sand	3 plants, 6m by 4m	6.3m ³ /h of effluent enters the reactor	8.0-8.5	Ca: 130	Ca(CO ₃) added as a source of Ca.	Between 70-80% removal of P from the influent	Ca ₃ PO ₄ removed. Crystals are about .80mm in size and good quality	Continuous flow through reactor, with crystals being separated sent for recycling
								PO ₄ : 67 NH ₄ : 437				
'West Bari, Italy' Petruzzi <i>et al</i> (1983)	Rim-Nut ion exchange membrane	Continuous	Secondary effluent	No seed used	Full Scale	10m ³ /h	pH 9	Mg: 24	None added	160kg of dried struvite after 3 months	Good size MAP crystals used on plants with reasonable results as a slow release fertiliser	Continuous flow through ion exchange membrane that when the trapped P is eluted with Mg then MAP is produced
								PO ₄ : 139 NH ₄ : 914				
'Treviso, Italy' Battistoni <i>et al</i> , (2005)	FBR	Can be operated as both continuous and batch	Anaerobic supernatant from belt press	Quartz sand	Air stripping column=1.3-2.1m ³ , and FBR=1.3m ³	1-2m ³ /h	8.5	Mg: 48	NaOH to aid pH rise	60-75% removal of P from influent.	MAP collected on sand as agglomeration	
								PO ₄ : 42 NH ₄ : 272				

Table 2.3 Pilot plants operated onsite

Reference	Process	Method	Influent	Seed	Dimensions	Flow rates	pH adjustment	Influent constituent conc. (mg/L ⁻¹)	Chemicals added to aid precipitation	Phosphate removal	Product type and structure	Further information
'Slough STW, UK' Jaffer <i>et al.</i> , (2001)	Air stirred tank reactor	Continuous	Centrate Liquor	No seed used	13.6m ³ total volume, with 5.8m ³ for reaction zone	Max 7.2m ³ /hr, avg. m ³ /hr, with a HRT of 64mins	Average of 9	Mg: 22	MgCl ₂ used as an additional source of Mg. NaOH added to raise pH when necessary	68% P removal at pH 7.7, 80% at this pH with MG added. pH 8.5, 90%	MAP recovered from process, large sized crystals with little impurity	
								PO ₄ : 111				
'Michigan, USA' Miles and Ellis, (2001)	Anaerobic sequence batch (ASBR) reactor with separate clarifier for MAP precipitation	Continuous	Swine waste water	No seed used	ASBR=84L and clarifier=4.4L	0.0002m ³ /h into clarifier	9.4 was found to be optimum for MAP ppt	Mg: 67	Mg(OH) ₂ (50%) added with 0-46-0 phosphate fertiliser for pH raise. Changed to MgO and K ₃ PO ₄	100% removal of P though NH ₄ was main aim of paper. 98% removal of NH ₄	Only conformation of MAP in clarifier by X-Ray is presented in paper	It was found that magnesium hydroxide slurry was clogging inlet piping due to lack of complete solubility of slurry.
								PO ₄ : 480				
'Oxley Creek, Australia' Munch and Barr, (2000)	FBR	Continuous	Sludge from centrifuge dewatering	500g of MAP added	1365mm of liquid, with 2 inner chambers of diameters of 600mm and 300mm. Total volume= 143	Influent flow= 0.002m ³ /h. Air flow rate =7L/min, HRT of between 1-5h	pH of 8.5	Mg: 13	60% Mg(OH) ₂ used as a source of Mg and pH raiser	320g of MAP per day. 94% of P removed from influent	Small crystals with an average size of 110µm produced. High purity.	Different HRT's were tested but with no noticeable change in product size
								PO ₄ : 70				
								NH ₄ : 820				

Table 2.4: Pilot plants operated onsite

Reference	Process	Method	Influent	Seed	Dimensions	Flow rates	pH	Chemicals added to aid precipitation	Influent constituent conc. (mg/L ¹)	Phosphate removal	Product type and structure	Further information
Suzuki <i>et al</i> (2004)	FBR	Continuous	Swine Waste Water	No seed used	Mixing Reactor h=1.40m and d=0.74m. Settling reactor h=2.24m and d=1.5m	0.2m ³ /h. HRT of 3.6h for aeration column and 22h for total reactor	pH 8.0 achieved with air stripping CO ₂	Oil added to reactor to stop the build up of bubbles in the reactor due to aeration.	Mg: 48 PO ₄ : 68 NH ₄ : ?	95% of P	Struvite crystals of 0.2mm were grown in the experiment on the air on the inlet	
Kalyuzhnyi <i>et al</i> (2003)	FBR	Batch	Anaerobic digested pig manure	Floccular anaerobic sludge	Height=85cm and Diameter=6.8cm	0.005m ³ /h though this was changed occasionally to ensure good mixing	6.7-8.8 through air stripping	NaOH added to aid rise in pH from air stripping	Mg: ? PO ₄ : 190 NH ₄ : 242	Up to 80% P removal	MAP and HAP. No information given on structure of product	Operating temperature of ~22C
Burns <i>et al</i> (2001)	Stirred	Continuous	Secondary swine manure	None used	140,000L swine waste storage pool	Not available	9	MgCl ₂ added for source of Mg. 2000L of it	Mg: 858 PO ₄ : 572 NH ₄ : ?	90% achieved in field experiments	Struvite recovered in confirmed by X-Ray	The recovered product was sprayed directly onto fields as a fertiliser,
Szögi <i>et al</i> (1997)	Metal Ion Addition	Continuous	Pre-treated swine wastewater	Marl Gravel (Impure fine grained limestone)	Tank (ø=1.5mh=0.6m)	25m ³ /h	The pH of the liquors is not mentioned in paper	Not available	Not available	37-52% over 1-4 cycles removal, though 100% was achieved in bench scale	No information given on MAP crystal size or quality	Liquid cycled between 1-4 times

Table 2.5 Laboratory scale struvite recovery reactors

Reference	Process	Method	Influent	Seed	Dimensions	Flow rates	pH	Chemicals added to aid precipitation	Influent constituent conc. (mg/L ⁻¹)	Phosphate removal	Product type and structure	Further information
Mamais <i>et al.</i> (1994)	FBR	Continuous	Activated sludge and primary sludge	No seed was used. FeCl ₃ was used to precipitate the MAP	V=225L though reduced to 4L later	HRT=12-15 days	7	Not available	Not available	91% removal of P	No information on structure or purity of product	
Wilsenach <i>et al.</i> (2007)	Stirred	Batch	Synthetic urine solutions	None	H=300mm d=100mm	Variable stirrer speed	9.4	MgCl ₂	Different MgCl ₂ ratios used in experiments	Up to 99% efficiency	Long needle like crystals up to 1mm in length	Mixing speed effected the amount of precipitate collected
Shimamura <i>et al.</i> (2003)	FBR	Continuous	Sludge liquors	Recirculated MAP crystals used for growth of larger crystals	Not available	0.045-0.3m ³ /h	8	MgCl ₂ added as source of Mg. And alkali added to raise pH to desired level	Mg:140 PO ₄ :90.3 NH ₄ :514	92% removal rate of P	Crystals of upto 2.1mm were grown after 3days of recirculation within tanks	Initial MAP seed crystal size were shown to effect the growth rate. Smaller seed crystals lead to the highest overall growth
Lee <i>et al.</i> (2004)	Hybrid anaerobic reactor.	Continuous	Food waste	Lake sediment	Total volume 59L, after packing material added 29.4L	HRT of up to 143 days was tested with reactor	8.3	MgCl ₂ added to solution. Alkali also added to increase pH	Mg:256 PO ₄ :570 NH ₄ :610	65% of P removed by reactor	Struvite crystals grown up to 700µm in length.	By applying extinction mode analysis 73% of P was removed

Table 2.6: HAP reactors

Reference	Process	Method	Influent	Seed	Dimensions	Flow rates	pH	Chemicals added to aid precipitation	Influent constituent conc. (mg/L ⁻¹)	Phosphate removal	Product type and structure	Further information
Battistoni <i>et al.</i> (1997)	FBR	Continuous	Supernatant of aerobically digested sludge	Quartz Sand	Air stripping column=	0.18-0.3m ³ /h	8-8.7	None	Ca: 48	Between 53-81% of P removed from the influent, on average 61% was removed, better results were shown at lab scale	HAP and Ca ₃ (PO ₄) ₂ produced though poor crystalline quality as demonstrated by X-Ray analysis	The pilot plant was tested over a course of 40 days at Treviso
									PO ₄ : 42			
									NH ₄ : 272			
Kim <i>et al.</i> (2006)	Stirred	Continuous	Water from industrial produced slag	Powdered converter slag	Not available	HRT of 2h	8.0-8.5	pH raised with NaOH. CaCl ₂ added to the reactor for Ca source	Ca: 111	75-98% of P recovery	HAP of good quality was produced, with little water content	
									PO ₄ :5			
									Total-N: 3.6			
Angel (1999)	FBR	Continuous	Secondary effluents	Not Available	D=17.6cm	0.012-0.120 L/h, most experiments carried out at 50L/h	10.2-10.5	CaSO ₄ added for source of Ca.	Ca: 240	>98% on lab scale, falling to 95% on pilot scale at STW	HAP was produced in the experiments of good quality	The recovered product from the pilot plant did not contain the P levels that the lab scale had done
									PO ₄ : 83			
									NH ₄ : 25			

a

2.6 References

Aage, H.K, Andersen, B.L., Blom, A., Jensen, I. (1997) The solubility of struvite. *Journal of Radioanalytical and Nuclear Chemistry* **223** (1-2) 213-215

Abbona, F., Lundager-Madsen, H.E., Boistelle, R. (1982) Crystallisation of two magnesium phosphates, struvite and newberyite: effect of pH and concentration. *Journal of Crystal Growth* **57**, 6-14.

Abbona, F. and Boistelle, R. (1985) Nucleation of struvite. *Crystal Reasearch Technology* **20**, 133-140.

Abe, S. (1995) Phosphate removal from dewatering filtrate by MAP process at Seibu treatment plant in Fukuoka City *Sewage Works in Japan* 59-64.

Ali, M. I. and Schneider, P.A. (2006) A fed batch design approach of struvite system on controlled supersaturation. *Chemical engineering sciences* **62**, (12) 3951-3961.

Ali, M. I. and Schneider, P.A. (2005) Crystallization of struvite from metastable region with different types of seed crystal. *Journal of Non-Equilibrium Thermodynamics* **30**, (2) 95-111.

Angel, R. (1999) Removal of phosphate from sewage as amorphous calcium phosphate. *Environmental Technology* **20**, (7) 709-720.

Atkins, P.W., *Physical Chemistry* 5th Edition, Oxford University Press

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.

Battistoni, P., Pavan, P., Prisciandaro, M., Cecchi, F. (2000) Struvite crystallization: A feasible and reliable way to fix phosphorus in anaerobic supernatants. *Water Research* **34**, (11) 3033-3041.

Battistoni, P., Paci, B., Fatone, F., Pavan, P. (2005) Phosphorus removal from supernatants at low concentration using packed and fluidized-bed reactors *Industrial and Engineering Chemistry Research* **44**, (17) 6701-6707.

Battistoni, P., Pavan, P., Cecchi, F., Mata-Alvarez, J. (1998) Phosphate removal in real anaerobic supernatants: Modelling and performance of a fluidized bed reactor *Water Science and Technology* **38**, (1 pt 1) 275-283

Battistoni, P., Paci, B., Fatone, F., Pavan, P. (2006) Phosphorus removal from anaerobic supernatants: Start-up and steady-state conditions of a fluidized bed reactor full-scale plant. *Industrial and Engineering Chemistry Research*. **45**, (2):663-669

Battistoni, P., Fava, G., Pavan, P., Musacco, A., Cecchi, F. (1997) Phosphate removal in anaerobic liquors by struvite crystallization without addition of chemicals: Preliminary results. *Water Research* **31**, (11) 2925-2929.

Benisch, M., Clark, C., Sprick, R.G., Baur, R., (2000) Struvite deposits: a common and costly nuisance. *WEF Operations Forum*.

Bhattacharai, Mohajit, Taiganides, E.Paul, Yap, B.C. (1989) Struvite deposits in pipes and aerators. *Biological Wastes* **30**, (2) 133-147.

Burns, R.T., Moody, L.B., Walker, F.R., Raman, D.K. (2001) Laboratory and in-situ reductions of soluble phosphorus in swine waste slurries *Environmental Technology* **22**, (11) 1273-1278.

Booker, N.A., Priestley, A.J. and Fraser I.H., (1999) Struvite formation in wastewater treatment plants: opportunities for nutrient recovery *Environmental Technology* **20**, 777-782.

Borgerding, J. (1972) Phosphate deposits in digestion systems. *J Water Pollution Control Fed* **44**, 813-9.

Bouropoulos, N.Ch., Koutsoukos, P.G. (2000) Spontaneous precipitation of struvite from aqueous solutions. *Journal of Crystal Growth* **213**, (3-4) 381-388.

Bridger G. L., Salutsky M. L. and Starostka R. W. (1961) Metal ammonium phosphates as fertilisers. In *140th meeting of the American Chemical Society*. Chicago, Illinois.

Çelen, I., Türker, M. (2001) Recovery of ammonia as struvite from anaerobic digester effluents. *Environmental Technology*. **22**, (11) 1263-1272.

Choi, E., Oa, S.-W., Lee, J.-J. (1997) Nightsoil treatment plant converted into a sequencing batch reactor to improve removal of pollutants and nutrients. *Water Science and Technology* **35**, (1) 233-240.

Choi, E., Eum, Y. (2002) Strategy for nitrogen removal from piggery waste. *Water Science and Technology* **46**, (6-7) 347-354.

Coe, F.L., Evan, A., Worcester, E. (2005) Kidney stone disease. *Journal of Urology* **174**, (4 II) 1711-1714.

Cullen, D.J. (1988) Mineralogy of nitrogenous guano on the Bounty Islands, SW Pacific. *Ocean Sedimentology* **35**, (3) 421-428.

Doyle, J.D., Parsons, S.A. (2002) Struvite formation, control and recovery. *Water Research* **36**, 3925-3940.

Doyle, J.D., Oldring, K., Churchley, J., Parsons, S.A. (2002) Struvite formation and the fouling propensity of different materials. *Water Research* **36**, (16) 3971-3978.

DeRooij, J.F., Heughebaert, J.C., Nancollas, G.H. (1984) pH study of calcium phosphate seed recovery. *Journal of Colloid and Interface Science* **100**, (2) 350-358.

Dunn, S., Impey, S.A., Kimpton, C.M., Parsons, S.A., Doyle, J., Jefferson, B. (2004) Surface diagnostics for scale analysis. *Water Science and Technology* **49**, (2) 183-190.

Edge, D. (1999) Perspectives for nutrient removal from sewage and implications for sludge strategy. *Environmental Technology* **20**, (7) 759-763.

Fujimoto, N., Mizuochi, T., Togami, Y. (1991) Phosphorus fixation in the sludge treatment system of a biological phosphorus removal process. *Water Science and Technology* **23**, (4-6) 635-340.

Gaterell, M.R., Gay, R., Wilson, R., Gochin, R.J., Lester, J.N. (2000) An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertiliser markets. *Environmental Technology* **21**, (9) 1067-1084.

Hafner, S.D., Bisogni Jr., J.J., Jewell, W.J. (2006) Measurement of un-ionized ammonia in complex mixtures. *Environmental Science and Technology* **40**, (5) 1597-1602.

Hirasawa, I. (1999) Study of the recovery of ions from wastewater. *Memoirs of the school of science and engineering* **60**, 97-119

Huang, H. Mavinic, D.S., Lo, K.V., Koch, F.A. (2006) Production and basic morphology of struvite from a pilot scale crystallisation process. *Environmental Technology* **27**, (3) 233-245.

Ishikawa, H., (2004) Development of a high-efficiency phosphorous recovery method using a 2 tank type fluidised bed MAP reactor. *Struvite: Its role in phosphorus recovery and reuse* Cranfield, UK.

Jaffer, Y., Clark, T.A., Pearce, P., Parsons, S.A. (2002) Potential phosphorus recovery by struvite formation. *Water Research* **36**, (7) 1834-1842.

Jardin, N., Johannes Pöpel, H. (1996) Influence of the enhanced biological phosphorus removal on the waste activated sludge production *Water Science and Technology* **34**, (1-2 pt 1) 17-23.

Jeong, Y.-K., Kim, J.-S. (2001) A new method for conservation of nitrogen in aerobic composting processes *Bioresource Technology* **79**, (2) 129-133.

Jeyanayagam, S. (2005) True confessions of the Biological Nutrient Removal process. *Florida water resources journal* **1**, pp. 37-46

Johnson, A. Hammond, R., Lewington, M., Ratnam, A. (2004) Struvite potential as an ingredient in horticultural fertiliser. *Struvite: Its role in phosphorus recovery and reuse* Cranfield, UK.

Kalyuzhnyi, S., Sklyar, V., Epov, A., Arkhipchenko, I., Barboulina, I., Orlova, O., Kovalev, A. (2003) Sustainable treatment and reuse of diluted pig manure streams in Russia: From laboratory trials to full-scale implementation *Applied Biochemistry and Biotechnology - Part A Enzyme Engineering and Biotechnology* **109**, (1-3) 77-94.

Kaneko, S., Nakajima, K. (1988) Phosphorus removal by crystallization using a granular activated magnesia clinker *Journal of the Water Pollution Control Federation* **60**, (7) 1239-1244.

Khan, F.A., Ansari, A.A. (2005) Eutrophication: An ecological vision. *Botanical Review* **71**, (4) 449-482.

Kim, E.-H., Lee, D.-W., Hwang, H.-K., Yim, S. (2006) Recovery of phosphates from wastewater using converter slag: Kinetics analysis of a completely mixed phosphorus crystallization process. *Chemosphere* **63**, (2) 192-201.

Kofina, A.N., Koutsoukos, P.G. (2005a) Spontaneous precipitation of struvite from synthetic wastewater solutions. *Crystal Growth and Design* **5**, (2) 489-496.

Kofina, A.N., Koutsoukos, P.G. (2005b) The crystallization of struvite from municipal wastewater: Investigation of crystal growth competition between different crystalline materials. *VDI Berichte* **1901**, (I) 499-504.

Langman, S.J., Hodson, M.E., Bain, D.C., Skeffington, R.A., Wilson, M.J. (1995) A preliminary review of weathering rates in relation to their method of calculation for acid sensitive soil parent materials. *Water, Air, and Soil Pollution* **85**, (3) 1075-1081.

Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A. (2005) Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth* **283**, (3-4) 514-522.

Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A (2006) Impact of reactor operation on the success of struvite precipitation from synthetic liquors. *Environmental Technology* (Waiting for publication)

Lee, J.J., Choi, C.U., Lee, M.J., Chung, I.H., Kim, D.S. (2004) A study of NH₃-N and P refixation by struvite formation in hybrid anaerobic reactor. *Water Science and Technology* **49**, (5-6) 207-214.

Lee, S.I., Weon, S.Y., Lee, C.W., Koopman, B. (2003) Removal of nitrogen and phosphate from wastewater by addition of bittern. *Chemosphere* **51**, (4) 265-271.

Levin, G.J. and Shapiro, J. (1965) Metabolic uptake of phosphorus by wastewater organisms. *Journal of the Water Pollution Control Federation* **37**, 800-821.

Lowenthal, R.E., Kornmuller, U.R.C., van Heerden, E.P. (1994) Modelling struvite precipitation in anaerobic treatment systems. *Water science and technology* **30**, (12) 107-116.

Mamais, D., Pitt, P.A., Yao Wen Cheng, Loiacono, J., Jenkins, D. (1994) Determination of ferric chloride dose to control struvite precipitation in anaerobic sludge digesters. *Water Environment Research* **66**, (7) 912-918.

Mangin, D. (2004) Struvite crystallisation reaction in a semi continuous stirred reactor, *Struvite: Its role in phosphorus recovery and reuse*, Cranfield, UK

Maqueda, C., Perez-Rodriguez, J.L., Lebrato, J. (1995) Anaerobic digestion of wastewater and solid waste using raw clays as supports. *Fresenius Environmental Bulletin* **4**, (2) 129-134.

McPherson, A. (1988) The use of heterogeneous and epitaxial nucleation to promote the growth of proteins. *Journal of crystal growth* **90**, (1-3) 47-50.

Miles, A., Ellis, T.G. (2001) Struvite precipitation potential for nutrient recovery from anaerobically treated wastes. *Water Science and Technology* **43**, (11) 259-266.

Bhattarai, Mohajit, Taiganides, E. P., Yap, B.C. (1989) Struvite deposits in pipes and aerators. *Biological Wastes* **30**, (2) 133-147.

Momberg, G.A., Oellermann, R.A. (1992) The removal of phosphate by hydroxyapatite and struvite crystallisation in South Africa. *Water Science and Technology* **26**, (5-6) 987-996.

Morse, G.K., Lester, J.N., Perry, R. (1994) The economic impact of phosphorus removal from wastewater in the European Union. *European Water Pollution Control* **4**, (3) 46-55.

Munch, E.V., Barr, K. (2001) Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams. *Water Research* **35**, (1) 151-159.

Neethling J.B. and Benisch M. (2005) Struvite control through process and facility design as well as operation strategy. *Water Science and Technology* **49**, (2) 191-199.

Ohlinger, K.N., Young, T.M., Schroeder, E.D. (1998) Predicting struvite formation in digestion. *Water Research* **32**, 3607-14.

Ohlinger, K.N., Young, T.M., Schroeder, E.D. (1999) Kinetics effects on preferential struvite accumulation in wastewater. *Journal of Environmental Engineering* **125** (8) 730-737.

Ohlinger, K.N., Young, T.M., Schroeder, E.D. (2000) Postdigestion struvite precipitation using a fluidized bed reactor. *Journal of Environmental Engineering* **126**, (3) 361-368.

Perez Rodriguez, J.L., Maqueda, C., Lebrato, J., Carretero, M.I. (1992) Influence of clay minerals, used as supports in anaerobic digesters, in the precipitation of struvite. *Water Research* **26**, (4) 497-506.

Petruzzelli, D., De Florio, L., Dell'Erba, A., Liberti, L., Notarnicola, M., Sengupta, A.K. (2003) A new phosphate-selective sorbent for the Rem Nut® process. Laboratory investigation and field experience at a medium a wastewater treatment plant. *Water Science and Technology* **48**, (1) 179-184.

Pierzynski, G.M., Vance, G. F., and Sims, J.T. (2000) Soils and Environmental Quality. *CRC Press*

Piekema, P.G. (2004) The case study of a phosphorus recovery sewage treatment plant at Geesterambacht, Holland- design and operation. *Phosphorus in Environmental Technologies, principles and applications* Valsami-Jones, E. (Ed), pp. 428-469, IWA Publishing.

Potjer, B., (2001) Economic/ environmental costs assessment of phosphate recycling possibilities at Thermphos' plant, Vlissingen, The Netherlands. *Second International Conference on the recovery of phosphorus from sewage and animal wastes*

Rawn, A.M., Perry, A., Pomeroy, R. (1939) Multiple stage sewage digestion. *Trans Am Soc Agric Eng* **105**, 93-105

Richards, I.R., Johnston, A.E. (2001) The effectiveness of different precipitated phosphates as sources of phosphorus for plants. *IACR*, Rothamstead, UK and Ecopt, Suffolk, U.K.

Sharpley, A.N., Chapra, S.C., Wedepohl, R., Sims, J.T., Daniel, T.C., Reddy, K.R. (1994) Managing agricultural phosphorus for protection of surface waters: Issues and options. *Journal of Environmental Quality* **23**, (3) 437-451.

Schulze-Rettmer, R (1991) The simultaneous chemical precipitation of ammonium and phosphate in the form of magnesium-ammonium-phosphate. *Water Science and Technology* **23** (4-6) 659-667.

Sen, D., Randall, C.W. (1988) Factors controlling the recycle of phosphorus from anaerobic digesters sequencing biological phosphorus removal systems. In: Hazardous and Industrial Waste. 20th Mid-Atlantic Industrial Waste and Hazardous Material Conference Papers, 286-298.

Shimamura, K., Tanaka, T., Miura, Y., Ishikawa, H. (2003) Development of a high-efficiency phosphorus recovery method using a fluidized-bed crystallized phosphorus removal system. *Water Science and Technology* **48**, (1) 163-170.

Snoeyink, V.L., Jenkins, D. (1980) Water Chemistry. *John Wiley and Sons. New York.*

Stratful, I., Brett, S., Scrimshaw, M.B., Lester, J.N. (1999) Biological phosphorus removal its role in phosphorus recycling. *Environmental Technology* **20**, (7) 681-695

Strickland, J. (1999) Perspectives for phosphorus recovery offered by enhanced biological P removal. *Environmental Technology* **20**, (7) 721-725.

Suschka, J., Poplawski, S. (2004) Free ammonia mechanism- Struvite precipitation and simultaneous ammonia removal. *Struvite: Its role in phosphorus recovery and reuse conference*, Cranfield, UK.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y. (2005) Recovery of phosphorous from swine wastewater through crystallization. *Bioresource Technology* **96**, (14) 1544-1550.

Szogi, A.A., Humenik, F.J., Rice, J.M., Hunt, P.O. (1997) *Swine wastewater treatment by media filtration Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes* **32**, (5) 831-843.

Taylor, A.W. Frazier, A.W., and Gurney, E.L., (1963). Solubility product of magnesium ammonium. *Transaction Faraday Society* **59**, 1580–1589.

Thaller, C., Weaver, L.H., Eichele, G., Wilson, E., Karlsson, R., Jansonius, J.N. (1981) Repeated seeding technique for growing large single crystals of proteins *Journal of Molecular Biology* **147**, (3) 465-469.

Ueno, Y., Fujii, T., (2001) Three years experience of operating and selling recovered struvite from full-scale plant. *Environmental Technology* **22**, 1373-1381.

Van Dijk, J.C., Wilms, D.A. (1991) Water treatment without waste material- fundamentals and state of the art pellet softening. *Journal of Water SRT-Aqua* **40**, 263-280.

UWWTD. Council of the European Communities, Directive concerning the collection, treatment and discharge of urban wastewater from certain industrial sectors (91/271/EEC) Official J L, 135/40, 1991

Wang, J., Burken, J.G., Zhang, X. (2006) *Effect of seeding materials and mixing strength on struvite precipitation. Water Environment Research* **78**, (2) 125-132.

Webb, K.M., Ho, G.E. (1992) Struvite($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) solubility and its application to a piggery effluent problem. *Water Science and Technology* **26**, (9-11) 2229-2232.

Wild, D., Kisliakova, A., Siegrist, H. (1996) P-fixation by Mg, Ca and zeolite a during stabilization of excess sludge from enhanced biological P-removal. *Water Science and Technology* **34**, (1-2 -2 pt 1) 391-398.

Wild, D., Kisliakova, A., Siegrist, H. (1997) Prediction of recycle phosphorus loads from anaerobic digestion. *Water Research* **31**, (9) 2300-2308.

Williams, S. (1999) *Struvite* precipitation in the sludge stream at Slough wastewater treatment plant and opportunities for phosphorus recovery. *Environmental Technology* **20**, 743-748

Yoshino, M., Yao, M., Tsuno, H., Somiya, I. (2003) Removal and recovery of phosphate and ammonium as struvite from supernatant in anaerobic digestion. *Water Science and Technology* **48**, (1) 171-178.

3 Experimental

3.1 Collection and characterisation of centrate liquors

Previous reports suggested the belt press (Battistoni *et al.*, 2006b) and the dewatering centrifuge (Doyle *et al.*, 2002 and Lee *et al.*, 2003) as the locations with the greatest potential for struvite formation. The supernatants of these processes have been identified as having the highest concentration of orthophosphate and magnesium (Jaffer *et al.*, 2002).

Initial tests on the supernatant of these two processes identified the dewatering centrifuge as the location with the highest orthophosphate concentration. Magnesium concentration was a secondary consideration, as further magnesium addition was already planned.

Samples were collected from sites operated by Severn Trent Water Ltd. The four sites sampled were Wanlip STW, Leicestershire; Derby STW, Derbyshire; Stoke Bardolph STW, Nottinghamshire; and Coleshill Sludge Destruction plant, Warwickshire (see Table 4.1 for sampling dates).

Sampling was carried out initially by dipping a bucket into the stream leading from the centrifuge. The samples were transported to Cranfield University in 25L containers, (acidification of the centrate samples has been shown by Sharp *et al.* (2003) to not stop changes in phosphate concentration and so was not carried out with the samples collected).

At Cranfield, samples were filtered through a 125 µm mesh sieve to remove gross particles. Characterisation of the samples was carried out using the methods outlined in Table 3.1. For samples where the range of the cell test was exceeded dilution of the sample by a factor of ten was carried out with distilled water. For cell test methodology refer to individual cell test instructions (Appendix 1). For calcium, alkalinity and suspended solid determination see

methodology outlined in ‘Standard Methods for the examination of water and wastewater 21st Edition’ (2006).

Table 3.1: Methods used to characterise liquor samples

Determinant	Method	Range (mg L ⁻¹)
Orthophosphate	Merck Cell Test	0.5-25
Soluble ammonia	Merck Cell Test	4-80
Total phosphorus	Merck Cell Test	0.5-25
Total nitrogen	Merck Cell Test	10-150
Chemical oxygen demand (COD)	Merck Cell Test	25-1500
Magnesium	ICP when available or estimated as 10% of calcium concentration	30µg L ⁻¹ -100mg L ⁻¹
Calcium	ICP when available or determination by titration against EDTA with Murexide indicator	10µg L ⁻¹ -100mg L ⁻¹
Suspended solids	Solids collected and dried from 100ml of liquor	NA
Alkalinity	Titration against HCl with Bromocresol green and methyl red indicators	NA
pH	pH meter (VWR pH 100, VWR, UK).	-2-15

3.2 Jar Tester precipitation

A series of jar tests have been undertaken to determine the dose of magnesium to be added to centrate liquors for optimum struvite precipitation.

The dosing tests were carried out using a jar test apparatus (Aztec sedimentation jar tester, Aztec Environmental Control, UK) to evaluate the required magnesium dosage for optimum struvite precipitation (see Figure 3.1)

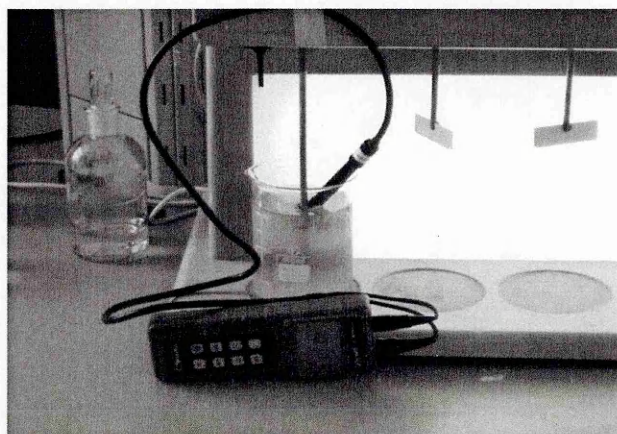


Figure 3.1: Image of jar tester setup for precipitation tests

The doses of magnesium were added to jars containing 500ml of centrate as magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 0.5mol/ Fisher Analytical Reagent Grade, UK). Doses were added as zero, 1mmol, 2mmol, 3mmol, 4mmol, 5mmol. The pH of the centrate was adjusted to 9 after initial tests suggested this to be the optimum pH for rapid precipitation. The pH adjustment was achieved with addition of sodium hydroxide solution (NaOH 2N/ Fisher Analytical Reagent Grade, UK). Solutions were mixed at 80 rpm after preliminary tests suggested this to be the lowest operating speed to ensure homogenous fluidisation of solids. The jars were stirred for two hours and the changes in pH monitored with a pH meter (VWR pH 100, VWR, UK).

At the end of each experiment particle size analysis was undertaken with a dynamic laser diffraction instrument (Malvern Mastersizer 2000, Malvern UK). Samples were filtered using 1.2 μm pore size glass filter paper (Munktell Filter AB, Sweden). The filtrate was used to measure the orthophosphate ($\text{PO}_4\text{-P}$) and soluble ammonia ($\text{NH}_4\text{-N}$) concentration remaining in solution using Merck cell tests (see Table 3.1). Samples collected on the filter paper were

analysed with X-ray diffraction (XRD, Siemens D5005, Germany) and scanning electron microscopy (SEM, Philips XL30 SFEG, Netherlands) coupled with energy dispersive X-ray analysis (Oxford 7321) (SEM-EDS).

3.3 Phase 1 fluidised bed reactor design and operation

A pilot scale crystallisation reactor has been developed at Cranfield University to study struvite nucleation and growth (Le Corre *et al.*, 2006c). The reactor was initially used to study struvite nucleation growth in synthetic liquors, while in the present work it has been used to study struvite crystallisation from centrifuge liquors.

The process consisted of a 10 L reactor made of Perspex with two side sampling ports and a drain valve which is illustrated in Figure 3.2. The reactor dimensions are as follows; height 0.7 m with a top section width 0.21 m and a bottom section width of 0.12 m.

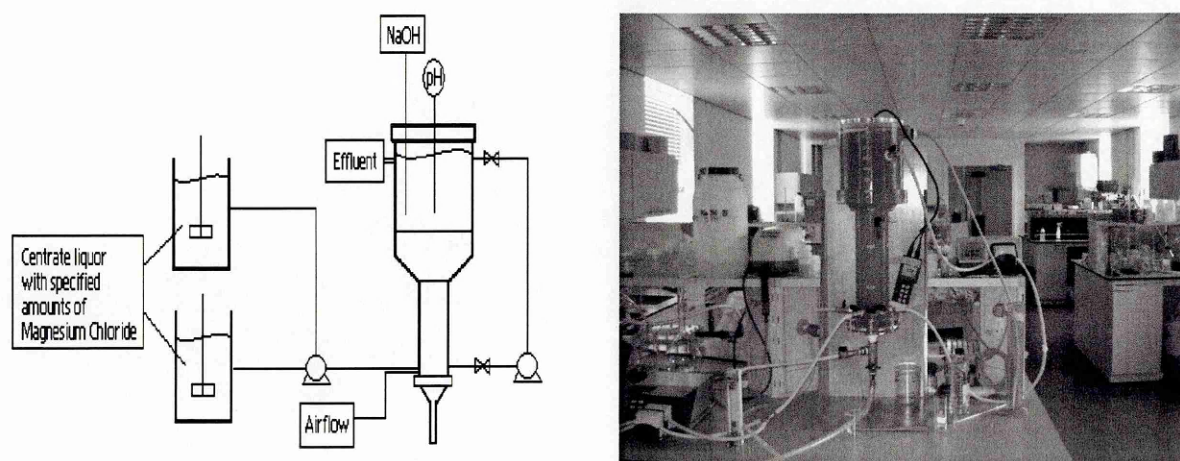


Figure 3.2: Schematic and picture showing the setup of the crystallisation reactor for struvite precipitation

Magnesium chloride hexahydrate solution ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ / Fisher Analytical Reagent Grade, UK) was added to two buckets each containing 4.5L of centrate liquor collected from Wanlip STW. The magnesium doses were 3, 3.5, 4, 4.5 and 5 mmol. After mixing the contents of both buckets with a mechanical stirrer (Eurostar Digital Stirrer, VWR, UK), both solutions were simultaneously injected into the reactor using a peristaltic pump.

After injection, a peristaltic pump was used to re-circulate the liquor through the reactor to increase the contact time. Air was pumped into the base of the reactor and adjusted between $5\text{-}12\text{ L min}^{-1}$ to ensure the mixing of the particles formed and maintain their fluidisation throughout the experiments. The pH was adjusted to 9 by the addition of sodium hydroxide (NaOH 2 N/ Fisher Analytical Reagent Grade, UK). A pH probe (VWR pH 100, VWR, UK) was used to monitor any changes in pH in the reactor.

To evaluate the efficiency of the reactor in precipitating struvite from liquors, between 3-5 mmol of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were added prior to pH adjustment. Each experiment was typically run for 2 hours.

At the end of each experiment 500 mL of sample were collected and filtered using $1.2\text{ }\mu\text{m}$ pore size glass filter paper (Munktell Filter AB, Sweden). The efficiency of the reactor in removing and recovering struvite was assessed by measurement of ortho-phosphate concentration left in the filtrate and by characterising the solids collected on the filter paper by XRD and SEM-EDS.

3.4 Accumulation system design and configuration

A system composed of 2 concentric meshes was designed for use as an accumulation system to grow struvite. Both meshes were made of stainless steel 1 mm hole, 0.35 mm wire (H&B Wire Fabrications Ltd, UK) and dimensioned to fit in the enlarged section of the reactor (Figure 3.3). The external mesh was 55 x 14 cm and the internal mesh was 39 x 9 cm.

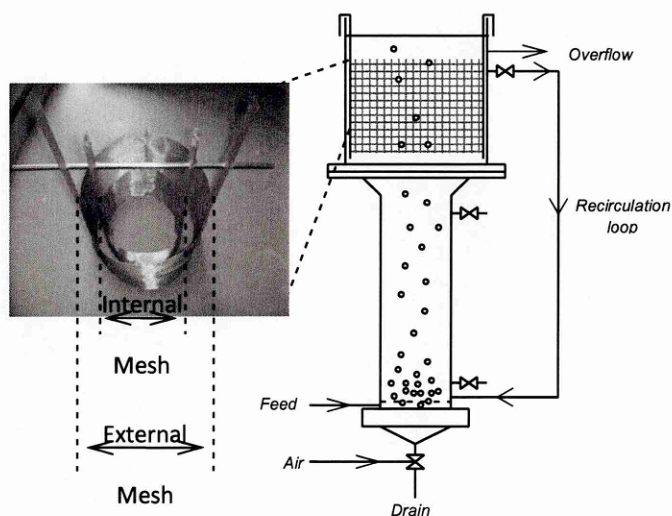


Figure 3.3: Image and schematic of the accumulation mesh used to collect struvite from the crystallisation reactor and its positioning within the reactor

3.5 Phase 1 stirred tank reactor

A 235 L water butt was used to simulate a stirred tank type reactor. A stirrer (Eurostar Digital Stirrer, VWR, UK) was placed in the centre of the tank and set at 1500rpm to ensure homogenous mixing of the solution. A pH probe (VWR, 100 pH, VWR, UK) was placed within the tank so the pH could be monitored over the course of the experiments.

50 L of centrate collected from Wanlip STW was added to the tank and stirred. For each experiment 5mmol of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ / Fisher Analytical Reagent Grade, UK) was added to the liquor. The pH of the solution was adjusted to 9 by suitable additions of sodium hydroxide (NaOH 2N/ Fisher Analytical Reagent grade, UK). The experiments were run for 2 hours during which samples were taken at specified intervals to measure the change in orthophosphate concentration using Merck cell tests over the experimental time. Unfortunately due to limitations with the reactor design solid samples were unobtainable.

3.6 Side-by-side operation of a FBR and stirred tank reactor

To compare the efficiency of both types of reactor in the precipitation of struvite, a side by side comparison was carried out when both reactors were run in a continuous mode for three hours with liquors collected from Wanlip STW (see Figure 3.4).

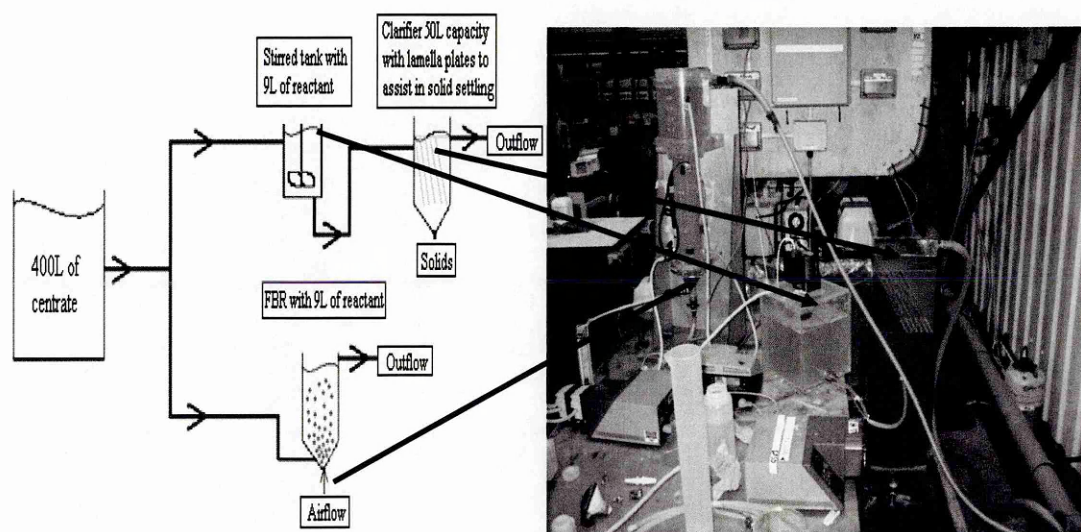


Figure 3.4: Set up for side by side analysis of each type of reactor

Like in the previous set of experiments the centrate was filtered through 125 μm mesh to remove the gross solids that are present in the liquors. The main storage container was filled with ~ 400 L of filtered centrate. Due to a degree of variability in the orthophosphate concentration in the samples that were collected, NaHPO_4 (Fisher analytical Reagent Grade, UK) was added to the centrate and the concentration adjusted to 1mmol L^{-1} of PO_4^{3-} .

Figure 3.4 shows the arrangement of reactors for the continuous operation. In these experiments the FBR was fed continuously from the centrate storage tank. Suitable amounts of magnesium sulphate hexahydrate solution ($1\text{N MgSO}_4 \cdot 6\text{H}_2\text{O}$ Fisher analytical Reagent Grade, UK) were manually added at ten minute intervals to maintain the magnesium

concentration. The pH of the liquors was maintained at pH 9 with the addition of (NaOH 2N/ Fisher analytical reagent grade, UK).

The stirred tank reactor has a 10 L capacity though for the reactions the fluid level was kept at 9 L to match the volume and retention time of the FBR. The clarifier was designed to store 50 L of reactant to allow the greatest time for the settling of any solid precipitate (see Figure 3.5 for details of the dimensions).

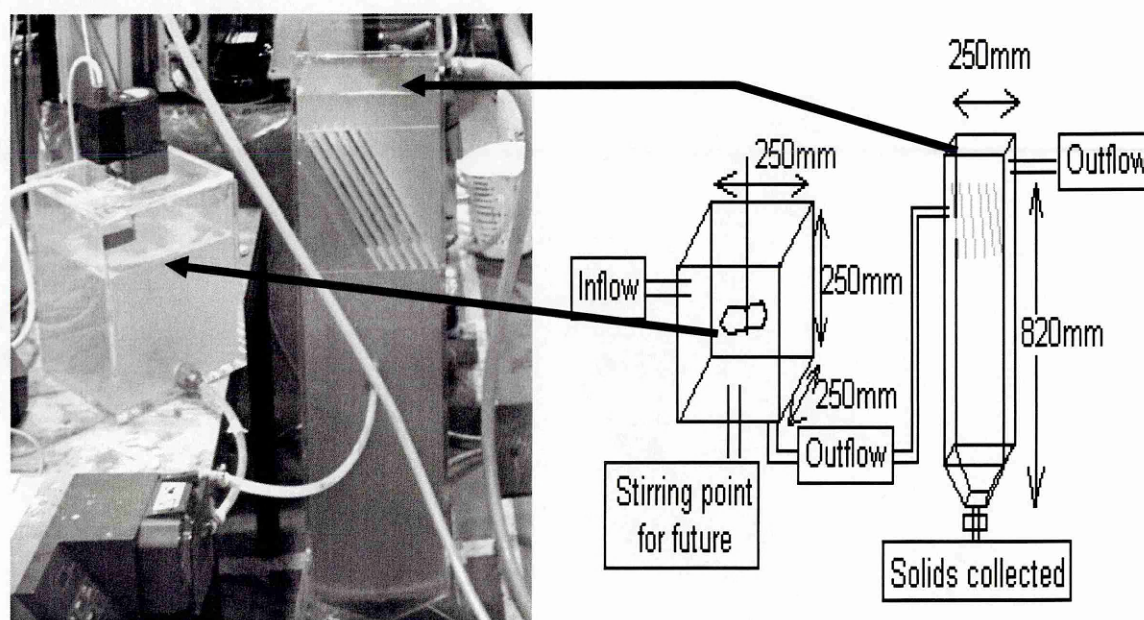


Figure 3.5: Image and schematic showing stirred tank reactor and clarifier

The chemistry of the liquors in the stirred tank was altered in the same manner as with the FBR. Suitable amounts of magnesium sulphate hexahydrate solution (1N $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ Fisher analytical Reagent Grade, UK) were added at ten minute intervals to maintain the magnesium concentration. The pH of the liquors was maintained at 9 with the addition of (NaOH 2N/ Fisher analytical reagent grade, UK).

Samples were collected from the bottom of the clarifier and the average ($d_{0.5}$) size of particles was determined using laser diffraction (Mastersizer 2000, Malvern Instruments, UK). The samples were then filtered using 1.2 μ m pore size glass filter paper (Munktell Filter AB, Sweden). The solids were dried at room temperature for 48 hours and the dried solids were characterised with XRD, SEM and EDS.

4 Results

4.1 Physiochemical results

The physiochemical characteristics of the liquors collected from the four sites are presented in Table 4.1 and show how between the four sites there is a significant variation in the main constituents of struvite i.e. Mg, PO₄ and NH₄. This data suggests that magnesium is generally the limiting constituent of struvite precipitation, which is expected as it is often added in struvite recovery operations e.g. Ueno and Fujii (2001). Here it varies between 3 and 24 mg L⁻¹ and when compared to the phosphate levels it can be seen that Coleshill and Stoke Bardolph are magnesium limited with respect to phosphate and surprisingly Derby is phosphate limited. The surprise is that Derby operates a BNR plant and it is generally thought that BNR plants rerelease a great deal of bound orthophosphate into the supernatants after anaerobic digestion (Jeyanayagam, 2005).

The majority of the data collected was from Wanlip STW, where a total of nine separate samples were collected over nine months. The data collected from Wanlip STW shows a degree of variability in magnesium, with the magnesium concentration varying from 5 to 15 mg L⁻¹, with a mean value of 10 mg L⁻¹. The soluble phosphate concentration also shows a large range of concentrations, with the concentration varying between 44 and 136 mg L⁻¹, with a mean value of 88 mg L⁻¹. This variability means that at some points Wanlip can be considered magnesium limited and whilst at other times it is phosphate limited. This means that constant monitoring would be required for a recovery plant so that suitable chemical additions can be made. The ratio of PO₄:Total P shows that there is no link between the concentrations.

Calcium levels also show a great variability across all the sites sampled and is likely related to water hardness, with levels going from 29 mg L⁻¹ at Coleshill to 147 mg L⁻¹ at Wanlip. Calcium has been shown to have a detrimental effect on the precipitation of struvite by Le Corre, *et al.* (2005), so the concentration of Ca within the liquors is important when

considering struvite precipitation, especially if its future sale value is to be considered. Ammonia levels are in the range expected and are significantly higher (in mmols) than any limiting value. The ammonia concentration compares well with that reported elsewhere e.g. 710 mg L⁻¹ Ueno and Fujii 2001; 522 mg L⁻¹ Yoshino *et al.* 2003.

Table 4.1: Concentrations of selected determinants taken from four sites

Sample Number	1	2	3	4	5	6	7	8	9	10	11	12	13
Determinant	Derby (01.03.06)	Stoke Bardolph (24.04.06)	Coteshill (01/05/06)	Wanlip (24.06.06)	Wanlip (19.06.06)	Wanlip (3.07.06)	Wanlip (17.07.06)	Wanlip (24.07.06)	Wanlip (10.08.06)	Wanlip (17.08.06)	Wanlip (8.01.07)	Wanlip (15.01.07)	Wanlip (22.01.07)
Orthophosphate (PO ₄ -P)	65	89	98	136	82	53	66	97	65	98	57	44	55
Ammonium (NH ₄ - N)	656	601	724	419	660	546	621	495	564	764	612	520	424
Magnesium	24	17	3	5	9.9	12.2	NM	NM	NM	NM	8.3*	14.7*	12*
Calcium	63	116	29	94	109	115	NM	NM	NM	NM	83	147	120
PO ₄	0.7	0.9	1	1.4	0.9	0.6	0.7	1	0.7	1	0.6	0.5	0.6
Mg	1	0.7	0.1	0.2	0.4	0.5	NM	NM	NM	NM	0.3	0.6	0.5
NH ₄	36.4	33.4	40.2	23.3	36.7	30.3	34.3	27.5	31.3	42.4	34.0	28.9	23.6
Ca	1.6	2.9	0.7	2.3	2.7	2.9	NM	NM	NM	NM	2.7	3.7	3.0
Mg:PO ₄ ratio	1.4 : 1	0.7 : 1	0.1 : 1	0.14 : 1	0.4 : 1	0.8 : 1	NM	NM	NM	NM	0.5 : 1	1.2 : 1	0.83 : 1
Mg:Ca ratio	0.6 : 1	0.24 : 1	0.14 : 1	0.09 : 1	0.14 : 1	0.17 : 1	NM	NM	NM	NM	0.11 : 1	0.13 : 1	0.16 : 1
COD	308	466	564	439	390	346	471	534	495	424	392	548	457
Total Phosphorus	NM	40	33	35	44	33	57	56	23	31	31	32	47
Total Nitrogen	1260	1020	1280	1100	960	980	1100	1060	890	1160	820	1030	960
Suspended Solids	124	197	634	223	211	346	2430	201	187	254	321	541	278
Alkalinity	3990	2414	2779	3251	4156	3278	2744	3146	3287	2987	3452	3270	2890
pH	7.56	7.90	8.34	7.72	7.88	7.92	7.93	7.82	7.94	7.73	7.76	7.88	7.90

*=Estimation from calcium concentration; NM=Not measured

Previous studies of the physiochemical characteristics of Wanlip and Coleshill have been made (see Table 4.2). Comparison of the mean values for the data collected from Wanlip with that of Doyle (2002) and Wall (2000) shows 15% less orthophosphate present and nearly 10 times less magnesium though this is comparing one samples set of data with 9 separate sample collections data. The orthophosphate data for Coleshill matches the data reported by Wall (2000) but is 40% less than that reported by Doyle (2002). Magnesium concentration is again lower than that recorded by the other authors.

Table 4.2: Reports by other authors on the concentrations of PO₄, Mg, NH₄ and Ca recorded at Wanlip STW and Coleshill sludge destruction plant (all figures in mmol)

Author	Site	PO ₄ -P (mmoles)	Mg (mmoles)	NH ₄ -N (mmoles)	Ca (mmoles)
Doyle (2002)	Wanlip	1.0	2.0	38.1	4.0
Wall (2000)	Wanlip	1.0	1.7	53.4	4.7
Doyle (2002)	Coleshill	1.4	0.2	59.8	1.6
Sharp (2000)	Coleshill	1.0	0.8	49.7	2.3

Doyle (2002) made a similar study of the physiochemical characteristics of liquors collected from Coleshill over a period of five months. The authors reported a comparable lack of consistency in the liquor's physiochemical qualities, with the magnesium, orthophosphate and calcium concentrations all varying over the sampling period. This again shows the need for constant monitoring of the physiochemical properties of the liquors so that additions of chemicals are correct for the quality liquor at any given time.

4.2 Jar tester precipitation tests

A series of bench scale experiments were undertaken to determine whether struvite could be precipitated from the four STW sites selected. Experiments investigated the effect of magnesium dose on orthophosphate removal and precipitate quality. Centrate was collected from Wanlip STW, Derby STW, Stoke Bardolph STW and Coleshill sludge destruction plant on the dates given in Table 4.1 (sample number 1-4).

The data presented in Tables 4.3-4.6 and Figure 4.1 show that 60-75% removal of orthophosphate was achievable with no magnesium addition for the Derby, Wanlip and Stoke Bardolph samples. Coleshill's liquor required an addition of 1mmol of magnesium to achieve comparable phosphate removal due to its low initial Mg concentration. These levels of orthophosphate removal are in close comparison to those achieved by Doyle (2002) for Coleshill; Wall (2000) for Wanlip; Jaffer (2001) for Slough STW with similar Mg:PO₄ ratios.

Increasing the Mg:PO₄ ratio to 3:1 meant that Wanlip, Stoke Bardolph and Coleshill all achieved >80% orthophosphate removal whilst a ratio of 5:1 was required for Derby to achieve a similar removal. The reason for Derby's result is not clear but it may be linked to the low initial orthophosphate concentration (see Table 4.1). Similar results have been reported by Suzuki *et al.* (2005) where the influent orthophosphate concentrations was 68 mg L⁻¹ and a Mg:PO₄ ratio of 2:1 but only 50% of the influent orthophosphate was removed.

Table 4.3: Derby STW centrate liquor PO₄ removal as a function of Mg:PO₄ and the change in pH over the course of experiment. Sample number 1 (for pH data see Appendix 2)

Mg:PO₄ ratio	1.4 : 1 (Natural)	3.5 : 1	3.9 : 1	5 : 1	6.4 : 1	8.6 : 1
PO₄ removal (%)	61	65	77	80	83	88
pH initial	9	9	9	9	9	9
pH final	8.83	8.9	8.93	8.92	8.85	8.83

Table 4.4: Stoke Bardolph STW centrate liquor PO₄ removal as a function of Mg:PO₄ and the change in pH over the course of experiment. Sample number 2 (for pH data see Appendix 2)

Mg:PO₄ ratio	0.7 : 1 (Natural)	1.9 : 1	3 : 1	4.1 : 1	5.2 : 1	6.3 : 1
PO₄ removal (%)	75	75	83	91	92	93
pH initial	9	9	9	9	9	9
pH final	8.88	8.9	8.89	8.82	8.82	8.81

Table 4.5: Coleshill STW centrate liquor PO₄ removal as a function of Mg:PO₄ and the change in pH over the course of experiment. Sample number 3 (for pH data see Appendix 2)

Mg:PO₄ ratio	0.1 : 1 (Natural)	1.1 : 1	2.1 : 1	3.1 : 1	4.1 : 1	5.1 : 1
PO₄ removal (%)	21	61	85	89	92	93
pH initial	9	9	9	9	9	9
pH final	8.93	8.92	8.84	8.85	8.84	8.82

Table 4.6: Wanlip STW centrate liquor PO₄ removal as a function of Mg:PO₄ and the change in pH over the course of experiment. Sample number 4 (for pH data see Appendix 2)

Mg:PO₄ ratio	0.14 : 1 (Natural)	0.85 : 1	1.6 : 1	2.3 : 1	3 : 1	3.9 : 1
PO₄ removal (%)	76	79	89	94	94	91
pH initial	9	9	9	9	9	9
pH final	8.91	8.91	8.88	8.85	8.87	8.83

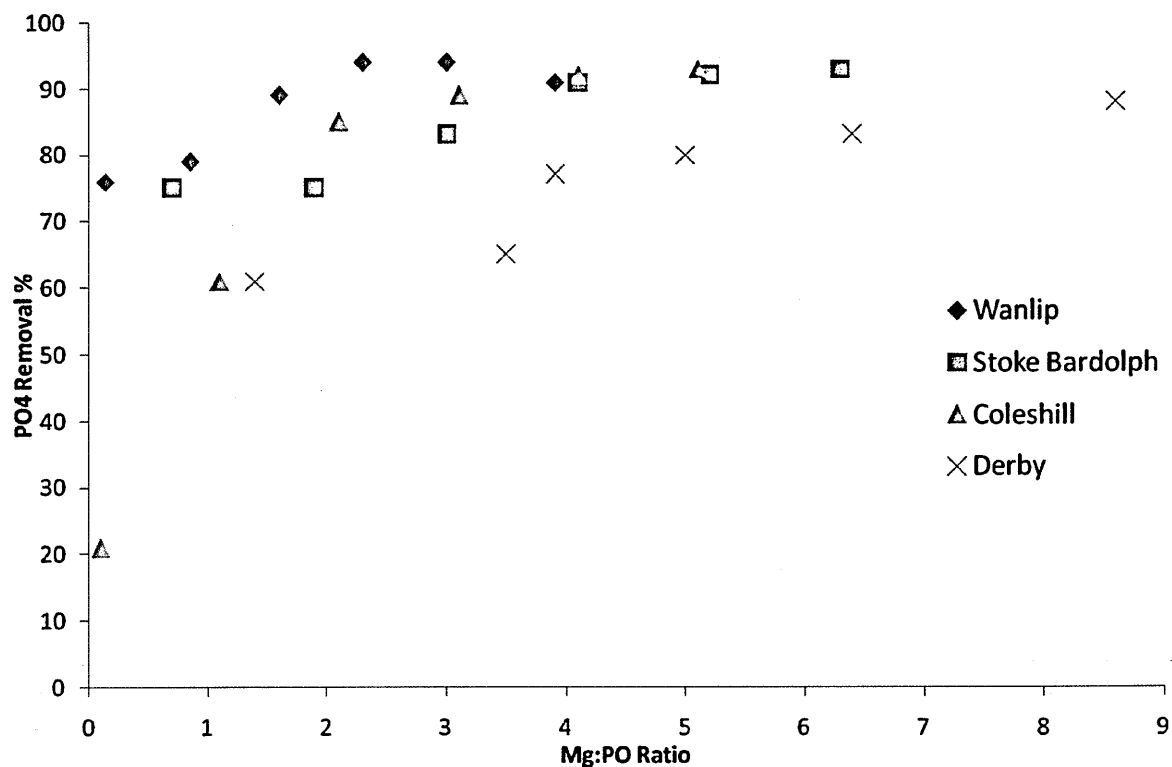


Figure 4.1: The impact on orthophosphate removal % with an increase in Mg:PO₄ ratio

Changing the Mg:PO₄ ratio also impacted the particle size of precipitate generated (Figure 4.2, original data in Appendix 3). The data shows what is thought to be individual crystals after comparison with the data obtained by the SEM. It can be seen at Mg:PO₄ ratios of <1:1 (>1.1 Ca:Mg) the d_{0.5} (50% of particles sized) is >200µm for the four sites. As the Mg:PO₄ ratio is increased past 1:1 (<Ca:Mg 1:1) there is a decrease in the d_{0.5} particle size to <200µm, with all four site's d_{0.5} particle sizes converging in a similar pattern at <80µm when the Mg:PO₄ ratio ≥2:1 (<Ca:Mg 1:2).

Similar results have been reported by Le Corre *et al.* (2005), where the Ca concentration affected the crystalline properties of the precipitate i.e. when the Ca:Mg ratio was ≥2:1, an amorphous material was observed with XRD analysis which was seen to have similarly large d_{0.5} particle size after analysis. When the Ca:Mg ratio was altered to 1:2, a defined crystalline material was produced of ~30µm in size, very much in agreement with the results

reported here. It was proposed that this change in particle size is related to the precipitation of amorphous calcium phosphates when the $\text{Mg}:\text{PO}_4$ is $<1:1$. As the $\text{Mg}:\text{PO}_4$ is increased past a ratio of 2:1 a precipitate that is $<100\mu\text{m}$ is produced due to the production of a crystalline struvite. Small size of the struvite crystals has been previously linked to the highly supersaturated conditions ($\text{Mg}:\text{PO}_4$ ratios and a pH of 9) leading to rapid nucleation (Ali and Schneider (2006); Battistoni *et al.* (2005); Munch and Barr (2002) reported a maximum d0.5 particle size of $110\mu\text{m}$ of produced in an FBR using $\text{Mg}(\text{OH})_2$.

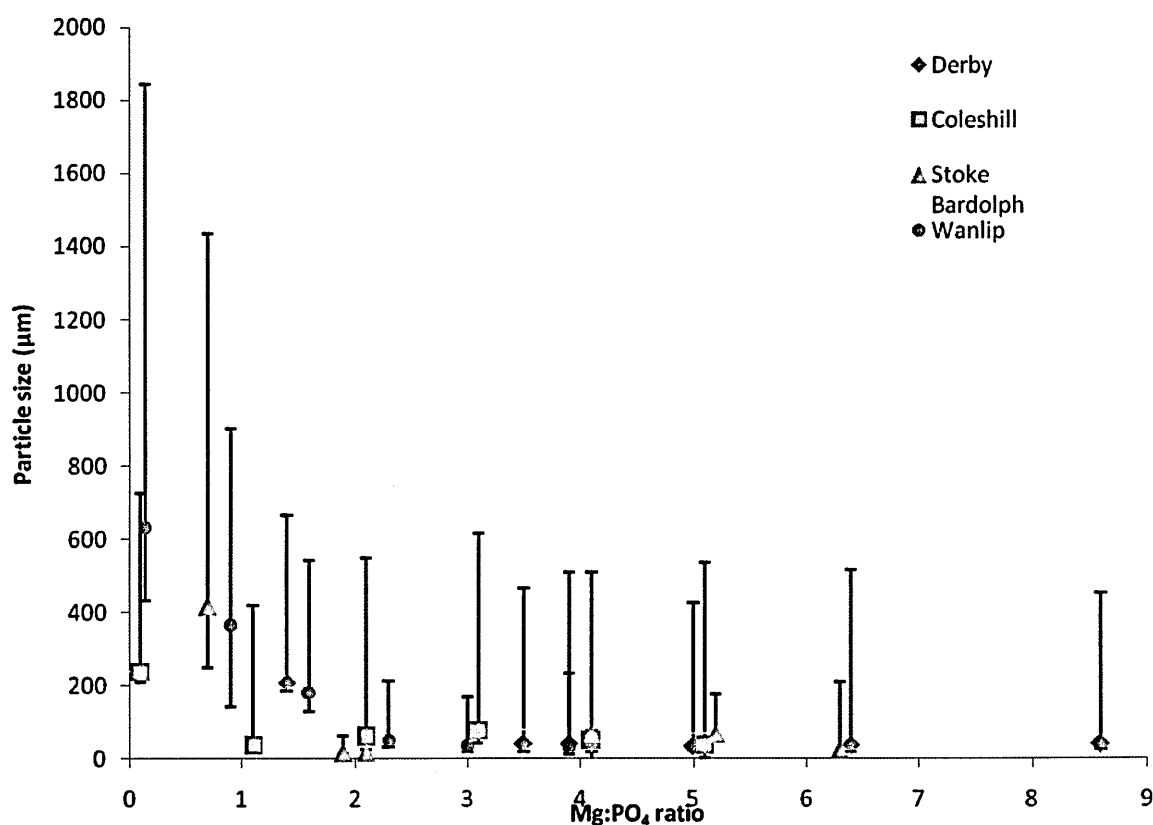


Figure 4.2: The impact of $\text{Mg}:\text{PO}_4$ increase on the d0.5 particle size of precipitate

SEM images of the precipitate produced by variation of the $\text{Mg}:\text{PO}_4$ ratio are shown in (Figure 4.3) (EDS analysis in Appendix 4). It can be seen there is considerable difference in the morphology of the precipitate produced at a $\text{Mg}:\text{PO}_4$ ratio of 0.1:1 and the images produced at higher ratios. The image at a ratio of 0.1:1 shows the precipitate is amorphous and may be calcium phosphate. Le Corre *et al.* (2005) reported similar findings when the

Ca:Mg ratio was 2:1 compared to the 7:1 Ca:Mg ratio reported here. The EDS analysis of the precipitate also shows 8% of the precipitate to be Ca again indicating the presence of calcium phosphates.

At a Mg:PO₄ ratio of 1.1:1 there are three types of material present in the sample; the typical 'coffin' like structure characteristic of struvite produced from STW liquors (Takiguchi *et al.*, 2004), a second 'dumbbell' like structure, possibly calcite as this often precipitates in small balls (Hirai *et al.*, 2000) and a third indefinable mass of material similar to that from the lower Mg:PO₄ ratio image (calcium phosphate). The EDS analysis showed a fall in the amount of Ca from 8% to 5%.

As the Mg:PO₄ ratio is raised above 1.1:1 the clumps of indefinable material are no longer present in the images and the material is clearly crystalline in nature, which is linked to the Mg:Ca ratio being greater >2:1 (Le Corre *et al.*, 2005). The images at ratios $\geq 2.1:1$ shows a small increase in the size of individual crystals, though this increase isn't linked to the predictions of the Mastersizer data. The amount of Ca present in the crystals falls from 2% to 0.71%. It is thought that the EDS analysis taken on the 4.1:1 ratio precipitate is not representative of the total sample and further analysis would show the steady decline seen in the other EDS analysis.

The morphology of the crystals grown from sludge liquors varies to those crystals grown from synthetic solutions (Stratful *et al.*, 2004). Crystals grown from synthetic solutions tend to be more elongated along the z-axis of growth i.e. needle like (Kofina and Koutsoukos, 2005). The crystals grown from the centrifuge liquors can be seen to be coffin shaped, this has been linked to the presence of other ions i.e. calcium, sodium and sulphate impeding the growth axis of the crystals (Kofina and Koutsoukos, 2005).

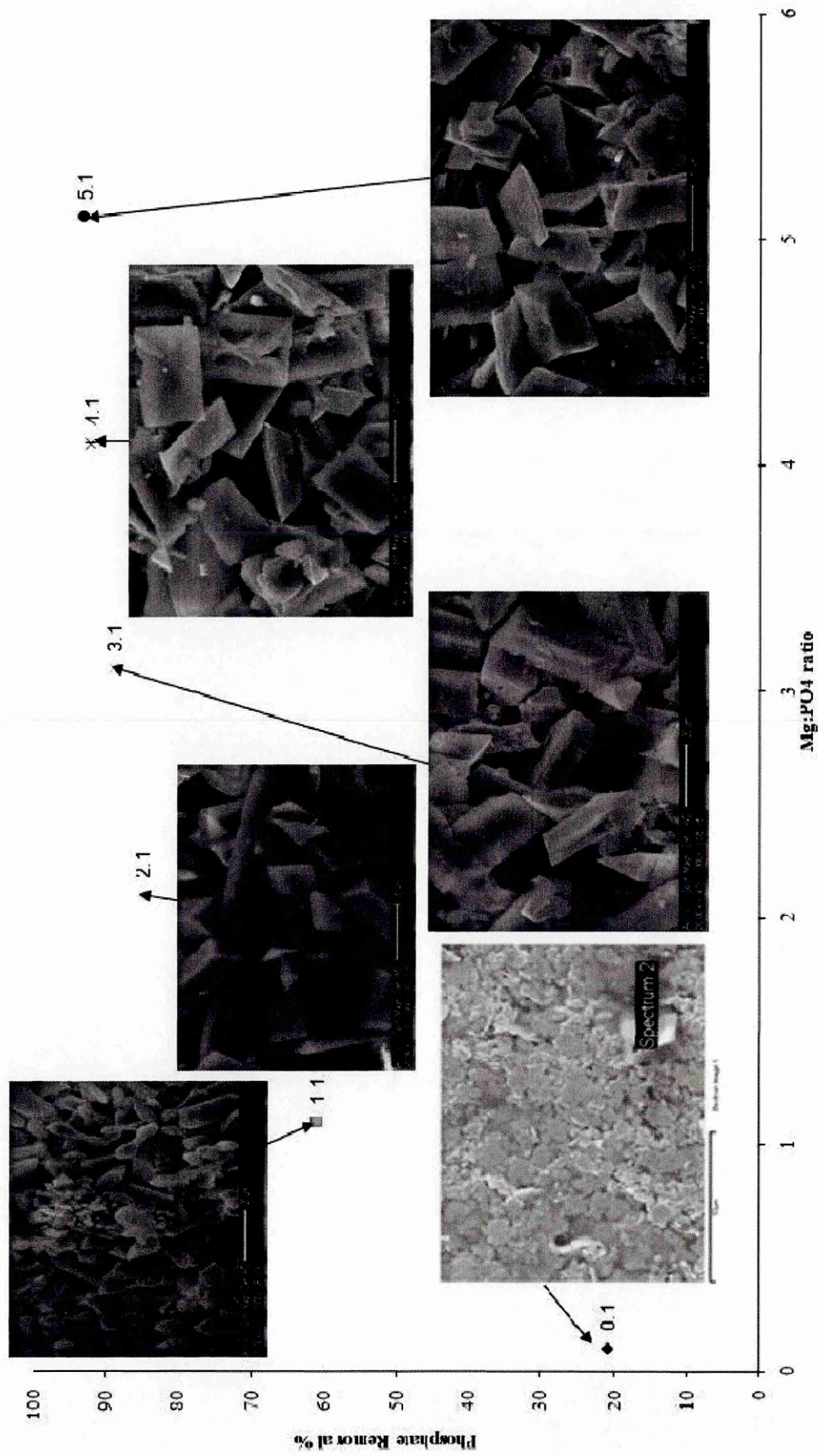
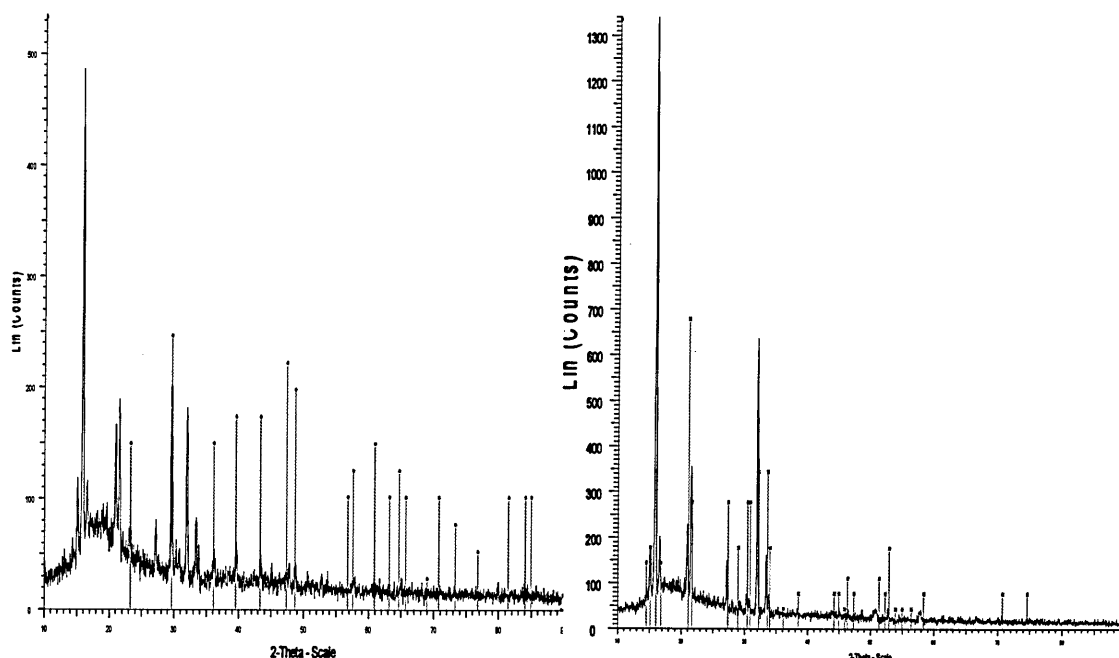


Figure 4.3: Analysis by SEM on the effect of changes in Mg:PO₄ ratio (same as Ca:Mg) on crystal morphology for the Coleshill centrate sample (8.06.06)

XRD analysis of the precipitates collected from Coleshill at Mg:PO₄ ratios of 1.1:1 and 3.1:1 was used to help in identification (Figure 4.4). This identification was done by use of peak matching software (PCPDFWIN database).

The sample taken from Mg:PO₄ ratio of 1.1:1 shows a mixture of calcite and struvite from the peak matching software. The result of a mixture of two materials is to be expected at such Ca:Mg ratios where competing reactions between Ca and Mg would be occurring. As previously mentioned, calcium phosphate is amorphous so its presence cannot be easily identified from XRD data. The identification of calcite and struvite is expected from the SEM-EDS results. At Mg:PO₄ ratio of 3.1:1 ratio, the XRD image shows struvite dominant.



1.1:1 Mg:PO₄ ratio. Calcite highlighted

3.1:1 Mg:PO₄ ratio. Struvite highlighted

Figure 4.4: XRD analysis of Mg:PO₄ ratios of 1.1:1 and 3.1:1 precipitates

The results from the jar tester precipitation tests have shown that effective removal of orthophosphate is easily achievable by simply raising the pH to 9 at three of the sites tested;

this only failed Coleshill due to the low starting Mg concentration (Tables 4.2-4.5). When the Mg:PO₄ is raised above 1:1 at pH 9, all the sites tested were able to remove >60% of the initial orthophosphate. This level of removal would remove a significant proportion of the struvite scaling potential and should lead to a reduction in the amount of scale formed in pipework. Decreasing the phosphate levels in the sludge recycle liquors should also lead to less on the biological P removal process such as Derby STW 1 mg L⁻¹ P discharge limit. Higher removals of orthophosphate were possible by significant increase in the Mg:PO₄ ratio though this is at added cost to any reactor operation.

The quality and particle size of precipitate produced was affected significantly by the ratio Mg:Ca selected. At low ratios, large amorphous particles were observed. At a ratio of 1.1:1, a more crystalline material is observed though the XRD data shows it not to be exclusively struvite. At ratios of $\geq 2:1$, struvite crystals are the main product though the crystals are on average a smaller size than at lower Mg:PO₄ ratios. Crystal size can be increased by allowing greater retention times in the reactor. Abe *et al.* (1995) reported the growth rate of struvite crystals to be 0.061 mm d⁻¹ at orthophosphate influents rates of ≤ 100 mg L⁻¹. The size may affect capture of the crystals in any reactor which explains the need of accumulation devices or seed materials often reported at full scale (Ueno and Fujii, 2001; Battistoni *et al.*, 2006; Suzuki *et al.*, 2007)

4.3 Phase 1: FBR results

A total of 12 experiments were undertaken in the Phase 1 tests using the FBR (Table 4.7). The initial 4 experiments were undertaken without the metallic mesh, and the remaining 8 were run with the metallic mesh over a range of reaction conditions and samples. All the experiments achieved >90% removal of available orthophosphate.

Table 4.7 Summary of experiment conditions tested with the FBR and the overall orthophosphate removal percentage

Date of experiment	Experiment Number	Reactor conditions	Reaction time (Hours)	Upward airflow (L min ⁻¹)	Magnesium added (mmol)	Initial PO ₄ concentration (mg L ⁻¹)	Initial NH ₃ concentration (mg L ⁻¹)	Final PO ₄ removal (%)
20.06.06	1	None	2	7	3.5	82	660	91
21.06.06	2	None	2	7	4	82	660	93
22.06.06	3	None	2	7	4.5	82	660	93
23.06.06	4	None	2	7	5	82	660	94
4.07.06	5	Mesh	2	7	3	53	546	91
5.07.06	6	Mesh	2	7	3	53	546	92
18.07.06	7	Mesh	2	12	5	66	621	93
19.07.06	8	Mesh	2	12	5	66	621	92
24.07.06	9	Mesh	3	12	5	97	495	91
25.07.06	10	Mesh	3	12	5	97	495	93
26.07.06	11	Mesh	3	12	5	97	495	95
27.07.06	12	Mesh	3	12	5	97	495	96

Experiments 1-4 achieved excellent orthophosphate removal (>90%) but there were considerable levels of suspended solids (fines) in the FBR effluent (Figure 4.5). No particle size measurements were possible during this period due to equipment problems. The precipitation of fines with this reactor is in agreement with the results of Le Corre *et al.* (2005) who also reported the precipitation of a similar amount of fines (200 mg L^{-1}). Munch and Barr (2000) reported fines ($d_{0.5} \sim 110 \mu\text{m}$) from a FBR with $\text{Mg}(\text{OH})_2$ dosing.

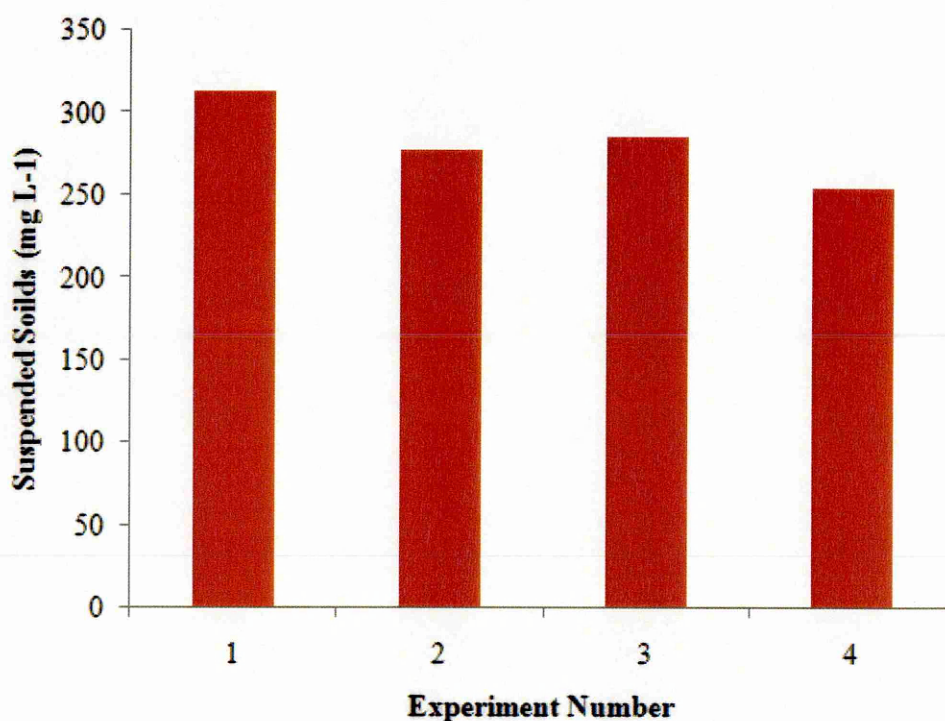


Figure 4.5: Suspended solids collected from the FBR effluent in experiments 1-4

To overcome the production of fines and to simplify the collection of these particles from the reactor, Le Corre *et al.* (2007) demonstrated the effectiveness of a metallic mesh system for the accumulation of fines from synthetic solutions. The impact of the metallic mesh system was investigated here on Wanlip liquors in experiments 5-12 (Figure 4.6).

The solids collected in experiments 5, 6, and 8 were due to accumulation of solid particles in gaps/rough surfaces of the mesh support structure (plastic struts used to support and hold mesh in place, see Figure 3.3), and not on the surface of the mesh as hoped.

In Experiment 7 there is significantly less suspended solids in the effluent and corresponds to an increase in the amount of material that was collected on the surface of the metallic mesh. No changes in variables were made between this experiment and experiment 8 but the patterning of the deposit suggests that there was contact between the mesh and the reactor wall as the deposit was restricted to two areas on the mesh and not an even covering like seen in experiments 9-12.

In experiments 9-12 the effluent suspended solids were reduced, while the amount of material collected on the mesh surface increased greatly. Two variables were changed between these experiments and experiment 7-8; firstly there was an increase in the reaction time from two to three hours and secondly the initial orthophosphate concentration changed from 66 to 97 mg L⁻¹ due to collection of new liquors. Visibly there were a large amount of suspended solids in the liquor up to two hours but after three hours the liquor suspended solids had cleared. It is thought that this reduction of solids in the liquor is due to the gradual accumulation of material on the surface of the metallic mesh due to the mesh acting as a filter (Le Corre, 2006; Suzuki *et al.*, 2007). It is only after 2 hours that enough of a coating of material is present on the surface of the mesh to allow for larger deposits of material to be observed. It was not possible to separate the two effects but it is likely that both played a role in the improved removal.

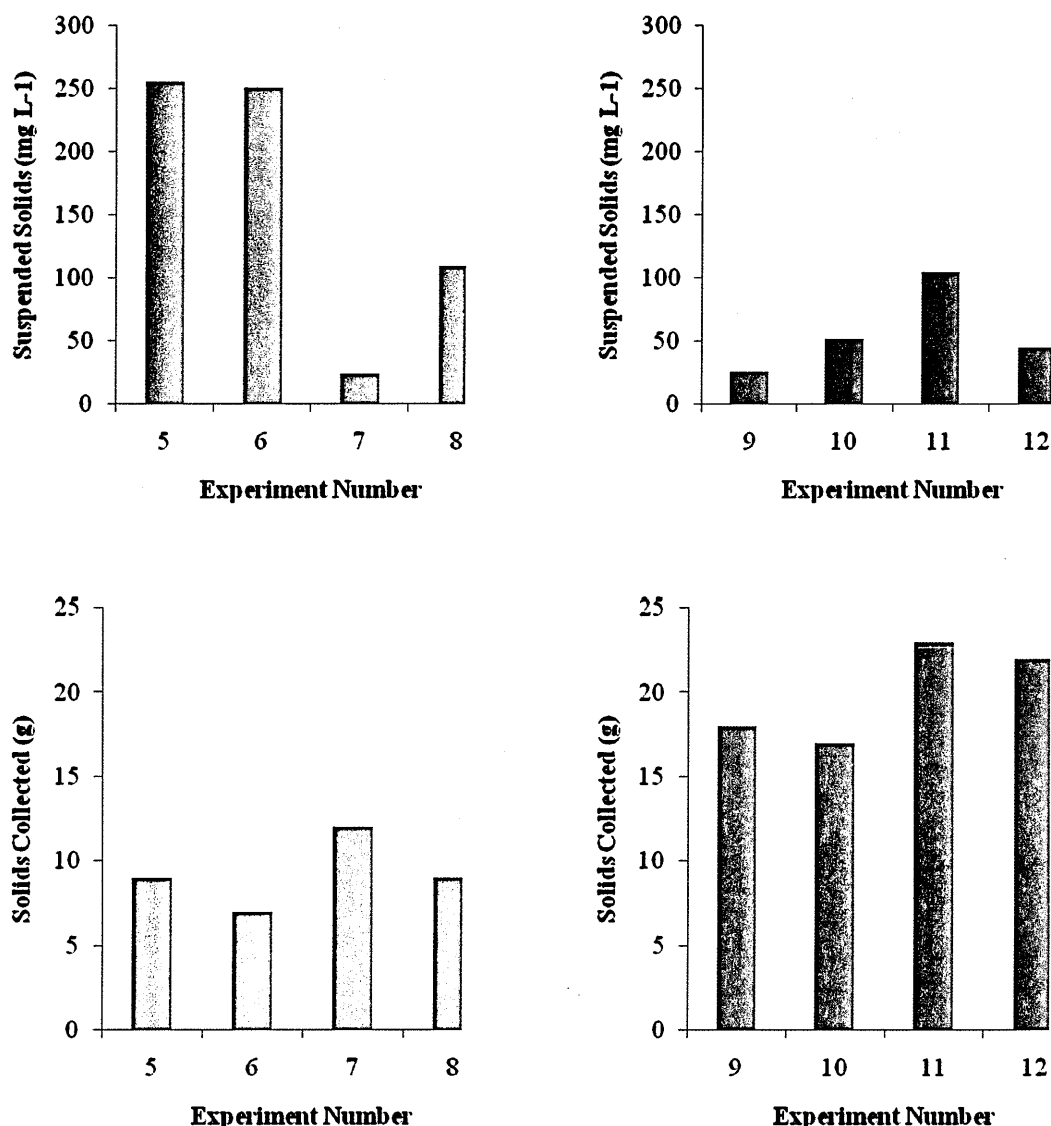


Figure 4.6: The suspended solids and solids collected on the mesh for experiments 5-12. (Experiment 5-6 with 53 mg L⁻¹ PO₄ run for 2 hours; Experiment 7-8 66 mg L⁻¹ PO₄; Experiment 9-12 with 97 mg L⁻¹ PO₄ run for 3 hours).

An examination of the struvite scaling rate for experiments 9-12 is shown below (see Figure 4.7). Le Corre (2006) reported the scaling rate of the metallic mesh in an optimum system to be 7.6 g m⁻² h⁻¹, which is ~10-20% better than the rate observed here. The main difference was that Le Corre's (2006) experiments were carried using synthetic liquors with a Mg:PO₄ of 1:2 as opposed to ratios of 5:1 trialled here. Interestingly Suzuki *et al.* (2005) reported the

scaling rate of a rectangular mesh system to be 1,037g over a 30 day period. If the best result here is extrapolated to a period of 30 days then the result of Suzuki *et al.* (2005) is twice as good. Why a square mesh would be better than a circular mesh is a question for future investigation.

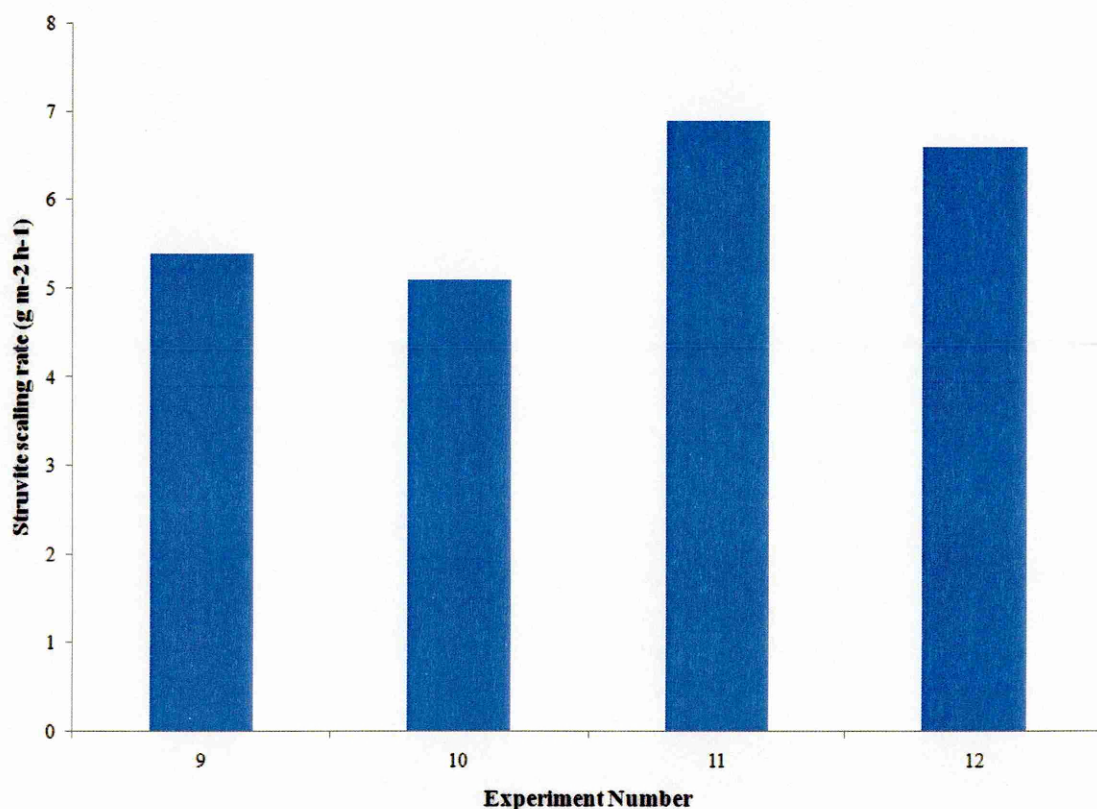


Figure 4.7: The struvite scaling rate of the metallic mesh system ($\text{g m}^{-2} \text{h}^{-1}$) in experiments 9-12

Analysis of the solid material collected from the mesh by SEM showed the majority of solids to be struvite (see Figure 4.8). The characteristic ‘coffin’ like structure of struvite is present in the image.

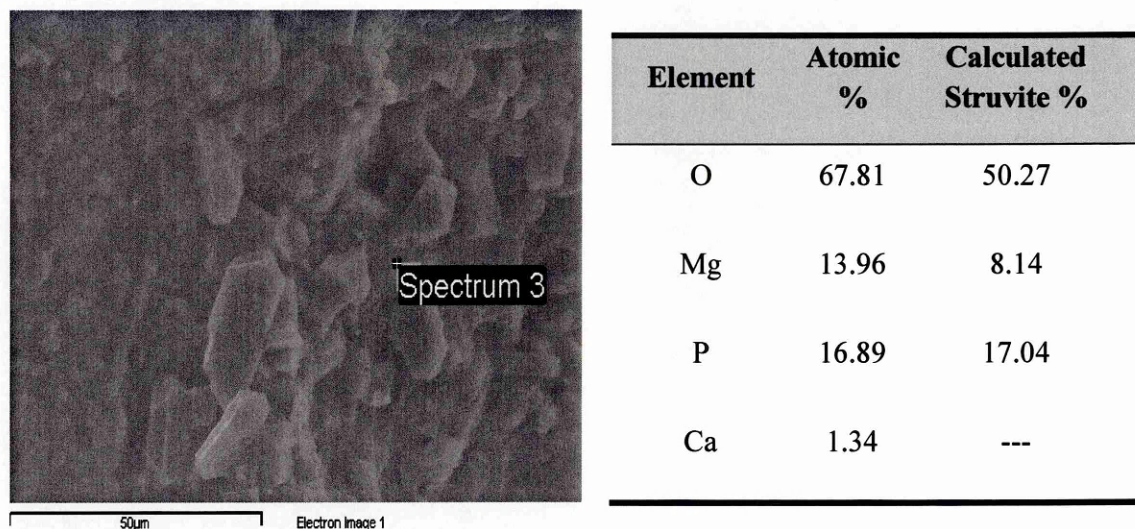


Figure 4.8 Image and EDS analysis of precipitate collected from metallic mesh after experiment 9

From the 12 experiments carried using the FBR it is seen that the reactor can always achieve excellent orthophosphate removal levels, >90%. The production of fines though is a problem that has been encountered by other authors but as shown here can it can be overcome by the introduction of the metallic mesh system to the reactor.

The metallic mesh system was shown by Le Corre (2006) to work by filtration instead of nucleation on the mesh surface. In these experiments it is thought to take two hours for the mesh to become coated in precipitate. Once a sufficient coating is present, visible accumulation is seen on the surface and a reduction in the suspended solids in the reactor effluent. The scaling rate of the metallic mesh during these experiments was lower than that reported by Le Corre (2006); Suzuki *et al.* (2005).

4.4 Phase 1 stirred tank results

The second reactor under investigation in this thesis is a stirred tank reactor. Initial tests used a 350 L water butt as the reactor and centrate collected from Wanlip STW on the 10th (sample number 9) and 17th of August 2006 (sample number 10). Details of experiments undertaken are given in Table 4.8.

Table 4.8: Summary of reaction conditions, initial liquor characteristics and the final orthophosphate removal %

Experiment Date	Experiment Number	Reaction Time (hours)	Magnesium Addition (mmol)	Initial PO ₄ conc. (mg L ⁻¹)	Initial NH ₃ conc. (mg L ⁻¹)	PO ₄ removal (%)	pH
12.08.06	13	2	5	65	564	40	9
13.08.06	14	2	5	65	564	61	9
14.08.06	15	2	5	65	564	53	9
18.08.06	16	2	5	98	764	79	9
19.08.06	17	2	5	98	764	49	9

The removal of orthophosphate with the stirred tank reactor was lower than with the FBR with a maximum of 79% achieved (see Figure 4.7) though lower removals were the norm. The majority of the orthophosphate is removed within the first 75 minutes of the reaction (Figure 4.8).

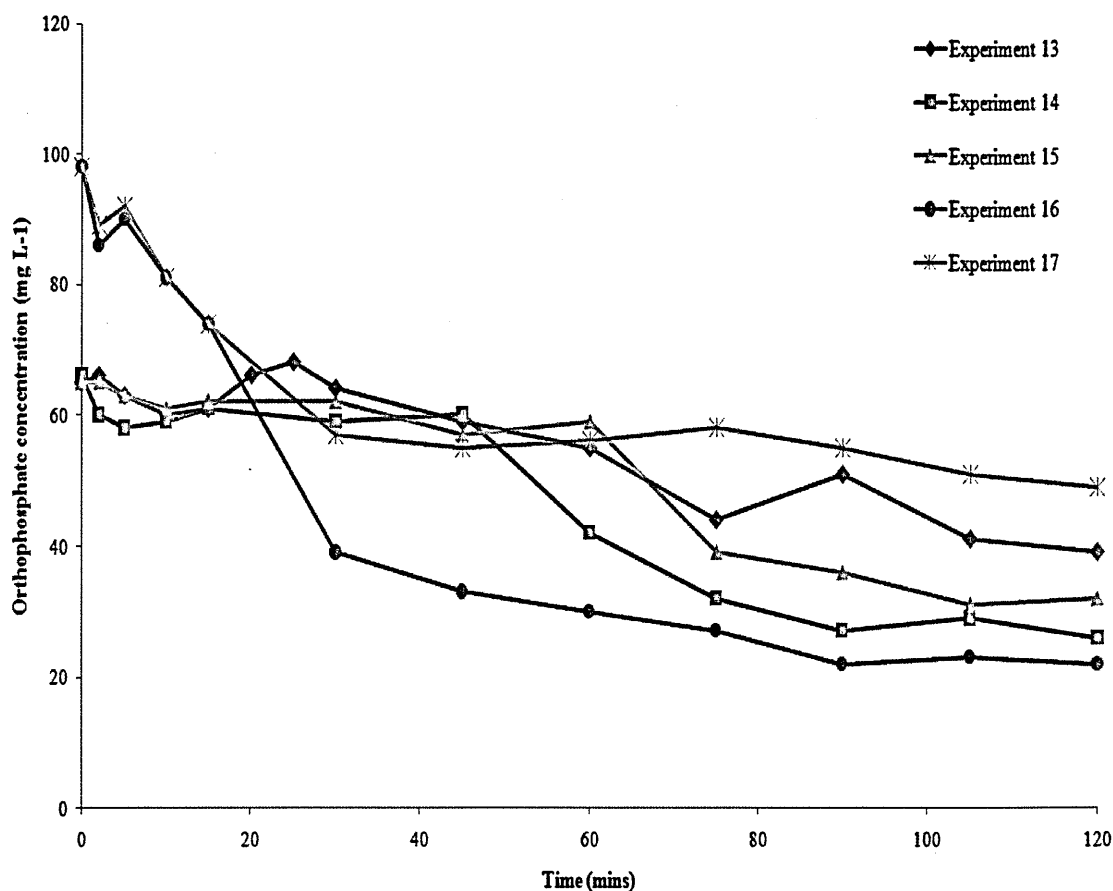


Figure 4.8: The change in orthophosphate concentration over time

The data shows there are significant differences in the removal of orthophosphate, even though the magnesium concentration is constant. The reason for this performance of this reactor isn't fully understood though it is believed that the stirrer might have been too small for such a large tank but this doesn't compare with the jar tester results for similar conditions. It is clear that the design doesn't match the jar test data so this design was no longer used also unfortunately due to the design of the tank it was not possible to collect any solid samples to confirm the precipitation of struvite.

4.5 Phase 2: Side-by-side comparison results

The results from Phase 1 showed excellent performance in orthophosphate removal by the FBR with and without the metallic mesh system and reasonable performance by the stirred tank (although this was an unoptimised reactor). The new stirred tank reactor (see materials and methods) was designed to allow a direct comparison between the two reactor designs by having the same influent flow rate and retention times. Due to time constraints only three conditions were selected for trials (see Table 4.9). The orthophosphate concentration for all experiments was 95 mg L^{-1} so each reactor could be compared easily.

As production of fines was a problem in the FBR, methods of fines capture were examined e.g. the metallic mesh and polyDADMAC. Le Corre *et al.* (2007) showed that a 1 mg L^{-1} polyDADMAC dose of a cationic polymer, polyDADMAC, could be used to form agglomerates of crystals to produce flocs.

Table 4.9: Outline of the operation conditions for each reactor

Experiment Number		18	19	20
Experiment Date		10.01.07	18.01.07	25.01.07
Conditions	FBR	No addition	Polydadmac (1 mg L^{-1})	Steel mesh
	Stirred Tank	No addition	Polydadmac (1 mg L^{-1})	Polydadmac (1 mg L^{-1})
Magnesium addition (mmol)	FBR	1	3	3
	Stirred Tank	1	3	3
pH	FBR +	9	9	9
	Stirred Tank			

The experimental results for 18-20 are shown in Table 4.9. Experiment 18 was run with only the addition of 1 mmol of magnesium. The stirred tank was able to remove 60% of the influent orthophosphate concentration as well as 20% of influent ammonia. The FBR was only able to remove 25% of influent orthophosphate concentration and 20% of ammonia. Particle size analysis of the stirred tank precipitate revealed large particles which is in agreement with previous results of low $\text{Mg}:\text{PO}_4$ ratios. The FBR precipitate was a lot smaller but was still considerably larger than if solely struvite. Both precipitates were shown by XRD (see Appendix 5) to be largely amorphous in nature though peaks matching struvite can be seen.

Experiment 19 was run with the addition of 3 mmol of magnesium and 1 mg L^{-1} of polyDADMAC coagulant. The stirred tank reactor was able to remove 70% of the influent orthophosphate concentration as well as 30% of ammonia. The FBR performed better than in previously, with 45% of influent orthophosphate removed and 30% of ammonia removed. As expected with the addition of larger amounts of magnesium the particle sizes recorded had fallen but had still remained high, particularly for the stirred tank precipitate. This is thought to be due to the additions of polyDADMAC forming larger masses of precipitate. A reduction in particle size was also recorded from the FBR precipitate.

In experiment 20 the FBR was run with the metallic mesh reported previously. The stirred tank was again run with 1 mg^{-1} of polyDADMAC. Both reactors had an addition of 3 mmol of magnesium added periodically. The FBR showed a further improvement with 65% of influent orthophosphate removed as well as 30% of the influent ammonia. The stirred tank reactor was able to remove 65% of the influent orthophosphate as well as 25% of the ammonia. Particle size analysis of both reactors' precipitate showed a considerable reduction particle size. This is thought to be due to the addition of more than 3mmol of magnesium.

Table 4.10: The results collected for the experiments ran with both reactor types

Determinant	Experiment 18		Experiment 19		Experiment 20	
	Stirred tank	FBR	Stirred tank	FBR	Stirred tank	FBR
Orthophosphate removal (%)	60	25	70	45	65	65
Ammonia removal (%)	20	20	30	30	25	30
Settled solids (g L ⁻¹)	20.04	4.85	37.89	7.07	14.06	$\frac{3.19}{4.1^*}$
Theoretical mass of settled solids if pure struvite (g)	26.95	7.35	30.87	19.86	28.68	28.68
d0.5 particle size (µm)	1039	239	630	120	90	50

* = Solids on mesh

In the polyDADMAC trials a problem was noted in that agglomerates of crystals were sticking to the Perspex used in the reactors (see Figure 4.9). This result would suggest that polyDADMAC is unsuitable for the formation of struvite flocs if a reactor was made of Perspex. Further investigations would be required to see if this was a problem with other materials except glass.

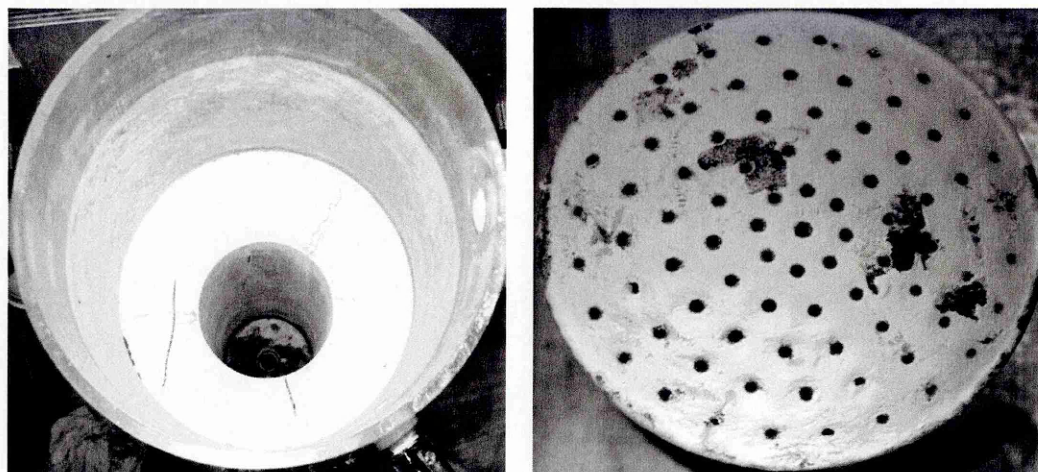


Figure 4.9: Images of precipitate sticking to the reactor sides and air diffuser (experiment 19)

Analysis of the precipitate with XRD and SEM-EDS was undertaken (Appendix 5 and 6 for complete results). The XRD analysis of the precipitates collected from experiment 18 showed the precipitates to have a significant amorphous character and led to the increase in magnesium addition for further experiments (see Figure 4.4). This led to the decision for the magnesium dose to be increased in experiments 19 and 20.

Below are shown the XRD spectra of the precipitate collected from the mesh in experiment 20. Clearly struvite is the prominent species in the precipitate position and intensity of the peak match lines of the database matching software (PCPDFWIN database) though there are a number of other peaks in the spectra.

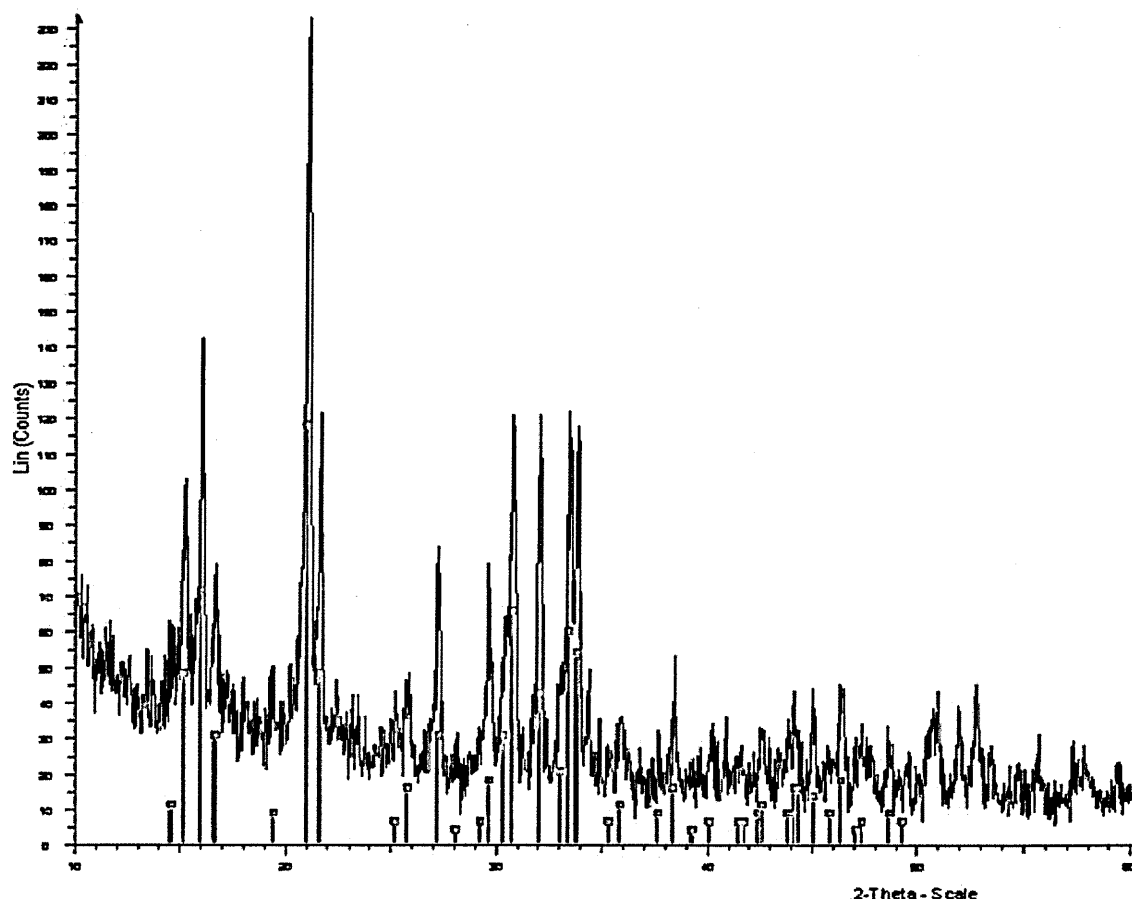


Figure 4.11: XRD trace of the solids collected from experiment 20, metallic mesh. Highlighted lines on spectra show database comparison for struvite

The precipitate collected from the stirred tank shows struvite to be present (see Figure 4.10). The shape of the spectra collected for the precipitate of the stirred tank shows a lot of background noise. This background noise can be attributed to the presence of amorphous material either or both polyDADMAC and Ca in the samples collected.

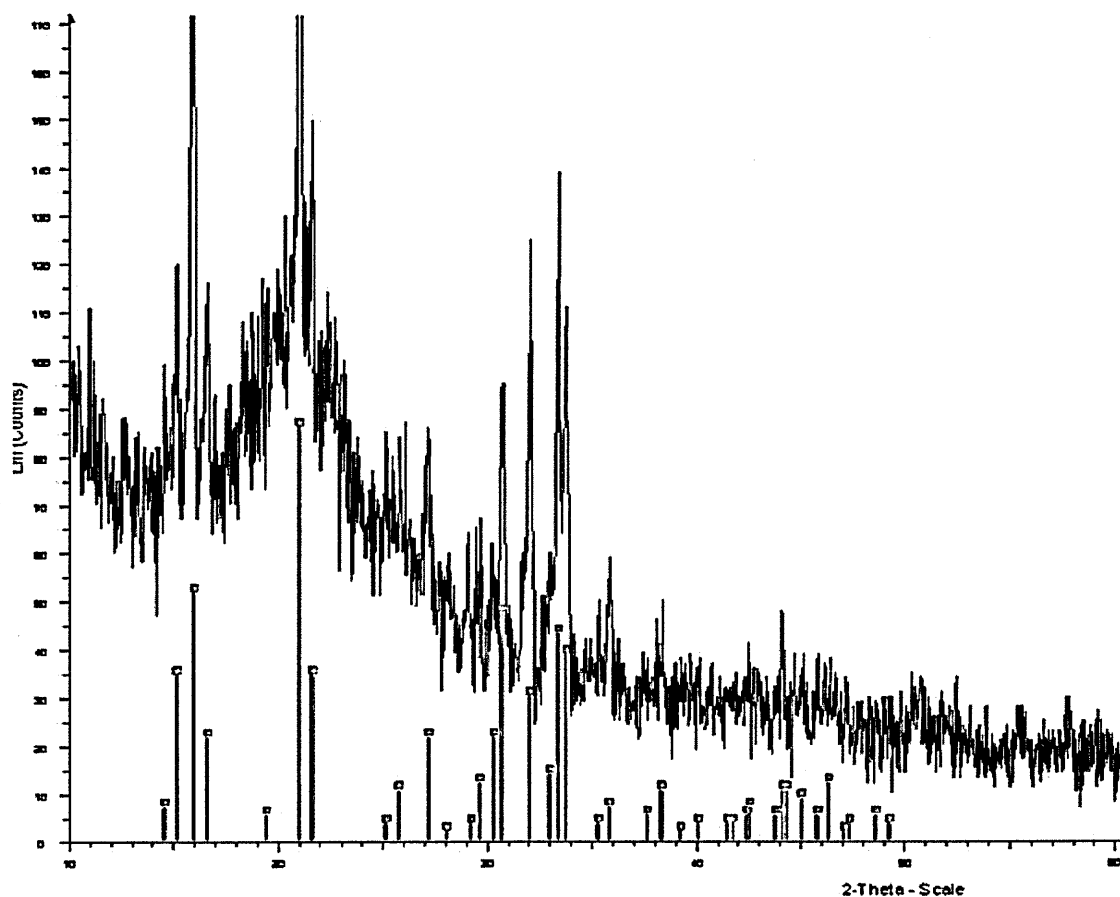


Figure 4.12: XRD trace of the solids collected from the stirred tank in experiment 19 with the addition of polyDADMAC. Lines show database comparison for struvite

The morphology of the crystals collected from the metallic mesh in experiment 20 (Figure 4.13) matches the struvite shape seen previously (see Figure 4.7). The crystals are a lot smaller, $\sim 10\ \mu\text{m}$, compared to $35\text{--}40\ \mu\text{m}$ seen previously though it is hoped that with time they can grow (Abe *et al.*, 2005). EDS analysis of the crystal marked 'Spectrum 1' is inconclusive for a positive struvite identification.

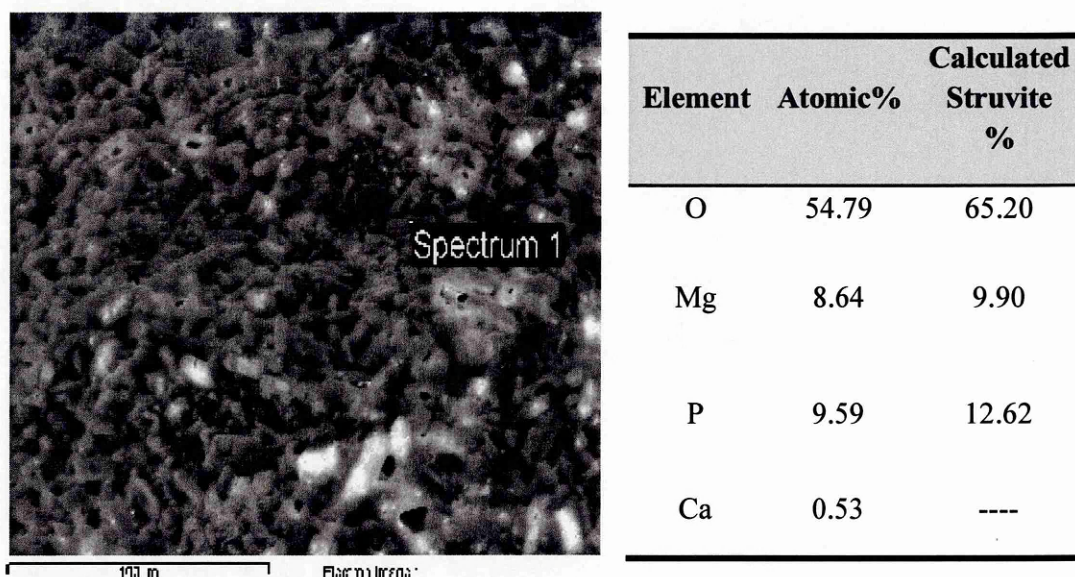


Figure 4.13: SEM and EDS analysis showing crystal morphology and elemental analysis of solids captured on the mesh accumulation device (experiment 20).

The image of the precipitate collected in experiment 19 (Figure 4.14) shows there to be struvite present from the shape of the crystals.

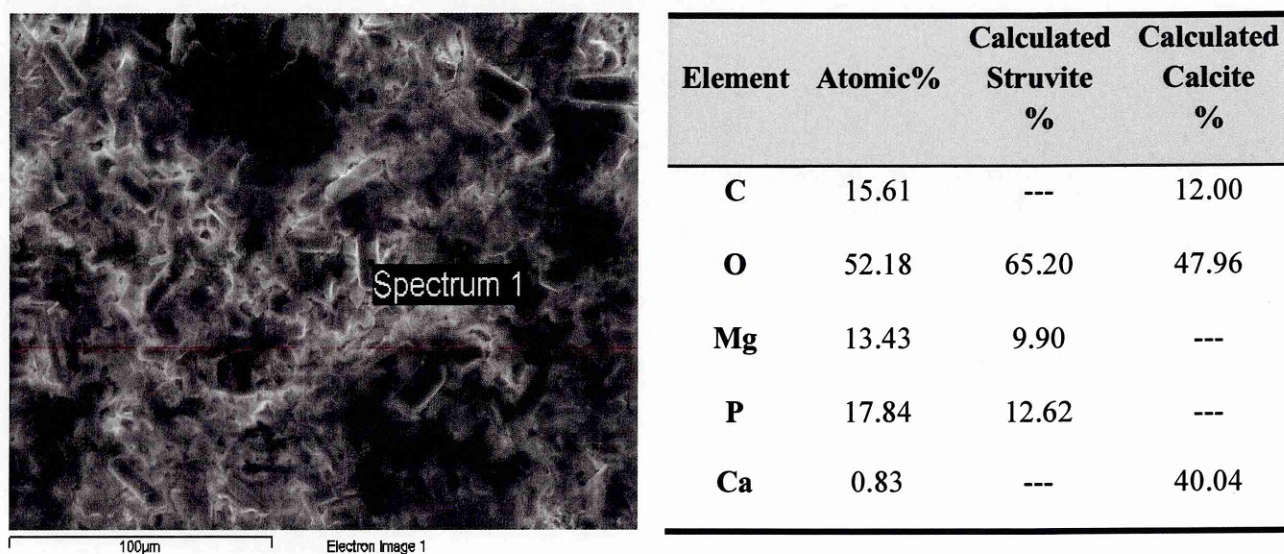


Figure 4.14: SEM and EDS analysis showing crystal morphology and elemental analysis of solids collected from the stirred tank reactor (experiment 19)

A comparison between the results of the Phase 1 and Phase 2 trials show some interesting results. Firstly, the FBR performance of orthophosphate removal in the Phase 2 trials isn't as good as in the Phase 1 trials. In the Phase 1 trials >90% of the influent orthophosphate was removed compared with the mixed results obtained here, 25-65% removal. The reason for the poorer performance is thought to be the relatively short retention time of 9 minutes compared to the 2-3 hour retention time of the Phase 1 trials.

The quality of the crystals produced by the FBR in the Phase 2 trials shows the reactor to perform well for producing struvite. The material produced by the mesh is a similar morphology though smaller than the material produced in the Phase 1 trials. Hopefully the size could be increased by the reactor being operated for longer periods of time e.g. Suzuki *et al.* (2007).

Results for using polyDADMAC as a coagulant in both types of reactor were mixed (see Table 4.11). Use of polyDADMAC in the FBR was found to be particularly unsuitable due to sticking of flocs to the reactor walls and air diffuser. The difference between theoretical and collected solids was greatest when no polyDADMAC was added, contrary to expected results. Comparison of the performance of polyDADMAC in the stirred tank was not possible and further experiments to test its effectiveness would be needed.

Table 4.11: Showing the differences in results in reactors with and without polyDADMAC

	With PolyDADMAC (Experiment 18)		Without PolyDADMAC (Experiment 19)	
	Difference between theoretical and collected solids (%)	d0.5 particle (µm)	Difference between theoretical and collected solids (%)	d0.5 particle (µm)
Stirred tank	122	630	NA	NA
FBR	36	120	49	50

5 Discussion

5.1 Implications of this study to the wastewater industry

This study set out to show how phosphorus could be removed and recovered from sludge liquors. The phosphorus was to be recovered as struvite, which is known to cause scaling problems at STW operated by Severn Trent Water Ltd (Wall, 1999; Doyle, 2002). Recovery of phosphorus as struvite has been demonstrated at full scale in four locations around the world; three in Japan and one in Italy. A number of other pilot scale operations have been demonstrated, though problems with the final product's structure and quality have been reported (Munch and Barr, 2002; Regy *et al.*, 2002). Previous work by Le Corre (2006) had shown methods to overcome these problems in quality and structure of struvite by understanding the effect of Ca on structure and the use of a metallic mesh accumulation device for the capture of fines. It was hoped to be able to transfer these findings of Le Corre (2006) from synthetic solutions to wastewater liquors. The project also set out to gain a better understanding of the merits of the two types of reactors available for the precipitation of struvite.

Two main reasons exist for why water companies wish to remove phosphorus from wastewater liquors. The first reason is due to the scaling problems that affect the operational efficiency of STW. To reduce scaling problem, Antiplax is added to the centrate collecting wells at the sites sampled to inhibit the formation of struvite in later pipework. Antiplax costs ~£900 per cubic metre, with on average 1 m³ being required per week at Wanlip STW. Estimations of the operating cost of a struvite recovery reactor by Jaffer *et al.* (2002) showed the chemical and energy costs to be £50,000, mostly arising from addition of NaOH, but the revenue from the sale of struvite to be between £18,000-20,000, meaning a net cost of £30,000-32,000 a year. This is substantially less than the £46,800 per year cost of addition of Antiplax at Wanlip STW. It should be noted that at present no market exists for the sale of struvite within Europe unlike in Japan.

The second reason the wastewater industry wishes to remove phosphorus is to lower the concentration of phosphorus within the discharges from the STW e.g. the sludge produced from metal salt removal of P and releases to watercourses. The chemical precipitation of phosphorus with metal ion salts, namely iron, is carried out at 50 STW operated by Severn Trent Water Ltd. Struvite precipitation offers a method for P removal in an easier to handle and dispose of product unlike the sludge that is produced from metal salt addition. The sludge that is produced is normally spread on farmland but is increasingly unpopular with farmers due to the buying policies of supermarkets insisting produce not be grown on land fertilised by sludge arising from wastewater treatment (Towers and Horne, 1997).

For the successful recovery of phosphorus as struvite the physiochemical characteristics of the liquor entering a reactor need to be monitored. This study and a study by Doyle (2002) have shown inconsistency in the concentration of struvite constituents over time at two sites operated by Severn Trent Water. In this study, the most noteworthy change, at Wanlip STW, was in the concentration of orthophosphate, which varied from 44 to 136 mg L⁻¹ over the sampling period of twelve months. Magnesium, often the limiting constituent in struvite recovery operations and subsequently added, also showed a large variability over the sampling period between 5 to 14.7 mg L⁻¹. Doyle (2002) found similar variability in the physiochemical characteristics of liquors collected from Coleshill. Doyle (2002) reported the orthophosphate concentration to vary between 104 to 195 mg L⁻¹ and the magnesium concentration to vary between 6 to 24 mg L⁻¹. These changes in the concentration of struvite constituents at Wanlip STW would mean that at some points the liquors are magnesium limited and at others orthophosphate limited with respect to struvite precipitation. This finding would have an impact on the operation of a struvite recovery reactor as it would likely need a system of monitoring and controlling the addition of chemicals to the influent liquors. This could be carried out automatically by machine though it would still require regular checking by a skilled technician.

If struvite is to be recovered from wastewater liquors, then it is hoped that the recovered product could be recycled as a fertiliser for domestic and industrial use (Johnson *et al.*, 2004). For this to be achieved the product needs to be of a high quality for easier processing into a

marketable product. The calcium concentration has been shown by Le Corre *et al.* (2005) to inhibit the formation and quality of struvite crystals. Different ratios have been given by these authors as to eliminate the detrimental effect of calcium on the formation of struvite, though a ratio of >2:1 Mg:Ca is generally accepted. The SEM-EDS and XRD analysis of the precipitate produced from the Coleshill liquors showed that at a ratio >2.1:1, struvite was the principal product. This study and the study by Doyle (2002) have shown there to be considerable variation in the concentration of calcium over the sampling period, with a Wanlip varying between 83-147 mg L⁻¹.

The difference between the two reactor designs has been examined in this study and obvious benefits can be seen for each reactor design. The FBR is the design of choice in operational reactors around the world. Three FBR are operated in Japan and one in Italy for the precipitation of struvite. There is also an operational FBR for the removal of phosphorus in the form of HAP at Geestmerambacht, Netherlands. All these FBRs use a form of seed material for the building of larger particles/pellets. The reactor at Shimane, Japan is able to produce crystals that range in size from 0.5-1.0mm, with the product then sold as 'green' fertilisers (Ueno and Fujii, 2001). At Treviso, Italy sand is used as the seed material and agglomerated particles of up to 1.4mm in size have been reported (Battistoni *et al.*, 2006). Initial results for the FBR operated in this study showed the production of a large amount of fines though the reactor was able to remove >90% of influent orthophosphate. Results from the Phase 2 trials showed that the present FBR was unsuitable for a continuous operation as it was unable to collect significant amounts of solids. The orthophosphate removal was also significantly reduced from the Phase 1 trials but this is thought to be due to the relatively short retention time and could be altered with the use of a larger reactor with a longer retention time. Fines are an unwanted product as there collection and possible reuse as a fertiliser is unfeasible. Battistoni *et al.* (2002) even reported that the production of fines might hamper operational efficiency if the crystals found their way back into the STW via the liquor recycle stream.

It was shown in Phase 1 that a metallic mesh system could be used as an effective accumulation device for struvite. The metallic mesh system was able to remove >90% of the

influent orthophosphate and recover the majority of the precipitated solids in the Phase 1 testing. The material collected on the mesh was easily removed by light brushing after a 24 hour drying period. During the Phase 2 side-by-side trial, the mesh system collected slightly less material on the surface of the mesh, with 65% of orthophosphate being removed during this trial. Results reported by Suzuki *et al.* (2007) showed a mesh system in a FBR over a 3.5 year study to be suitable for the collection of struvite from swine waste liquors. One issue surrounding the use of the metallic mesh system would be the amount of sludge particles in the liquors and the possible collection on the surface of the mesh compromising the purity of recovered struvite. Another challenge is how to recover, at an industrial scale, the struvite from the mesh whilst operating continuously. A number of mesh systems would be required so that at a mesh change over struvite would not re-enter the STW recycle lines and cause problems later in the site.

The stirred tank type reactor operated in the Phase 1 testing was able to remove ~55% of the orthophosphate present in the liquors much less than at similar conditions in the jar tester experiments. The majority of orthophosphate removal occurred within the first 75 mins of the experiment. The Phase 1 experiments were carried out in at what could be considered highly supersaturated conditions (high $\text{Mg}:\text{PO}_4$ ratio and pH 9), where it is thought that high concentrations of magnesium allow the rapid production of struvite crystals, leading to a large amount of fines due to the depletion of available Mg. If the orthophosphate was being removed as struvite in such high supersaturated conditions, then it should follow that the orthophosphate removal would occur within the first ten minutes as reported by Momberg (1992). This was not the case in these initial experiments and reason for this is thought to be due to the stirrer not being sufficiently large for the reactor unlike in the jar tester experiments where the stirrer was matched to the jar size.

The stirred tank reactor for the Phase 2 testing performed better than the stirred tank operated in the Phase 1 testing i.e. ~65% removal of orthophosphate from the influent. Analysis of the precipitate that was collected from experiments showed that it was not exclusively struvite. SEM-EDS showed there to be a considerable amount of calcium in the precipitate collected. XRD analysis showed the presence of struvite in experiments 18 and 19 though the material

had a amorphous nature. In experiment 20 SEM-EDS and XRD analysis showed the precipitate to be calcite.

The Mg:PO_4 is an important selection for both types of reactor. it can be seen from the results that at a Mg:PO_4 ratio 1:1 the stirred tank reactor removes 60% of influent orthophosphate whilst the FBR removes 25%. This would suggest that if the objective of the reactor was to remove orthophosphate alone the stirred tank could be run at this ratio and achieve good removal. If the desired product was struvite then the results from Phase 2 show that a Mg:PO_4 ratio of 3:1 is required to achieve recovery as struvite. A method for recovery was also investigated here with polyDADMAC and the metallic mesh. polyDADMAC failed to achieve the same success as that seen by Le Corre *et al.* (2007). Problems in both reactors with material sticking to the Perspex parts were noted which would cause further problems later on. The metallic mesh system on the other hand worked particularly well. Material was produced on the surface and struvite was the recovered product. These results would suggest the metallic mesh as the better choice as an accumulation device for the recovery of struvite.

6 Conclusions

- The physiochemical characteristics of the centrate over the sampling period show a large variability in the concentrations of the constituents of struvite. The concentrations of these chemicals in an on-site plant would require a system of monitoring being put in place. The monitoring would could be attached to an automatic chemical adder but would still need some intervention
- The jar tester experiments were all able to show a >60% removal of orthophosphate at $\text{Mg:PO}_4 > 1:1$. Wanlip, Stoke Bardolph and Coleshill liquors were able to remove >80% of orthophosphate when the Mg:PO_4 ratio was adjusted to >2:1. The effect of calcium on the morphology of the struvite crystals was seen in the SEM-EDS results. It took only 2mmol of magnesium to overcome the detrimental effect of calcium on struvite morphology.
- In Phase 1 testing the FBR removed >90% of initial orthophosphate in all the experiments. Without the accumulation device, an average of $\sim 300 \text{ mg L}^{-1}$ of suspended solids was present in the effluent.
- The high suspended solids were also a feature of experiments 5, 6 and 8. Only when the reaction time was increased to three hours were the suspended solid levels decreased in experiments 9-12. The scaling rate of the mesh was calculated to be $\sim 6 \text{ g m}^{-2} \text{ h}^{-1}$. The material that collected on the mesh was easily removable with drying and light brushing.
- The Phase 1 stirred tank was able to achieve $\sim 55\%$ removal of orthophosphate from the liquors added with the majority removed in the first 75 mins. Collection of precipitate from the reactor was difficult due to the sampling port not being at the bottom of the tank.
- Phase 2 testing showed that each reactor type could achieve different results. The FBR could produce relatively pure amounts of struvite, particularly with the mesh system and remove 45% of influent orthophosphate. Whereas the stirred tank reactor could achieve good orthophosphate removal $\sim 65\%$ of the influent concentration but poor struvite purity.

- The use of the cationic polymer, polyDADMAC, was seen to be impractical for the capture of fines in both types of reactor trialled in Phase 2 testing.

7 Further work

- Further work on the mesh accumulation device. Optimisation of the FBR and mesh system in a continuous operation. Suzuki *et al.* (2007) has demonstrated a metallic mesh system over a period of three and a half years. The metallic mesh demonstrated that a square mesh worked better than a circular mesh with it being believed this was due to the surface area of the mesh. Possible new designs with increased surface areas could be a new focus for research of accumulation devices.
- Examine methods for the increase in particle size. At present the product is unsuitable for usage as a fertiliser. A more granular product is wanted by industry and so methods of producing a product like this are desirable.
- pH has been shown by other authors to allow the growth of larger particles at lower pH values. This is done by an increase in HRT of liquids which requires bigger reactors. An effective investigation with larger reactors or lower influent flow rates would provide useful results.
- Seed materials have been shown to work effectively at pH <8.80. At lower pH's less base is needed to raise the pH so a lower cost. An investigation of seed materials in reactors could offer a method for a lower operating cost reactor.
- Scaling up of the reactors trialled here to on-site pilot plant.

8 References

Abe, S. (1995) Phosphate removal from dewatering filtrate by MAP process at Seibu treatment plant in Fukuoka City *Sewage Works in Japan* 59-64.

Ali, M. I. and Schneider, P.A. (2006) A fed batch design approach of struvite system on controlled supersaturation. *Chemical engineering sciences* **62**, (12) 3951-3961.

Battistoni, P., De Angelis, A., Prisciandaro, M., Boccadoro, R., Bolzonella, D. (2002a) P removal from anaerobic supernatants by struvite crystallization: Long term validation and process modelling. *Water Research* **36**, (8) 1927-1938

Battistoni, P., Paci, B., Fatone, F., Pavan, P. (2006b) Phosphorus removal from anaerobic supernatants: Start-up and steady-state conditions of a fluidized bed reactor full-scale plant. *Industrial and Engineering Chemistry Research* **45**, (2) 663-669.

Battistoni, P., Paci, B., Fatone, F., Pavan, P. (2005) Phosphorus removal from supernatants at low concentration using packed and fluidized-bed reactors *Industrial and Engineering Chemistry Research* **44**, (17) 6701-6707.

Benisch, M., Clark, C., Sprick, R.G., Baur, R., Struvite deposits: a common and costly nuisance. *WEF Operations Forum*, December, 2000.

Doyle, J.D. (2002) Struvite formation and control in wastewater treatment. *PhD Thesis*, Cranfield University.

- Hafner, S.D., Bisogni Jr., J.J., Jewell, W.J. (2006) Measurement of un-ionized ammonia in complex mixtures. *Environmental Science and Technology* **40**, (5) 1597-1602.
- Jaffer, Y., Clark, T.A., Pearce, P., Parsons, S.A. (2002) Potential phosphorus recovery by struvite formation. *Water Research* **36**, (7), pp. 1834-1842.
- Jeyanayagam, S. (2005) True confessions of the Biological Nutrient Removal process. *Florida water resources journal* **1**, pp. 37-46
- Johnson, A. Hammond, R., Lewington, M., Ratnam, A. (2004) Struvite potential as an ingredient in horticultural fertiliser. *Struvite: Its role in phosphorus recovery and reuse* Cranfield, UK.
- Kofina, A.N., Koutsoukos, P.G. (2005) Spontaneous precipitation of struvite from synthetic wastewater solutions. *Crystal Growth and Design* **5**, (2) pp. 489-496.
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Jefferson, B., Parsons, S.A. (2007) Agglomeration of struvite crystals. *Water Research* **41**, (2) 419-425
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A. (2006b) Impact of reactor operation on the success of struvite precipitation from synthetic liquors. *Environmental Technology*; (Waiting for publication).
- Le Corre, K.S. (2006c) Understanding struvite crystallisation and recovery. *PhD Thesis*, Cranfield University

- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A. (2005) Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth* **283**, (3-4):514-522.
- Lee, S.I., Weon, S.Y., Lee, C.W., Koopman, B. (2003) Removal of nitrogen and phosphate from wastewater by addition of bittern. *Chemosphere* **51** (4) 265-271.
- Momberg, G.A., Oellermann, R.A. (1992) The removal of phosphate by hydroxyapatite and struvite crystallisation in South Africa. *Water Science and Technology* **26**, (5-6) 987-996.
- Munch, E.V., Barr, K. Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams. *Water Research* (2001) **35** (1) 151-159.
- Ohlinger, K.N., Young, T.M., Schroeder, E.D. (1998) Predicting struvite formation in digestion. *Water Research* **32** 3607-14
- Potjer, B., (2001) Economic/ environmental costs assessment of phosphate recycling possibilities at Thermphos' plant, Vlissingen, The Netherlands. *Second International Conference on the recovery of phosphorus from sewage and animal wastes*
- Regy, S., Mangin, D., Klein, J.P., Lieto, J. and Thornton, C. (2002). Phosphate recovery by struvite precipitation in a stirred reactor. *Lagep (Laboratoire d'Automatique et de Génie des Procédés) internal report/CEEP (Centre Européen d'Etude des Polyphosphates)*, 1-65
Accessed in 2004 at <http://www.nhm.ac.uk/mineralogy/phos/LagepReport.PDF>.
- Richards, I.R., Johnston, A.E. (2001) The effectiveness of different precipitated phosphates as sources of phosphorus for plants. *IACR*, Rothamstead, UK and Ecopt, Suffolk, U.K.

Standard Methods for the examination of water and wastewater 21st Edition (2006), AWWA, Washington DC.

(2006) Stratful, I., Brett, S., Scrimshaw, M.B., Lester, J.N. (1999) Biological phosphorus removal its role in phosphorus recycling. *Environmental Technology* **20**, (7) 681-695

Stratful, I., Scrimshaw, M.D. and Lester, J.N. (2004) Removal of struvite to prevent problems associated with its accumulation in wastewater treatment works. *Water Environment Research* **76**, 437-4199.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y. (2005) Recovery of phosphorous from swine wastewater through crystallization. *Bioresource Technology* **96**, (14) 1544-1550.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y., Yasuda, T., Waki, M. (2007) Removal and recovery of phosphorous from swine wastewater by demonstration crystallization reactor and struvite accumulation device. *Bioresource Technology* (2007) **98** (8) 1573-1578

Takiguchi, N., Kishino, M., Kuroda, A., Kato, J., Ohtake, H. (2004) A laboratory-scale test of anaerobic digestion and methane production after phosphorus recovery from waste activated sludge. *Journal of Bioscience and Bioengineering* **97** (6) 365-368

Turker, M., Celen, I. (2007) Removal of ammonia as struvite from anaerobic digester effluents and recycling of magnesium and phosphate. *Bioresource Technology* **98** (8) 1529-1534

Ueno, Y., Fujii, T., (2001) Three years experience of operating and selling recovered struvite from full-scale plant. *Environmental Technology* **22**, 1373-1381.

UWWTD. Council of the European Communities, Directive concerning the collection, treatment and discharge of urban wastewater from certain industrial sectors (91/271/EEC) Official J L, 135/40, 1991

Williams, S. (1999) *Struvite* precipitation in the sludge stream at Slough wastewater treatment plant and opportunities for phosphorus recovery. *Environmental Technology* **20**, 743-748.

Wall, F. (2000) Evaluation of the potential for struvite and calcite formation at seven sewage treatment works within the Severn Trent region. *MSc Thesis*, Cranfield University.

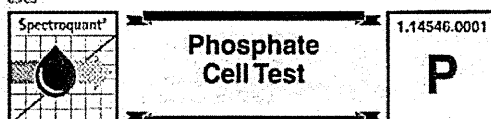
Yoshino, M., Yao, M., Tsuno, H., Somiya, I. (2003) Removal and recovery of phosphate and ammonium as struvite from supernatant in anaerobic digestion. *Water Science and Technology* **48**, (1) 171-178

Appendix 1

Cell test instructions, concentration limits and accuracy

Orthophosphate

65/03



for the determination of orthophosphate

1. Method

In sulfuric solution, orthophosphate ions react with ammonium vanadate and ammonium heptamolybdate to form orange-yellow molybdovanadophosphoric acid that is determined photometrically (VM method).
The method is analogous to US Standard Methods 4500-P C.

2. Measuring range and number of determinations

Wavelength ¹⁾	Measuring range	Number of determinations
313 nm	0.5 - 25.0 mg/l PO ₄ -P 1.5 - 76.7 mg/l PO ₄ -P 1.1 - 57.3 mg/l P ₂ O ₅	25

¹⁾ Maximum absorbance; the wavelength stored in system photometers may differ from this value

3. Applications

This test measures only orthophosphate

Sample material:

Groundwater and surface water, seawater
Wastewater
Industrial water
Boiler water
Nutrient solutions for fertilization
Soils after appropriate sample pretreatment

4. Influence of foreign substances

This was checked in solutions containing 10 and 0 mg/l PO₄-P. The concentrations of foreign substances given in the table lie below the limit at which the determination is interfered with.

The values in parentheses apply for the phosphate-free solution. In some cases, namely the tolerable concentration in this solution is lower than that in the phosphate-containing solution.

Concentrations of foreign substances in mg/l or %					
Ag ⁺	1000	Cu ²⁺	1000	Pb ²⁺	10
AsO ₄ ³⁻	100 (10)	Fe ²⁺	10	S ²⁻	10
Ca ²⁺	1000	H ₂ P ⁺	1000	SCN ⁻	1000
Co ²⁺	1000	Mg ²⁺	1000	SO ₄ ²⁻	1000 (100)
CN ⁻	1000	Mn ²⁺	1000	SO ₃ ²⁻	1000
Co ³⁺	100	NH ₄ ⁺	1000	Zn ²⁺	1000
Cr ³⁺	100 (10)	NO ₃ ⁻	1000 (100)		
Cr ₂ O ₇ ²⁻	10 (1)				

5. Reagents and auxiliaries

Please note the warnings on the packaging materials!

The reagents in the test are stable up to the date stated on the pack when stored closed at +15 to +25 °C.

Package contents:

25 reaction cells
1 cell with blank (white screw cap); required only when using the SQ 118 photometer
1 sheet of round stickers for numbering the cells

Other reagents and accessories:

Merckoquant® Phosphate Test, Cat. No. 1.10428.0001,
measuring range 10 - 500 mg/l PO₄-P
Universal indicator strips pH 0 - 14, Cat. No. 1.09535.0001
Sulfuric acid 0.5 mol/l, Cat. No. 1.09072,
Phosphate standard solution CertiPUR®, 1000 mg/l PO₄-P,
Cat. No. 1.18998.0500

Pipette for a pipetting volume of 5.0 ml

6. Preparation

- Analyze immediately after sampling.
- Check the phosphate content with the Merckoquant® Phosphate Test.
Samples containing more than 25 mg/l PO₄-P (76.7 mg/l P₂O₅) must be diluted with distilled water.
- The pH must be within the range 0 - 10.
Adjust, if necessary, with sulfuric acid.
- Filter turbid samples.

7. Procedure

Prepared sample (10 - 40 °C)	5.0 ml	Pipette into a reaction cell; close the cell tightly, and mix.
Measure the sample in the photometer.		

Notes on the measurement:

- For photometric measurement the cells must be clean.
Wipe, if necessary, with a clean dry cloth.
- Measurement of turbid solutions yields false-high readings.
- The pH of the measurement solution must be within the range 0.5 - 1.0.
- The colour of the measurement solution remains stable for at least 60 min after the end of the reaction time stated above.

8. Analytical quality assurance

The measurement results can be officially recognized under the precondition that analytical quality-assurance measures are taken (ATV M 704).
To check the photometric measurement system (test reagents, measurement device, handling) and the mode of working, a dilute phosphate standard solution containing 15.0 mg/l PO₄-P can be used.
Sample-dependent interferences (matrix effects) can be determined by means of standard addition.

Characteristic data of the procedure:

In the production control, the following data were determined in accordance with ISO 8466-1 and DIN 38402 A51:

Standard deviation of the procedure	± 0.09 mg/l PO ₄ -P
Coefficient of variation of the procedure	± 0.72 %
Confidence interval ¹⁾	± 0.1 mg/l PO ₄ -P
Number of lots	12

Sensitivity: 0.010 A (absorbance) ± 0.13 mg/l PO₄-P

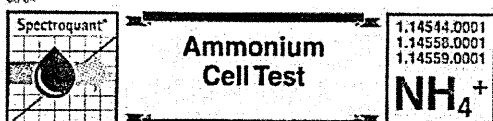
Accuracy of a measurement value: max. ± 0.5 mg/l PO₄-P

9. Notes

- Use only phosphate-free detergents to clean glassware. Otherwise fill with hydrochloric acid (approx. 10 %) and leave to stand for several hours.
- For information on disposal/return for disposal please contact your local Merck organization or Merck dealer.

Merck KGaA, 64271 Darmstadt, Germany, Tel. +49(0)6151 720, Fax +49(0)6151 722900,
environmental.analysis@merck.de <http://photometry.merck.de>

06/04



1. Method

Ammonium nitrogen ($\text{NH}_4\text{-N}$) occurs partly in the form of ammonium ions and partly as ammonia. A pH-dependent equilibrium exists between the two forms. In strongly alkaline solution ammonium nitrogen is present almost entirely as ammonia, which reacts with hypochlorite ions to form monochloramine. This in turn reacts with a substituted phenol to form a blue indophenol derivative that is determined photometrically. The method is analogous to EPA 350.1, US Standard Methods 4500- $\text{NH}_4\text{-N}$, D, and ISO 7150/1.

2. Measuring range and number of determinations

Cat. No.	Measuring range		Number of determinations
	$\text{mg/l NH}_4\text{-N}$	mg/l NH_4^+	
1.14558.0001	0.20 - 8.00	0.26 - 10.30	25
1.14544.0001	0.5 - 16.0	0.6 - 20.6	
1.14559.0001	4.0 - 80.0	5.2 - 103.0	

For programming data for selected photometers / spectrophotometers see the website.

3. Applications

This test measures both ammonium ions and dissolved ammonia.

Sample material:

Groundwater and surface water, seawater
Drinking water
Wastewater
Nutrient solutions for fertilization
Soils and food after appropriate sample pretreatment

4. Influence of foreign substances

This was checked in solutions with ammonium concentrations from the middle of the respective measuring range and with 0 $\text{mg/l NH}_4\text{-N}$. The concentrations of foreign substances given in the table lie below the limit at which the determination is interfered with.

	Concentrations of foreign substances in mg/l or %		
	1.14558	1.14544	1.14559
Al^{3+}	1000	1000	1000
Ca^{2+}	250	500	1000
Cd^{2+}	1000	1000	1000
CN^-	25	50	250
Cr^{3+}	10	25	100
CrO_4^{2-}	250	500	1000
Cu^{2+}	25	50	250
F^-	1000	1000	1000
Fe^{3+}	50	100	250
Hg^{2+}	50	100	500
Mg^{2+}	50	100	500
Mn^{2+}	10	25	100
Ni^{2+}	25	50	250
NO_3^-	500	1000	1000
Pb^{2+}	1000	1000	1000
PO_4^{3-}	250	500	1000
S^{2-}	5	10	50
SiO_4^{4-}	1000	1000	1000
Zn^{2+}	50	100	500

Reducing agents interfere with the determination.

¹ tested with methylamine

² tested with dimethylamine

³ tested with nonionic, cationic, and anionic surfactants

5. Reagents and auxiliaries

Please note the warnings on the packaging materials!

The reagents in the test are stable up to the date stated on the pack when stored closed at $+15$ to $+25$ °C.

Package contents:

1 bottle of reagent $\text{NH}_4\text{-1K}$ (contains granulate + desiccant capsule)
25 reaction cells
1 cell with blank (white screw cap); required only when using the SQ 118 photometer
1 blue dose-metering cap
1 sheet of round stickers for numbering the cells

Other reagents and accessories:

Universal indicator strips pH 0 - 14, Cat. No. 1.09535.0001
Sodium hydroxide solution 1 mol/l, Cat. No. 1.09137
Sulfuric acid 0.5 mol/l, Cat. No. 1.09072
Spectroquant® CombiCheck 10, Cat. No. 1.14676.0001
Spectroquant® CombiCheck 20, Cat. No. 1.14675.0001
Spectroquant® CombiCheck 70, Cat. No. 1.14689.0001

Pipette for a pipetting volume of 0.10 ml

Pipette for a pipetting volume of 0.50 ml

Pipette for a pipetting volume of 1.0 ml

6. Preparation

At the first use replace the black screw cap of the reagent bottle $\text{NH}_4\text{-1K}$ by the blue dose-metering cap. Hold the reagent bottle upright and, at each dosage, press the slide all the way into the dose-metering cap. Before each dosage ensure that the slide is completely retracted.

Reclose the reagent bottle with the black screw cap at the end of the measurement series, since the function of the reagent is impaired by the absorption of atmospheric moisture.

- Analyze immediately after sampling.
- The pH must be within the range 4 - 13. Adjust, if necessary, with sodium hydroxide solution or sulfuric acid.
- Filter turbid samples.

7. Procedure

	1.14558	1.14544	1.14559
Pipette into a reaction cell (20 ± 30 °C), close the cell, and mix.	1.0 ml	0.50 ml	0.10 ml
Reagent $\text{NH}_4\text{-1K}$	1 dose	1 dose	1 dose
Add, close the cell lightly, and shake vigorously until the reagent is completely dissolved.			
Leave to stand for 15 min (reaction time), then measure the sample in the photometer.			

Notes on the measurement:

- For photometric measurement the cells must be clean. Wipe, if necessary, with a clean dry cloth.
- Measurement of turbid solutions yields false-high readings.
- Ammonium-free samples turn yellow on addition of reagent $\text{NH}_4\text{-1K}$.
- The pH of the measurement solution must be within the range 11.5 - 11.8.
- The colour of the measurement solution remains stable for at least 60 min after the end of the reaction time stated above.
- In the event of ammonium concentrations exceeding 500 mg/l (Cat. No. 1.14558.0001), 1000 mg/l (Cat. No. 1.14544.0001), or 5000 mg/l (Cat. No. 1.14559.0001), other reaction products are formed and false-low readings are yielded. In such cases it is advisable to conduct a plausibility check of the measurement results by diluting the sample (1:10, 1:100).

8. Analytical quality assurance

The measurement results can be officially recognized under the precondition that analytical quality assurance measures are taken (ATV A 704). The Spectroquant® CombiCheck products given below can be used for this purpose. Each contains a standard solution for checking the photometric measurement system (test reagents, measurement device, handling) and the mode of working and also an addition solution for determining sample-dependent interferences (matrix effects). The appropriate CombiCheck product can be found in the following table:

Ammonium Cell Test Cat. No.	CombiCheck Cat. No.	Standard solution $\text{mg/l NH}_4\text{-N}$
1.14558.0001	1.14676.0001, CombiCheck 10	4.00
1.14544.0001	1.14675.0001, CombiCheck 20	12.0
1.14559.0001	1.14689.0001, CombiCheck 70	50.0

Characteristic quality data:

In the production control, the following data were determined in accordance with ISO 8486-1 and DIN 38402 A51:

	1.14558	1.14544	1.14559
Standard deviation of the procedure ($\text{mg/l NH}_4\text{-N}$)	± 0.043	± 0.15	± 0.49
Coefficient of variation of the procedure (%)	± 1.1	± 1.5	± 1.2
Confidence interval ($\text{mg/l NH}_4\text{-N}$)	± 0.10	± 0.3	± 1.2
Number of lots	23	19	23

Characteristic data of the procedure:

	1.14558	1.14544	1.14559
Sensitivity: Absorbance 0.010 A corresponds to ($\text{mg/l NH}_4\text{-N}$)	0.01	0.1	0.4
Accuracy of a measurement value ($\text{mg/l NH}_4\text{-N}$)	max. ± 0.20	max. ± 0.6	max. ± 2.0

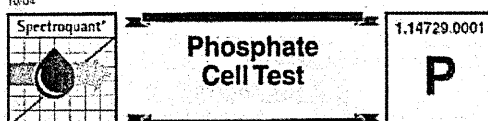
For quality and batch certificates for Spectroquant® test kits see the website.

9. Notes

- Reclose the reagent bottle immediately after use.
- Rinse glassware ammonium-free with distilled water. Do not use detergent!
- For information on disposal/return for disposal please contact your local Merck organization or Merck dealer.

Merck KGaA, 64271 Darmstadt, Germany, Tel. +49(0)6151 720, Fax +49(0)6151 722000, environmental analysis@merck.de <http://photometry.merck.de>

10/04



for the determination of orthophosphate and total phosphorus
USEPA approved for drinking water and wastewater

1. Method

In sulfuric solution orthophosphate ions react with molybdate ions to form molybdophosphoric acid. Ascorbic acid reduces this to phosphomolybdenum blue (PMB) that is determined photometrically.
The method is analogous to EPA 365.2+3, US Standard Methods 4500-P E, and ISO 6878.

2. Measuring range and number of determinations

Measuring range	Number of determinations
0.5 - 25.0 mg/l PO ₄ -P	25
1.5 - 76.7 mg/l PO ₄ -P	
1.1 - 57.3 mg/l P ₂ O ₅	

For programming data for selected photometers / spectrophotometers see the website.

3. Applications

This test measures only orthophosphate. Samples must be decomposed by digestion before total phosphorus can be measured (see section 6).

Sample material:

Groundwater and surface water, seawater
Drinking water
Wastewater
Nutrient solutions for fertilization
Soils after appropriate sample pretreatment
Food after appropriate sample pretreatment

4. Influence of foreign substances

This was checked in solutions containing 15 and 0 mg/l PO₄-P. The concentrations of foreign substances given in the table lie below the limit at which the determination is interfered with.

Concentrations of foreign substances in mg/l or %					
Ag ⁺	1000	F ⁻	250	Pb ²⁺	100
AsO ₄ ³⁻	1.0	Fe ³⁺	1000	Si ⁴⁺	10
Ca ²⁺	1000	H ₂ O ₂	50	SiO ₂	1000
Co ²⁺	1000	Mg ²⁺	1000	SO ₄ ²⁻	1000
Cu ²⁺	1000	Mn ²⁺	1000	Na-acetate	5 %
Cr ³⁺	1000	NH ₄ ⁺	1000	NaCl	20 %
Cr ₂ O ₇ ²⁻	25	Ni ²⁺	1000	NaNO ₂	10 %
Cu ⁺	1000	NO ₃ ⁻	1000	Na ₂ SO ₄	10 %

Reducing agents interfere with the determination.

¹⁾ Tested with nonionic, cationic, and anionic surfactants.

! A higher COD may impair the efficacy of the digesting mixture in the determination of total phosphorus and thus result in false-low readings. Up to a maximum of 1500 mg/l COD, this can be avoided by adding 2 doses of reagent P-1K instead of 1.

5. Reagents and auxiliaries

Please note the warnings on the packaging materials!

The reagents in the test are stable up to the date stated on the pack when stored closed at +15 to +25 °C.

Package contents:

1 bottle of reagent P-1K
1 bottle of reagent P-2K
1 bottle of reagent P-3K
25 reaction cells
1 cell with blank (white screw cap); required only when using the SQ 118 photometer
1 green dose-metering cap
1 blue dose-metering cap
1 sheet of round stickers for numbering the cells

Other reagents and accessories:

Merckquant[®] Phosphate Test, Cat. No. 1.10428.0001, measuring range 10 - 500 mg/l PO₄-P
Universal indicator strips pH 0 - 14, Cat. No. 1.09535.0001
Sulfuric acid 0.5 mol/l, Cat. No. 1.09072
Spectroquant[®] CombiCheck 20, Cat. No. 1.14675.0001

Pipette for a pipetting volume of 1.0 ml
Thermoreactor

6. Preparation

At the first use replace the black screw caps of the reagent bottles P-1K and P-3K by the corresponding dose-metering caps:

Reagent P-1K: green dose-metering cap
Reagent P-3K: blue dose-metering cap

Hold the respective reagent bottle upright and, at each dosage, press the slide all the way into the dose-metering cap. Before each dosage ensure that the slide is completely retracted.

! Reclose the reagent bottles with the black screw caps at the end of the measurement series, since the function of the reagents is impaired by the absorption of atmospheric moisture.

- Analyze immediately after sampling.

- Digestion for the determination of total phosphorus (Wear eye protection!):

Pretreated sample	1.0 ml	Pipette into a reaction cell.
Reagent P-1K	1 dose ¹⁾	Add, close the cell tightly, and mix.

Heat the cell at 120 °C²⁾ in the preheated thermoreactor for 30 min. Allow the closed cell to cool to room temperature in a test-tube rack. Do not cool with cold water!

¹⁾ In the case of high COD values: 2 doses

²⁾ A digestion temperature of 100 °C may result in false-low readings (e.g. in the case of polyphosphates).

- Check the phosphate content with the Merckquant[®] PhosphateTest. Samples containing more than 76.7 mg/l PO₄-P must be diluted with distilled water prior to digestion.
- The pH must be within the range 0 - 10. Adjust, if necessary, with sulfuric acid.
- Filter turbid samples.

7. Procedure

Pretreated sample (10 - 35 °C)	1.0 ml	Pipette into a reaction cell and mix or - after digestion for total phosphorus - shake the tightly closed cell vigorously after cooling.
Reagent P-2K ¹⁾	5 drops	Add, close the cell tightly, and mix.
Reagent P-3K ¹⁾	1 dose	Add, close the cell tightly, and shake vigorously until the reagent is completely dissolved.

Leave to stand for 5 min (reaction time), then measure the sample in the photometer.

¹⁾ In the case of high chloride contents, it is recommended to switch the sequence of the reagents P-2K and P-3K.

Notes on the measurement:

- For photometric measurement the cells must be clean. Wipe, if necessary, with a clean dry cloth.
- Measurement of turbid solutions yields false-high readings.
- The pH of the measurement solution must be within the range 0.60 - 0.95.
- The colour of the measurement solution remains stable for at least 60 min after the end of the reaction time stated above.

8. Analytical quality assurance

The measurement results can be officially recognized under the precondition that analytical quality-assurance measures are taken (ATV A 704).

Spectroquant[®] CombiCheck 20 can be used for this purpose.

This article contains a standard solution with 8.0 mg/l PO₄-P for checking the photometric measurement system (test reagents, measurement device, handling) and the mode of working and also an addition solution for determining sample-dependent interferences (matrix effects).

Characteristic quality data:

In the production control, the following data were determined in accordance with ISO 8466-1 and DIN 38402 A51.

Standard deviation of the procedure (mg/l PO ₄ -P)	± 0.15
Coefficient of variation of the procedure (%)	± 1.2
Confidence interval (mg/l PO ₄ -P)	± 0.4
Number of lots	25

Characteristic data of the procedure:

Sensitivity: Absorbance 0.010 A corresponds to (mg/l PO ₄ -P)	0.08
Accuracy of a measurement value	max. ± 0.5

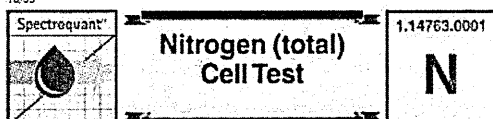
For quality and batch certificates for Spectroquant[®] test kits see the website.

9. Notes

- Reclose the reagent bottles immediately after use.
- Use only phosphate-free detergents to clean glassware. Otherwise fill with hydrochloric acid (approx. 10 %) and leave to stand for several hours.
- For information on disposal/return for disposal please contact your local Merck organization or Merck dealer.

Merck KGaA, 64271 Darmstadt, Germany. Tel. +49(0)6151 720, Fax +49(0)6151 722000.
environmental.analysis@merck.de <http://photometry.merck.de>

10/05



1. Method

Organic and inorganic nitrogen compounds are transformed into nitrate according to Koroleff's method by treatment with an oxidizing agent in a thermoreactor. In a solution acidified with sulfuric and phosphoric acid, this nitrate reacts with 2,6-dimethylphenol (DMP) to form 4-nitro-2,6-dimethylphenol that is determined photometrically.

The digestion is analogous to EN ISO 11905-1.

The determination of nitrate is analogous to ISO 7890-1.

2. Measuring range and number of determinations

Measuring range	Number of determinations
10 - 150 mg/l N	25

For programming data for selected photometers / spectrophotometers see the website.

3. Applications

Sample material:
Groundwater, drinking water, and surface water
Industrial water
Wastewater
Inflow and outflow of wastewater-treatment plants
Nutrient solutions for fertilization
Soils after appropriate sample pretreatment
This test is **not** suited for seawater.

4. Influence of foreign substances

This was checked in solutions containing 75 and 0 mg/l N. The concentrations of foreign substances given in the table below the limit at which the determination is interfered with.

Concentrations of foreign substances in mg/l or %					
Al ³⁺	1000	Cu ²⁺	1000	Ni ²⁺	1000
Ca ²⁺	1000	F ⁻	1000	Pb ²⁺	1000
Co ²⁺	1000	Fe ²⁺	1000	PO ₄ ³⁻	1000
Cl ⁻	10 000	Hg ²⁺	1000	SiO ₄ ²⁻	1000
Cr ³⁺	100	Mg ²⁺	1000	Sn ²⁺	1000
Cr ₂ O ₇ ²⁻	100	Mn ²⁺	1000	Zn ²⁺	1000
				Surfactants ¹⁾	500
				CSB (K-hydrogen-phthalate)	3500
				Na ascorbate	10 %
				NaCl	2 %
				Na ₂ SO ₄	10 %

¹⁾ Tested with anionic, cationic, and amphoteric surfactants.

⚠ When the quantity of reagent N-1K is doubled, the tolerable COD increases to 7000 mg/l. In the event of higher COD values false-low results are obtained.

5. Reagents and auxiliaries

Please note the warnings on the packaging materials!

The test reagents are stable up to the date stated on the pack when stored closed at +15 to +25 °C.

Package contents:

1 bottle of reagent N-1K
1 bottle of reagent N-2K
1 bottle of reagent N-3K
25 reaction cells
1 cell with blank (white screw cap): **required only when using the SQ 118 photometer**
1 sheet of round stickers for numbering the cells

Other reagents and accessories:

Spectroquant[®] COD Cell Test, Cat. No. 1.14555.0001, measuring range 500 - 10 000 mg/l
Spectroquant[®] CombiCheck 70, Cat. No. 1.14669.0001
Merckoquant[®] Peroxide Test, Cat. No. 1.10011.0001, measuring range 0.5 - 25 mg/l H₂O₂
Water for on-line analysis, Cat. No. 1.01051.5000
Sodium sulfite anhydrous GR for analysis, Cat. No. 1.06657
Empty cells 16 mm with screw caps (25 pcs), Cat. No. 1.14724.0001
Pipettes for pipetting volumes of 1.0 and 9.0 ml
Thermoreactor²⁾

6. Preparation

- Analyze immediately after sampling.
- Check, where necessary, the COD with the Spectroquant[®] COD Cell Test. In the event of COD values of more than 7000 mg/l, the sample must be diluted with distilled water.

7. Procedure

Digestion:

Pretreated sample	1.0 ml	Pipette into an empty cell.
Distilled water ³⁾	9.0 ml	Add and mix.
Reagent N-1K ⁴⁾	1 level blue microspoon (in the cap of the N-1K bottle)	Add and mix.
Reagent N-2K	6 drops	Add, close the cell tightly, and mix.

Heat the cell at 120 °C in the preheated thermoreactor for 1 hour.
Allow the closed cell to cool to room temperature in a test tube rack.
Do not cool with cold water!
Shake the cell briefly after 10 min. (Turbidity or precipitation frequently occurs in the digestion solution.)

³⁾ It is recommended to use water for on-line analysis, Cat. No. 1.01051.5000.

⁴⁾ When using Spectroquant[®] CombiCheck 70, the quantity of reagent N-1K must be doubled in order to maintain the efficacy of the decomposition procedure.

⁵⁾ A digestion temperature of 100 °C may result in false-low readings. Check the samples digested at 100 °C for freedom from peroxide with the Merckoquant[®] Peroxide Test. If necessary, eliminate any peroxide by adding a spatula-tip of sodium ascorbate.

Preparation of measurement sample:

Digested, cooled sample (use clear supernatant or filtrate in the event of turbidity or precipitate)	1.0 ml	Pipette into a reaction cell. Do not mix contents!
Reagent N-3K	1.0 ml	Add with syringe, close the cell tightly, and mix (Wear eye protection! The cell becomes hot!). The cell must be held only by the screw cap!

Leave the hot cell to stand for 10 min (reaction time).
Do not cool with cold water!
Measure the sample in the photometer.

Notes on the measurement:

- For photometric measurement the cells must be clean. Wipe, if necessary, with a clean dry cloth.
- Measurement of turbid solutions yields false-high readings.
- The colour of the measurement solution remains stable for 30 min after the end of the reaction time stated above. (After 60 min the measurement value would have increased by 5 %.)

8. Analytical quality assurance

The measurement results can be officially recognized under the precondition that analytical quality-assurance measures are taken (ATV A 704).

Spectroquant[®] CombiCheck 70 can be used for this purpose. This article contains a **standard solution** with 50 mg/l N for checking the photometric measurement system (test reagents, measurement device, handling) and the mode of working and also an **addition solution** for determining sample-dependent interferences (matrix effects).

Characteristic quality data:

In the production control, the following data were determined in accordance with ISO 8466-1 and DIN 38402 A51:

Standard deviation of the method (mg/l N)	± 1.2
Coefficient of variation of the method (%)	± 1.4
Confidence interval (mg/l N)	± 3
Number of lots	15

Characteristic data of the procedure:

Sensitivity: Absorbance 0.010 A corresponds to (mg/l N)	2
Accuracy of a measurement value (mg/l N)	max. ± 6

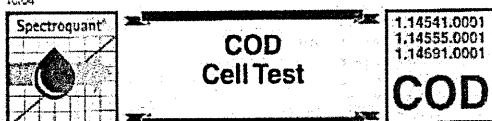
For quality and batch certificates for Spectroquant[®] test kits see the website.

9. Notes

- Reclose the reagent bottles immediately after use.
- For information on disposal/return for disposal please contact your local Merck organization or Merck dealer.

Merck KGaA, 64271 Darmstadt, Germany, Tel. +49(0)6151 720, Fax +49(0)6151 722000, environmental.analyses@merck.de <http://photometry/merck.de>

10/04



USEPA approved for wastewater

1. Definition

The COD (chemical oxygen demand) expresses the amount of oxygen originating from potassium dichromate that reacts with the oxidizable substances contained in 1 l of water under the working conditions of the specified procedure.

1 mol $K_2Cr_2O_7$ is equivalent to 1.5 mol O_2 .
Results are expressed as mg/l COD (= mg/l O_2)

2. Method

The water sample is oxidized with a hot sulfuric solution of potassium dichromate, with silver sulfate as the catalyst. Chloride is masked with mercury sulfate. The concentration of green Cr^{3+} ions is then determined photometrically. The method is analogous to EPA 410.4, US Standard Methods 5220 D, and ISO 15705.

3. Measuring range and number of determinations

Cat. No.	Measuring range mg/l COD	Number of determinations
1.14541.0001	25 - 1600	25
1.14691.0001	300 - 9500	
1.14555.0001	500 - 10 000	

For programming data for selected photometers / spectrophotometers see the website.

4. Applications

This test measures organic and inorganic compounds oxidizable by dichromate. Exceptions: some heterocyclic compounds (e.g. pyridine), quaternary nitrogen compounds, and readily volatile hydrocarbons.

Sample material:
In-process controls
Wastewater

5. Influence of foreign substances

The concentrations of foreign substances given in the table lie below the limit at which the determination is interfered with.

Cat. No.	Cl ⁻	Concentrations of foreign substances in mg/l or %							
		Cr ⁶⁺	CrO ₄ ²⁻	NO ₂ ⁻	SO ₄ ²⁻	H ₂ O ₂	NaNO ₃	Na ₂ SO ₄	Na ₃ PO ₄
1.14541.0001	2000	25	50	50	25	50	10 %	10 %	10 %
1.14691.0001	2500	50	100	50	25	50	20 %	20 %	20 %
1.14555.0001	5000	25	50	50	25	10	10 %	10 %	10 %

6. Reagents and auxiliaries

Please note the warnings on the packaging materials!

Store the pack protected from light!

The reagents in the test are stable up to the date stated on the pack when stored closed at +15 to +25 °C.

Package contents:

25 reaction cells
1 cell with blank (white screw cap); required only when using the SQ 118 photometer
1 sheet of round stickers for numbering the cells

Other reagents and accessories:

Merckoquant® Chloride Test, Cat. No. 1.10079.0001,
measuring range 500 - 3000 mg/l Cl⁻
Spectroquant® CombiCheck 20, Cat. No. 1.14675.0001
Spectroquant® CombiCheck 70, Cat. No. 1.14689.0001
Spectroquant® CombiCheck 80, Cat. No. 1.14738.0001

Pipette for a pipetting volume of 1.0 ml
Pipette for a pipetting volume of 2.0 ml
Pipette for a pipetting volume of 3.0 ml
Thermoreactor

7. Preparation

- Analyze immediately after sampling.
- Homogenize the samples.
- Check the chloride content with the Merckoquant® Chloride Test. Samples containing more chloride than is stated for the respective test kit in section 5 must be diluted with distilled water prior to determining the COD.

8. Procedure

	1.14541.	1.14691.	1.14555.
Suspend the bottom sediment in the reaction cell by swirling			
Pipetted sample	3.0 ml	2.0 ml	1.0 ml
Carefully allow to run from the pipette down the inside of the tilted reaction cell onto the reagent (Wear eye protection! The cell becomes hot!)			
Tightly attach the screw cap to the cell.			
In all subsequent steps the cell must be held only by the screw cap!			
Vigorously mix the contents of the cell.			
Heat the cell at 148 °C in the preheated thermoreactor for 120 min.			
Remove the hot cell from the thermoreactor and allow to cool in a test-tube rack. Do not cool with cold water!			
Wait 10 min, invert the cell, and return to the rack for complete cooling to room temperature (cooling time at least 30 min).			
Measure the sample in the photometer.			

Notes on the measurement:

- For photometric measurement the cells must be clean. Wipe, if necessary, with a clean dry cloth.
- Measurement of turbid solutions yields false-high readings.
- The measurement value remains stable over a long term.

9. Analytical quality assurance

The measurement results can be officially recognized under the precondition that analytical quality-assurance measures are taken (ATV A 704). The Spectroquant® CombiCheck products given below can be used for this purpose. Each contains a standard solution for checking the photometric measurement system (test reagents, measurement device, handling) and the mode of working and also an addition solution for determining sample-dependent interferences (matrix effects). The appropriate CombiCheck product can be found in the following table:

COD Cell Test Cat. No.	CombiCheck Cat. No.	Standard solution mg/l COD
1.14541.0001	1.14675.0001, CombiCheck 20	750
1.14691.0001	1.14738.0001, CombiCheck 80	1500
1.14555.0001	1.14689.0001, CombiCheck 70	5000

Characteristic quality data:

In the production control, the following data were determined in accordance with ISO 6456-1 and DIN 38402 A51:

	1.14541.	1.14691.	1.14555.
Standard deviation of the procedure (mg/l COD)	± 5.6	± 18.1	± 85.2
Coefficient of variation of the procedure (%)	± 0.73	± 1.01	± 0.65
Confidence interval (mg/l COD)	± 14	± 33	± 80
Number of lots	30	30	23

Characteristic data of the procedure:

	1.14541.	1.14691.	1.14555.
Sensitivity: Absorbance 0.010 A corresponds to (mg/l COD)	17	32	47
Accuracy of a measurement value (mg/l COD)	max. ± 30	max. ± 75	max. ± 130

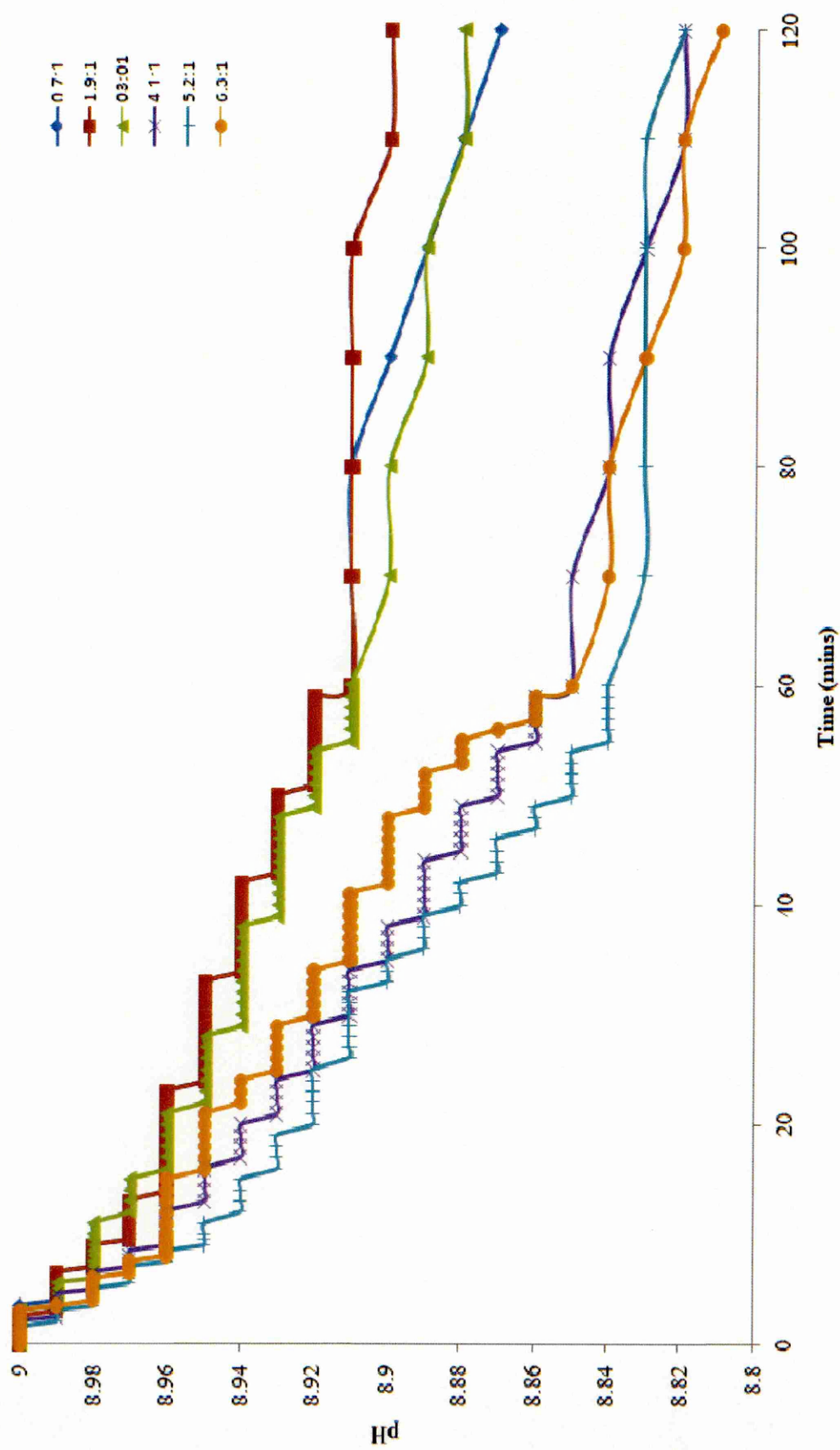
For quality and batch certificates for Spectroquant® test kits see the website.

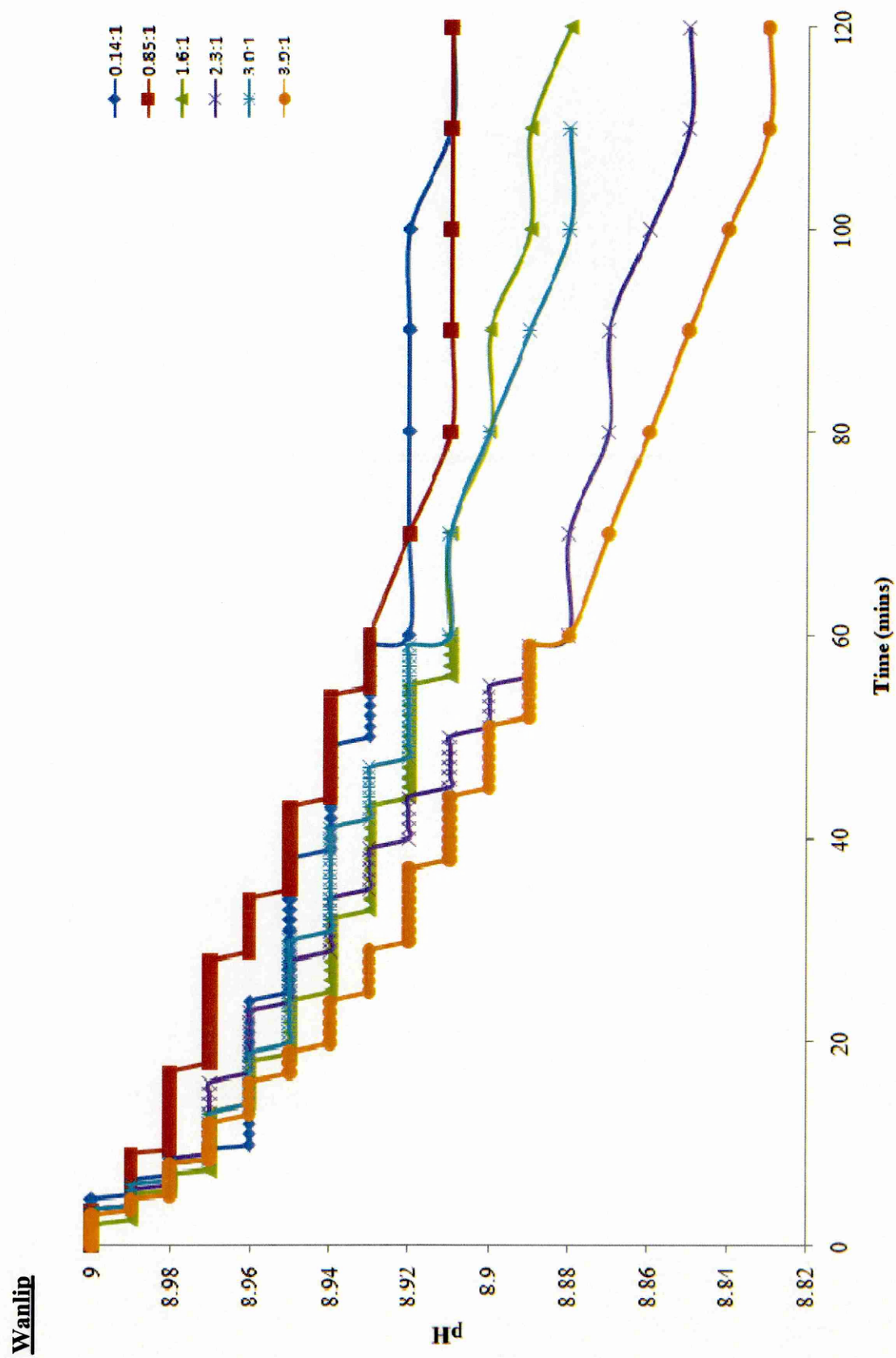
10. Note

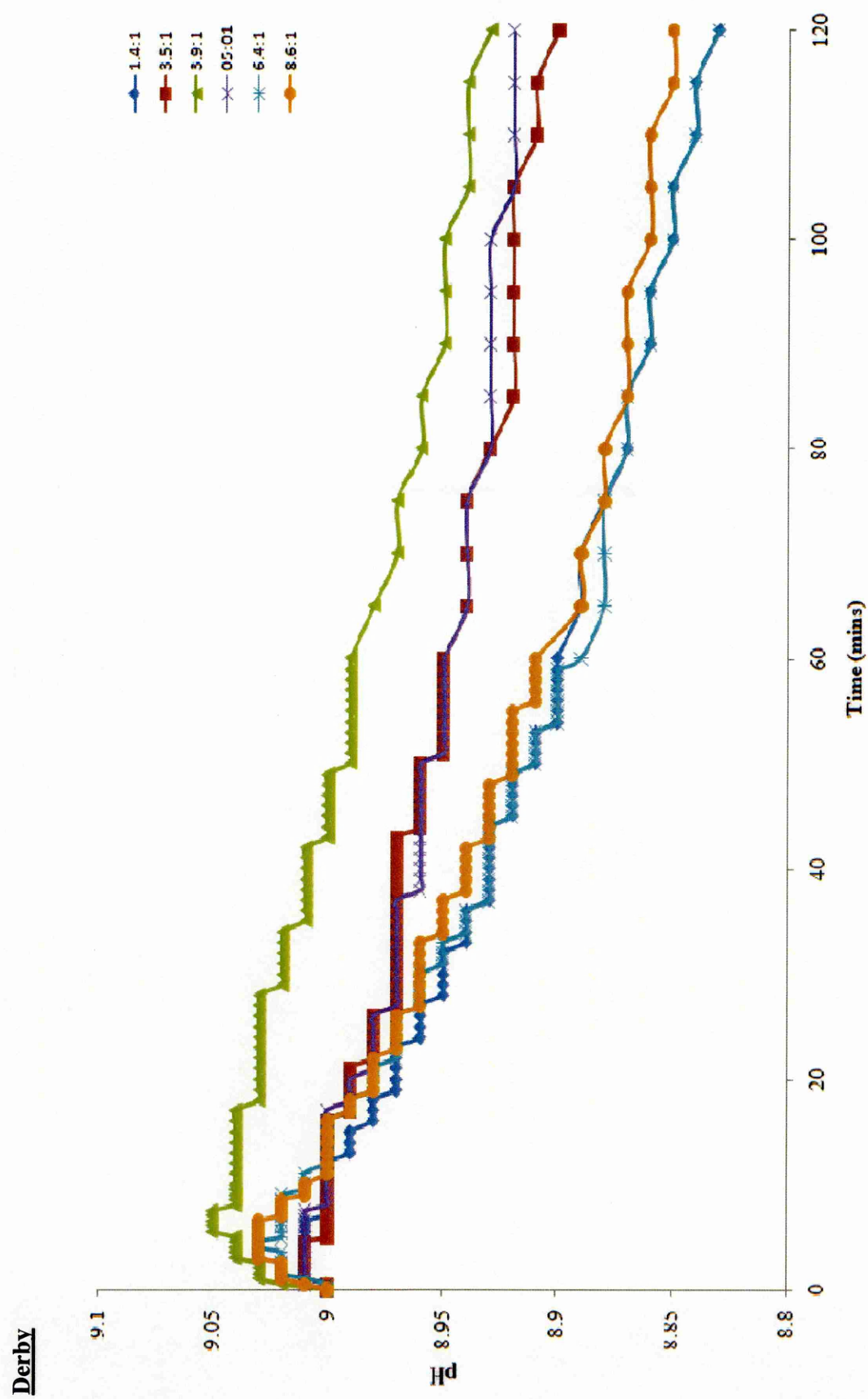
The test reagents must not be run off with the wastewater!
For information on disposal/return for disposal please contact your local Merck organization or Merck dealer.

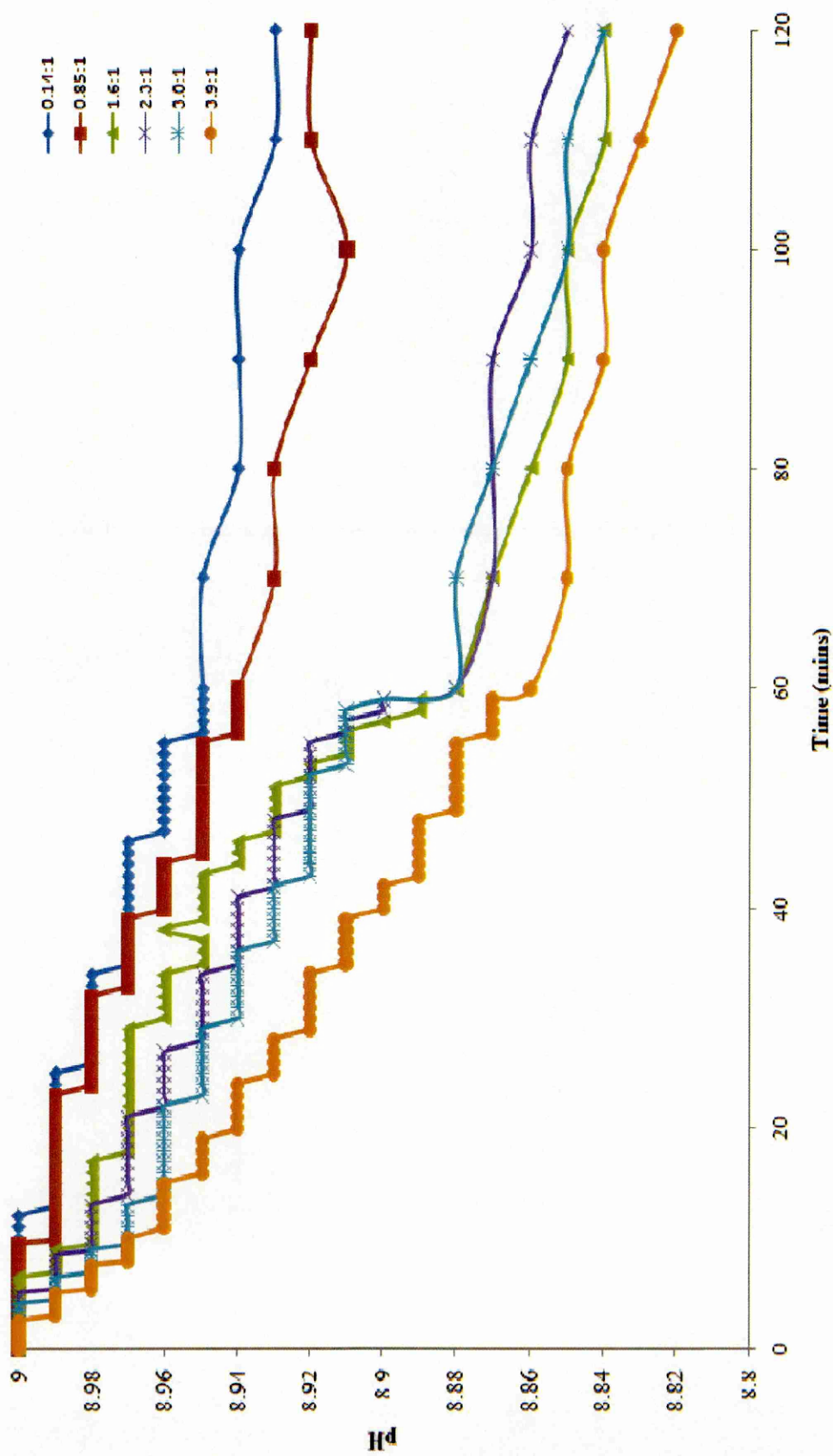
Appendix 2

pH change data for the jar tester precipitation tests

Stoke Bardolph

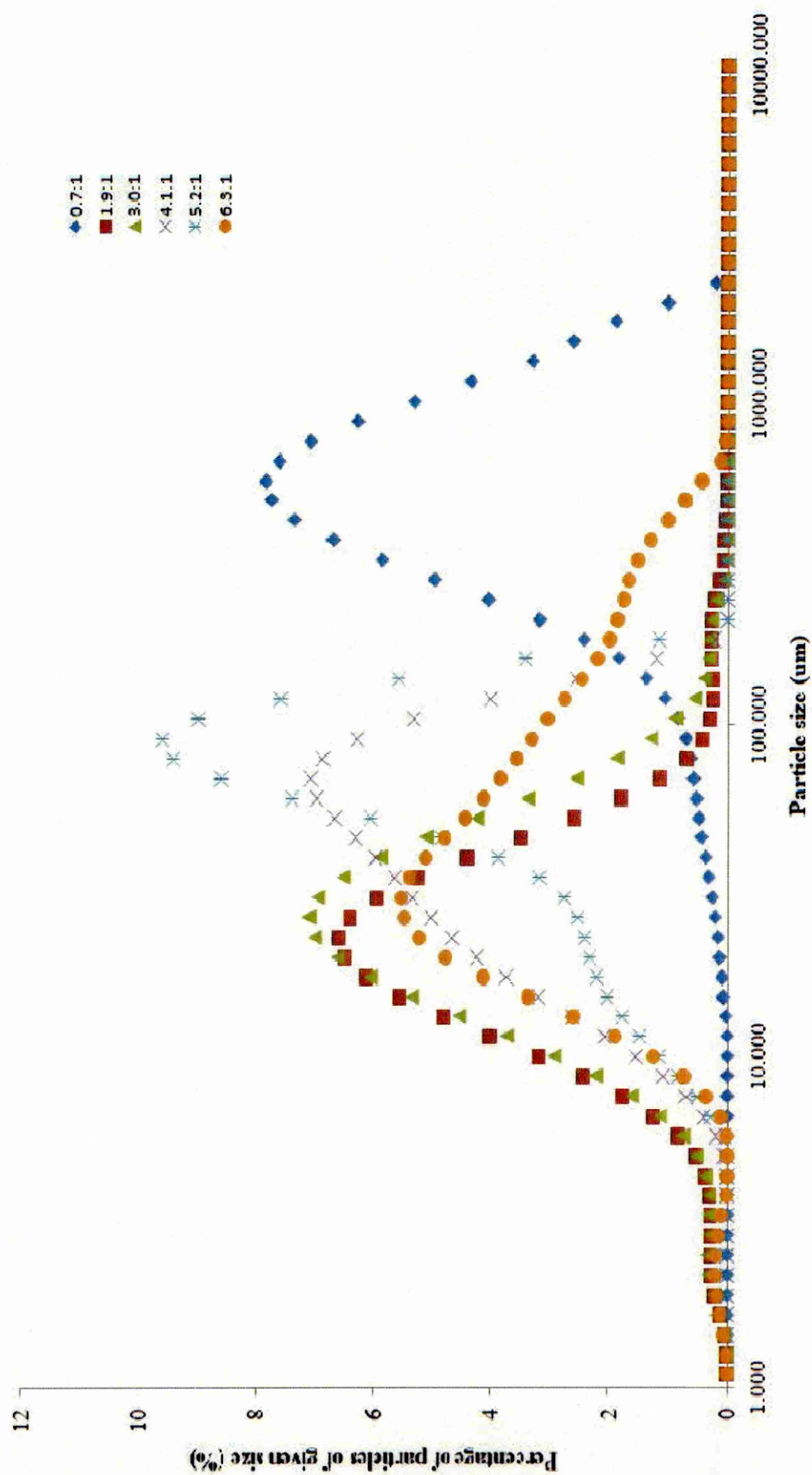


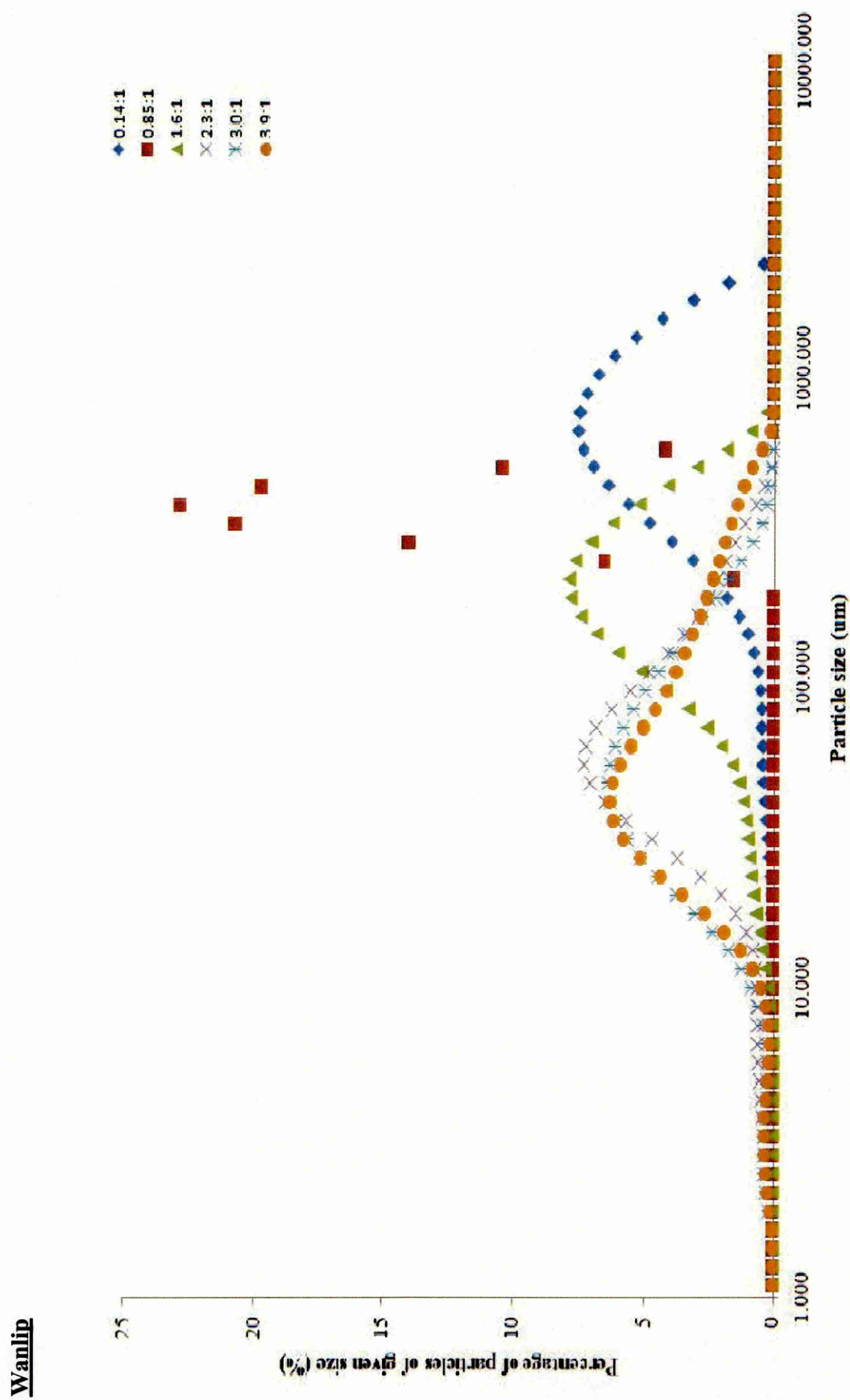


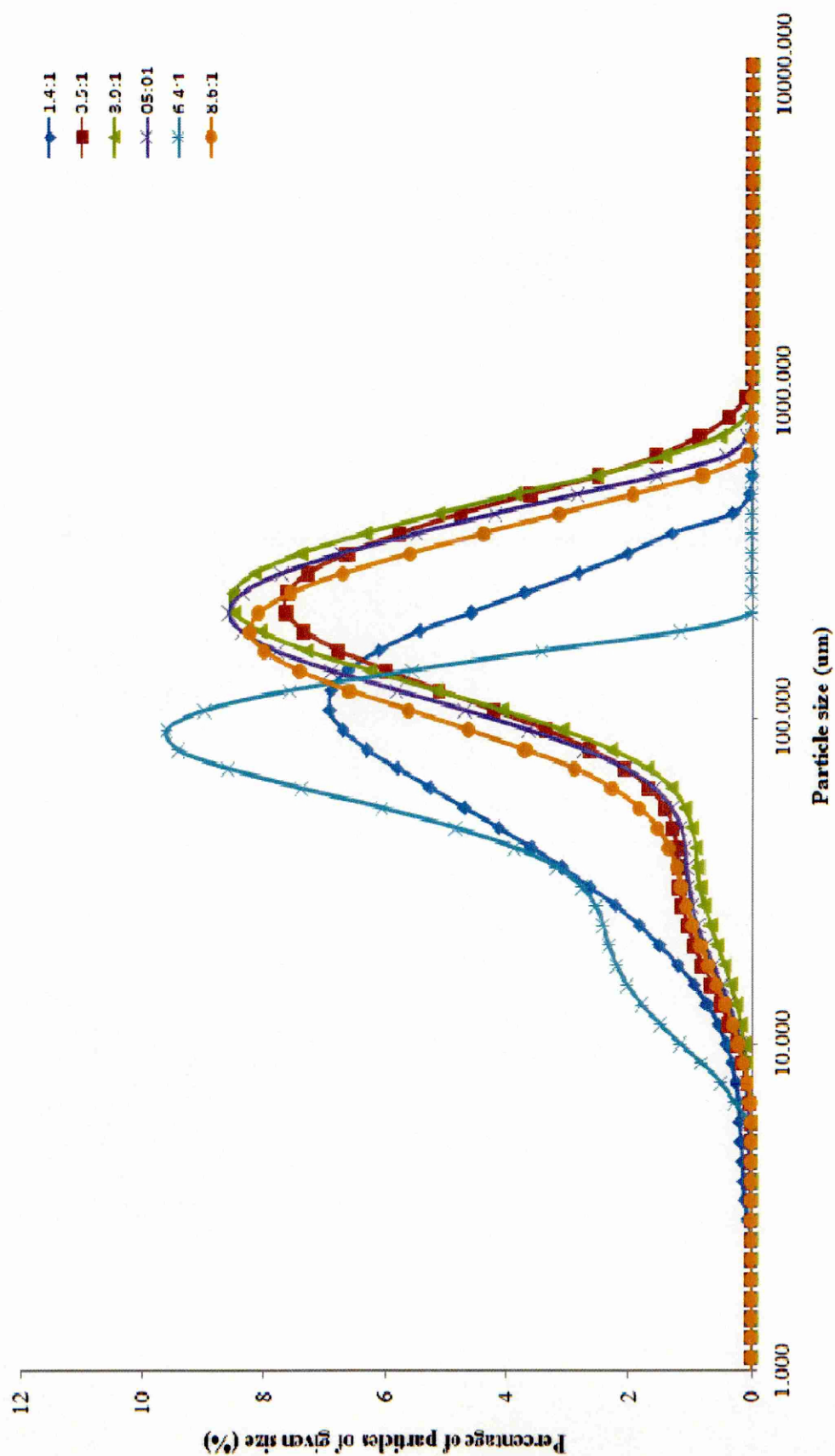
Coleshill

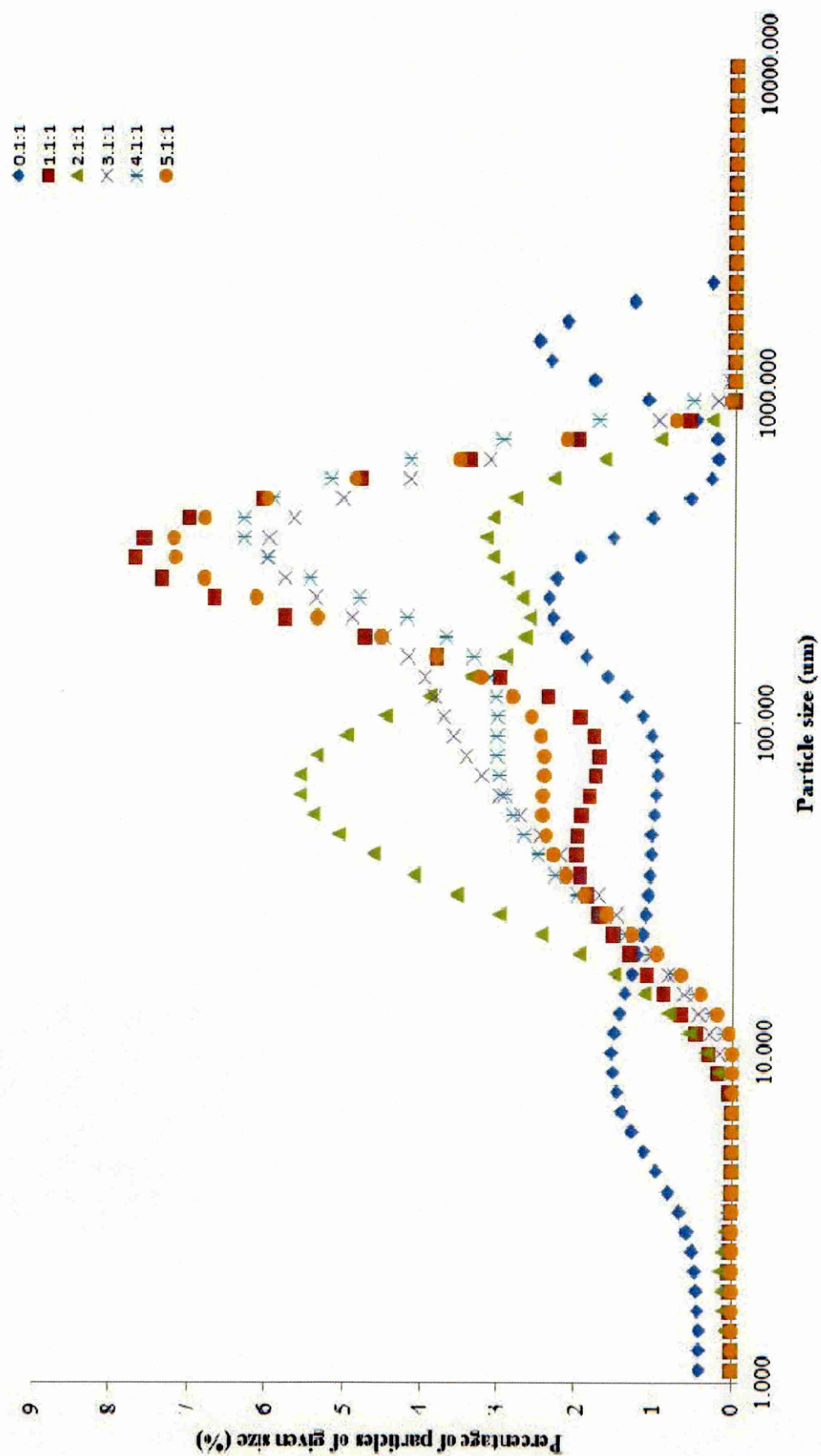
Appendix 3

Particle size analysis of the precipitate produced in for each site during the jar tester experiments

Stoke Bardolph



Derby

Coleshill

Appendix 4

EDS analysis of the precipitate collected from Coleshill STW

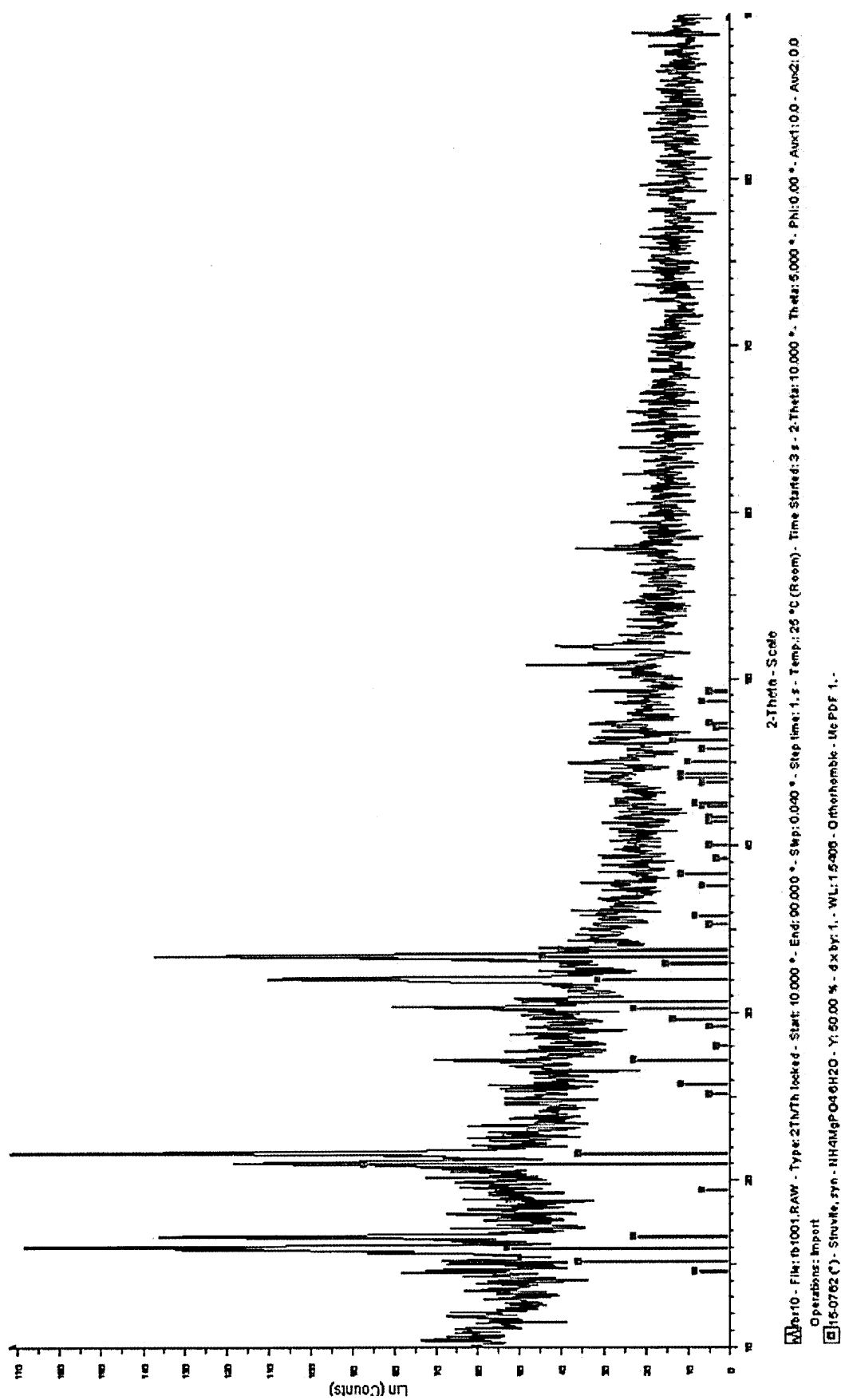
EDX analysis of Coleshill precipitate

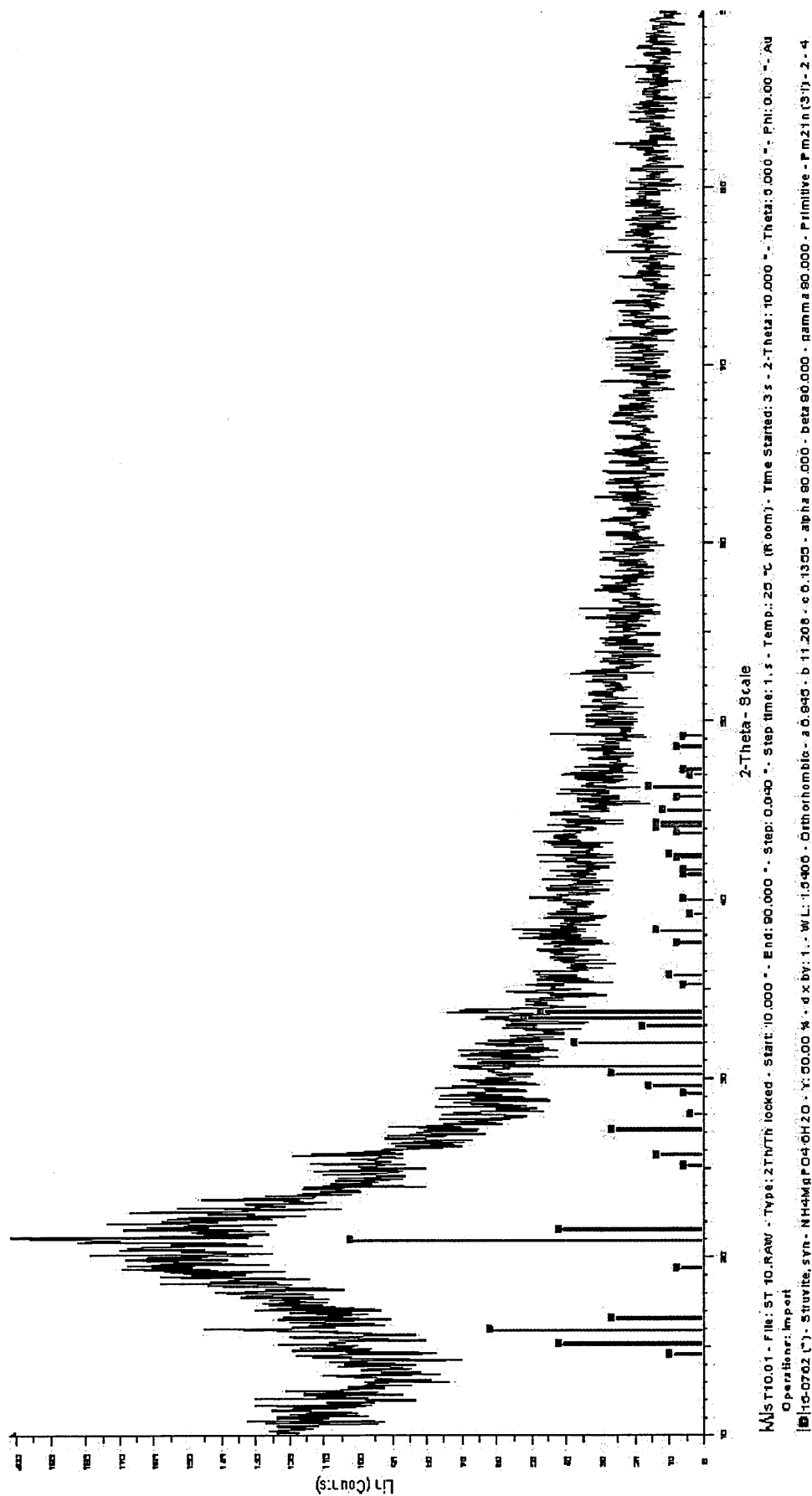
Ratio 0.1:1	Ratio 1.1:1	Ratio 2.1:1	Ratio 3.1:1	Ratio 4.1:1	Ratio 5.1:1
Element	Element	Element	Element	Element	Element
Weight%	Weight%	Weight%	Weight%	Weight%	Weight%
CK	CK	CK	CK	CK	CK
15.07	15.59	0	9.90	9.61	14.01
NK	NK	NK	NK	NK	NK
9.99	3.65	5.31	5.99	6.50	4.86
OK	OK	OK	OK	OK	OK
34.90	41.00	42.97	52.22	48.27	39.00
Mg K	Mg K	Mg K	Mg K	Mg K	Mg K
10.59	13.61	19.33	13.84	13.61	14.68
P K	P K	P K	P K	P K	P K
21.17	21.09	30.38	17.06	19.92	26.31
Ca K	Ca K	Ca K	K K	Cl K	K K
8.27	5.06	2.01	0.18	0.52	0.39
			Ca K	Ca K	Ca K
			0.81	1.57	0.74
Totals	Totals	Totals	Totals	Totals	Totals
100.00	100.00	100.00	100.00	100.00	100.00

Appendix 5

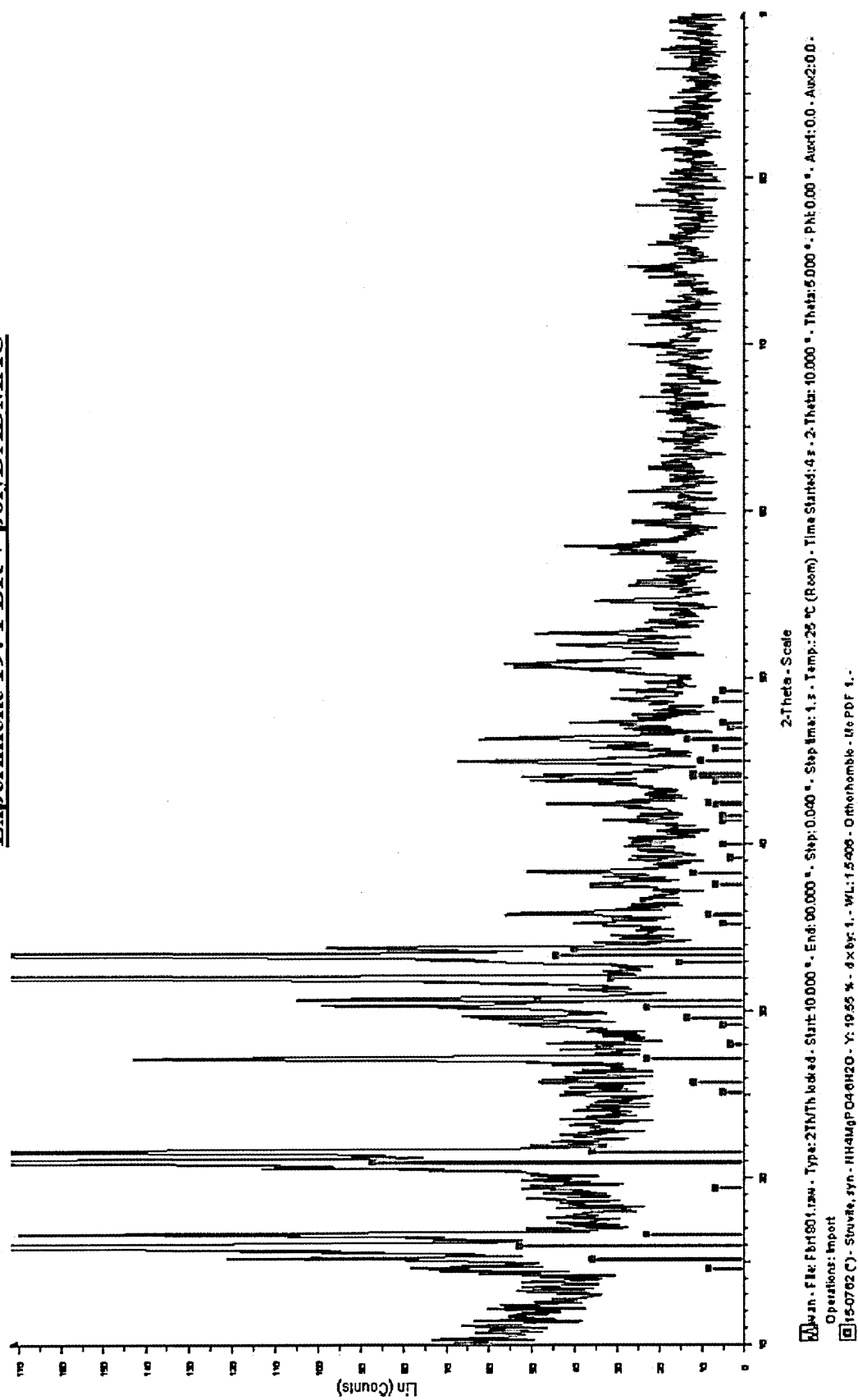
XRD data from experiments 18-20

Experiment 18: FBR precipitate

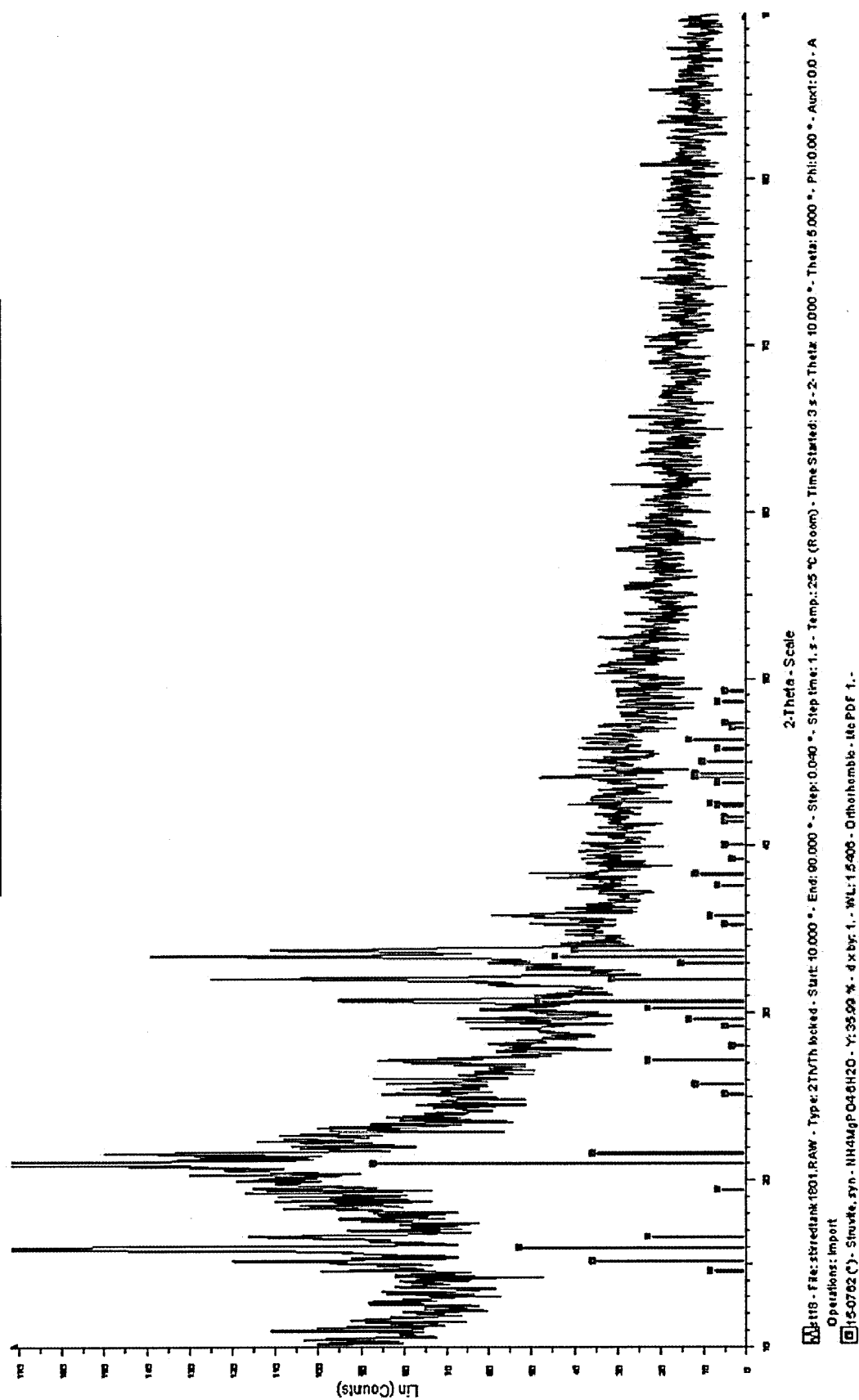


Experiment 18: Stirred tank reactor solids

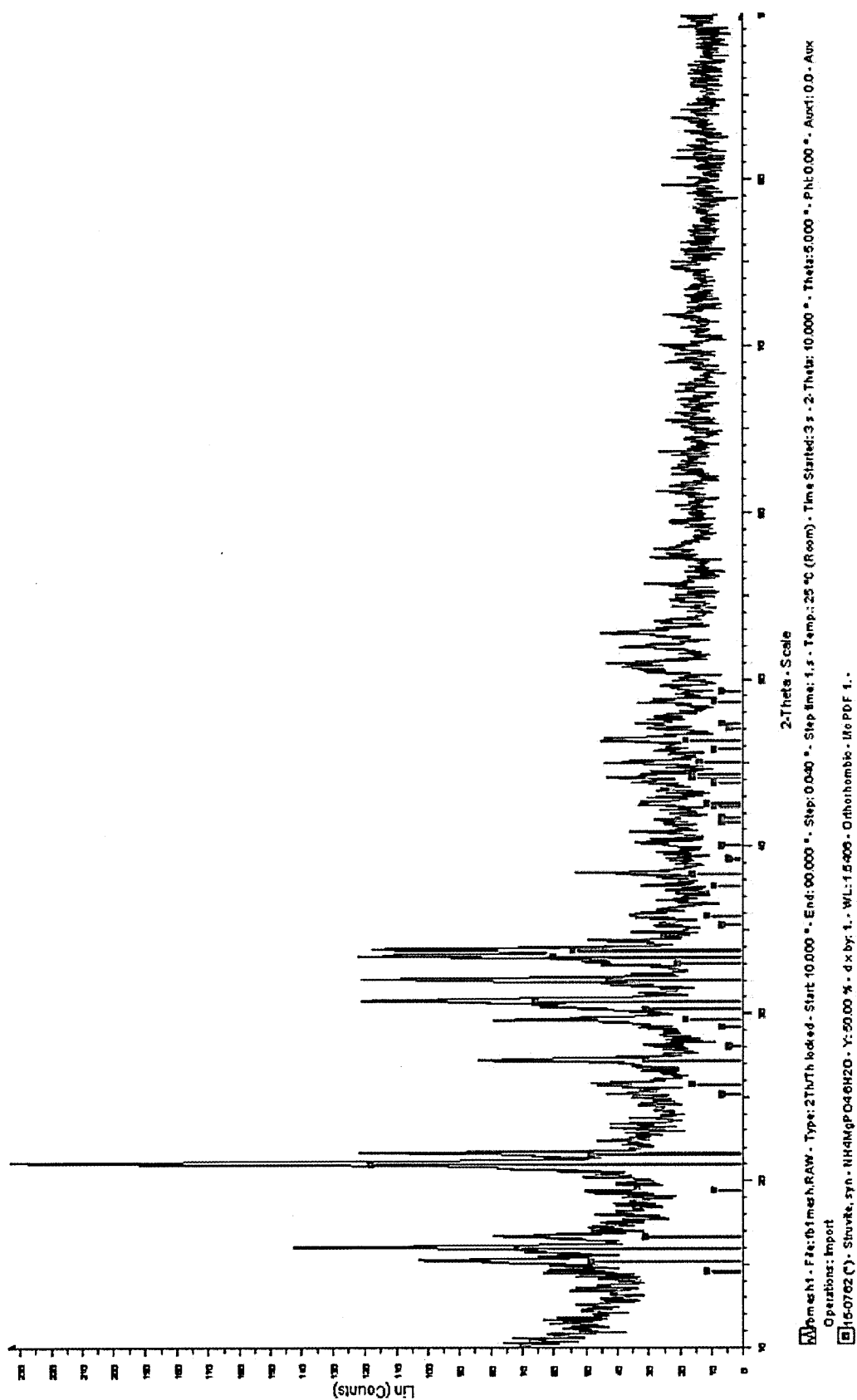
Experiment 19: FBR + polyDADMAC



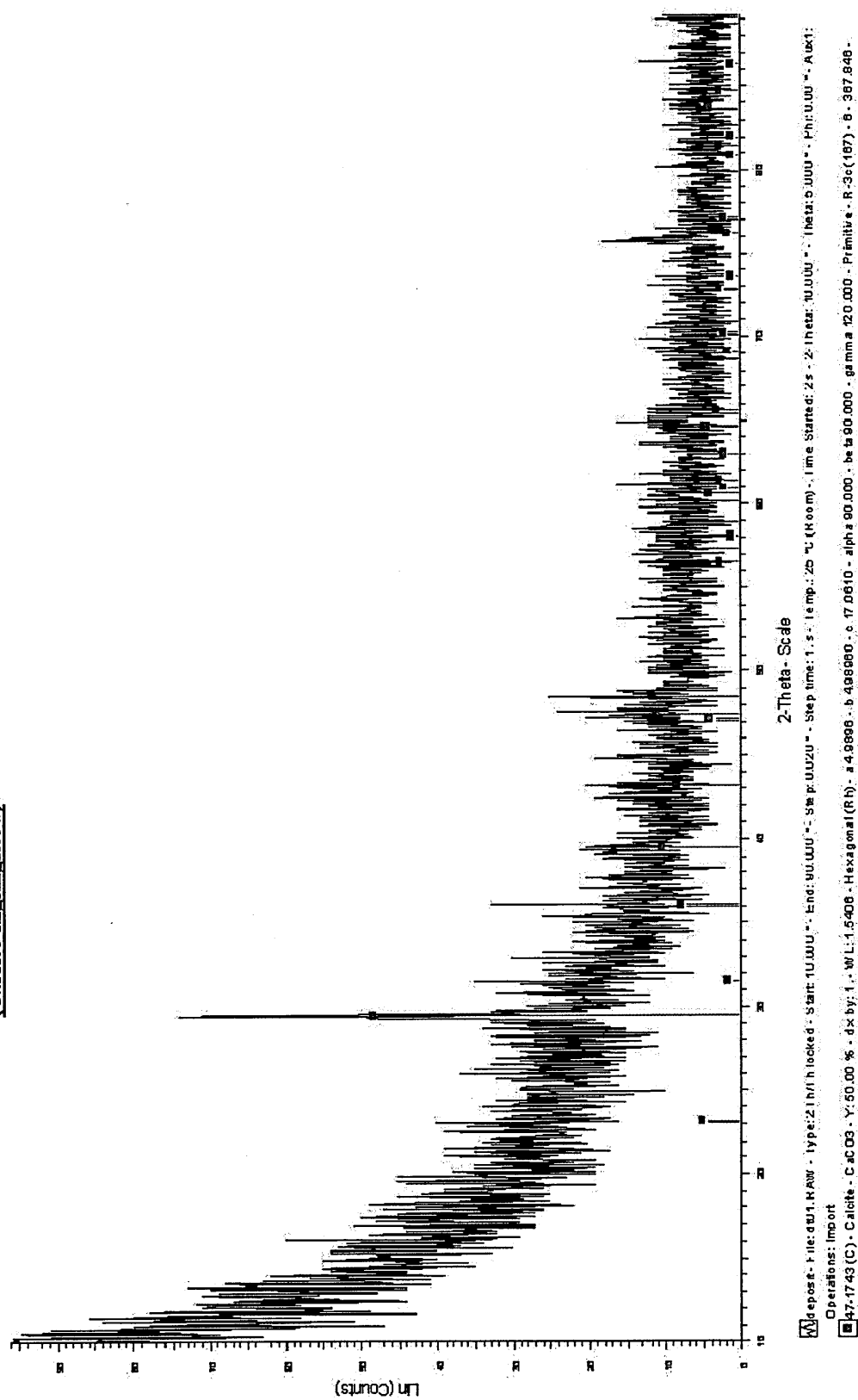
Experiment 19: Stirred tank + polyDADMAC



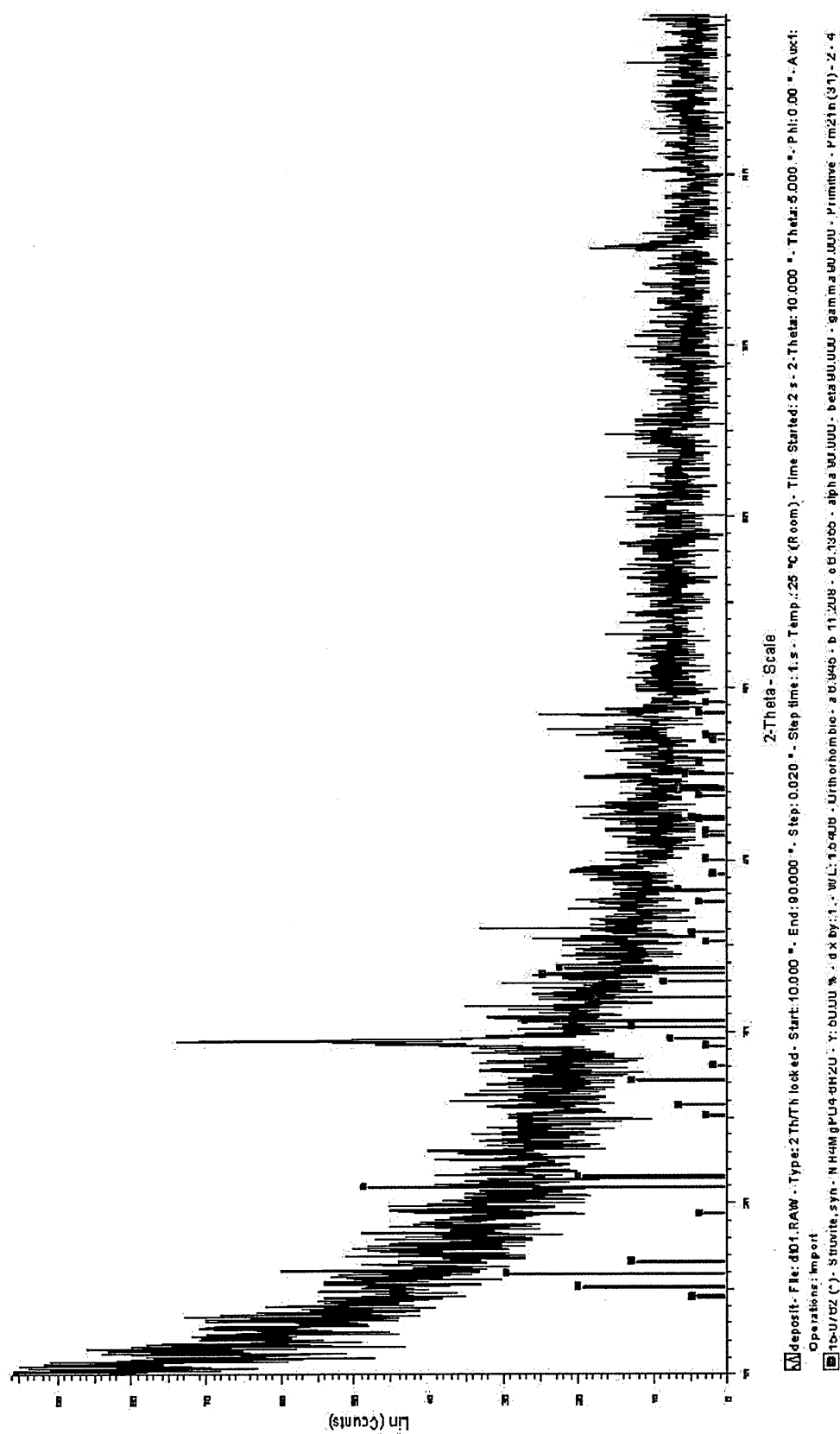
Experiment 20: FBR + Metallic Mesh



Experiment 20: Stirred tank + polyDADMAC
(calcite highlighted)



Experiment 20: Stirred tank + polyDADMAC
(struvite highlighted)



Appendix 6

SEM and EDS data

08/02/2007 12:35:20

Experiment 18: Stirred tank, Data 1

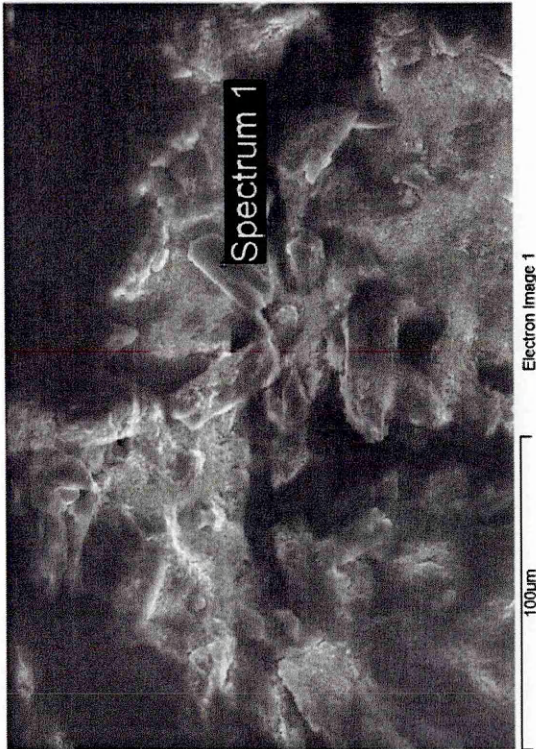
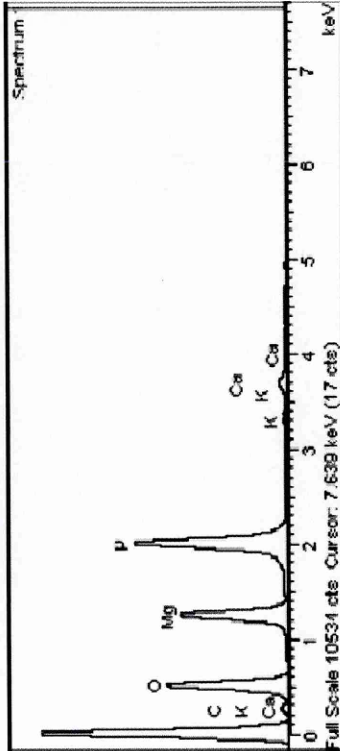
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :

- C CaCO3 1-Jun-1999 12:00 AM
- O SiO2 1-Jun-1999 12:00 AM
- Mg MgO 1-Jun-1999 12:00 AM
- P GaP 1-Jun-1999 12:00 AM
- K MAD-10 Feldspar 1-Jun-1999 12:00 AM
- Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	13.60	20.10
O K	53.02	58.82
Mg K	13.38	9.77
P K	18.88	10.82
K K	0.12	0.05
Ca K	0.99	0.44
Totals	100.00	



08/02/2007 12:36:23

Experiment 18: Stirred tank, data 2

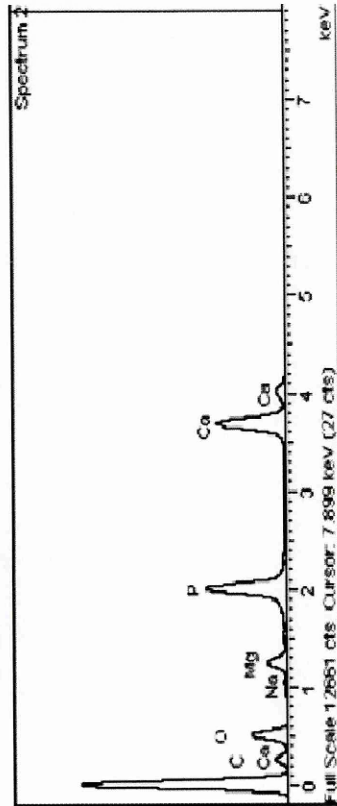
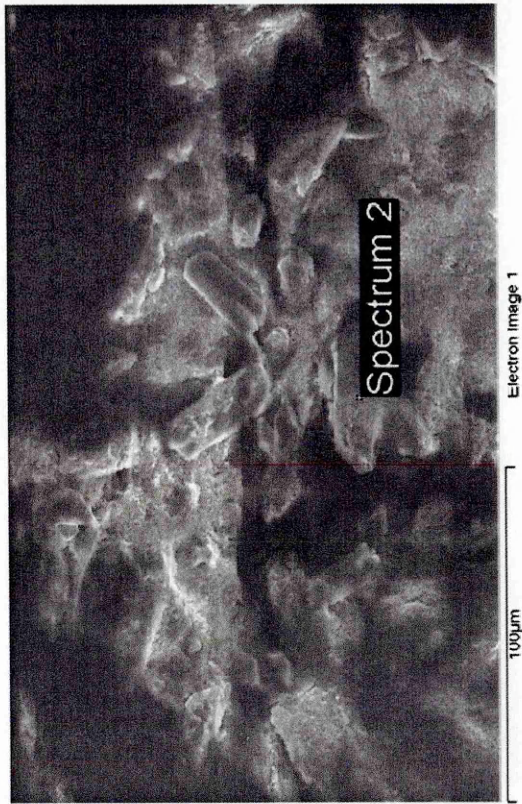
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :

C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	19.43	29.63
O K	44.27	50.69
Na K	0.39	0.31
Mg K	3.83	2.89
P K	14.00	8.28
Ca K	17.60	8.04
Fe K	0.49	0.16
Totals	100.00	



Experiment 19: FBR + polyDADMAC

08/02/2007 12:04:29

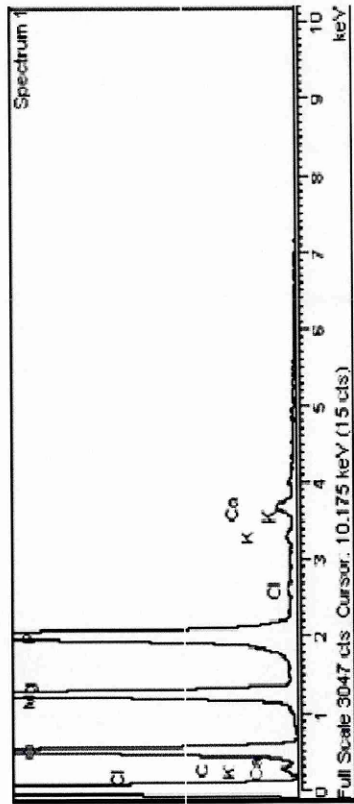
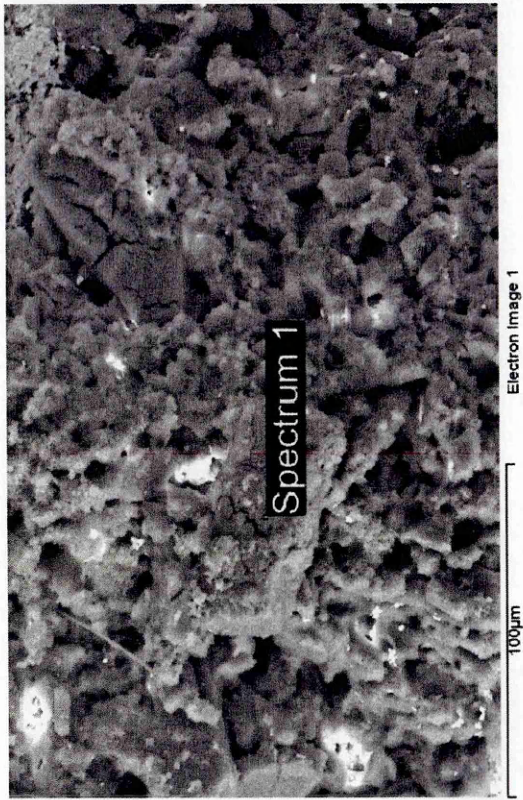
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
Cl KCl 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	15.06	22.43
O K	49.24	55.04
Mg K	13.25	9.75
P K	20.96	12.10
Cl K	0.19	0.10
K K	0.29	0.13
Ca K	1.01	0.45
Totals	100.00	



Experiment 19: Stirred tank + polyDADMAC

08/02/2007 12:33:51

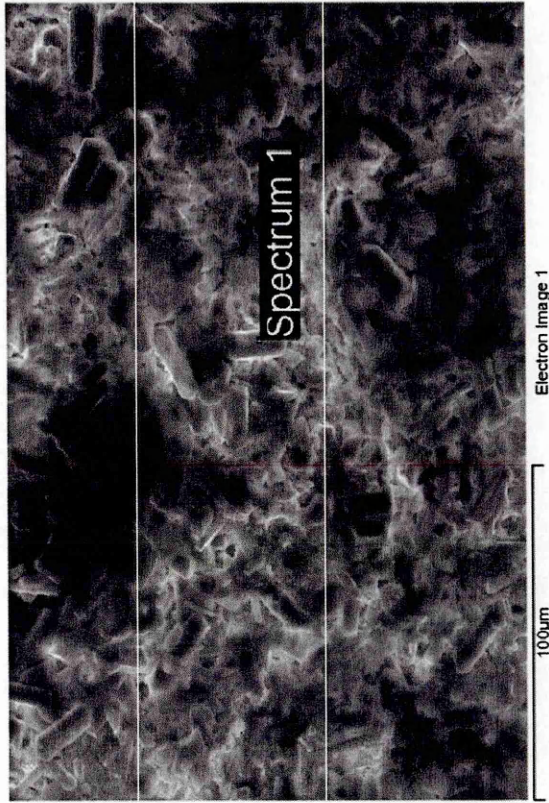
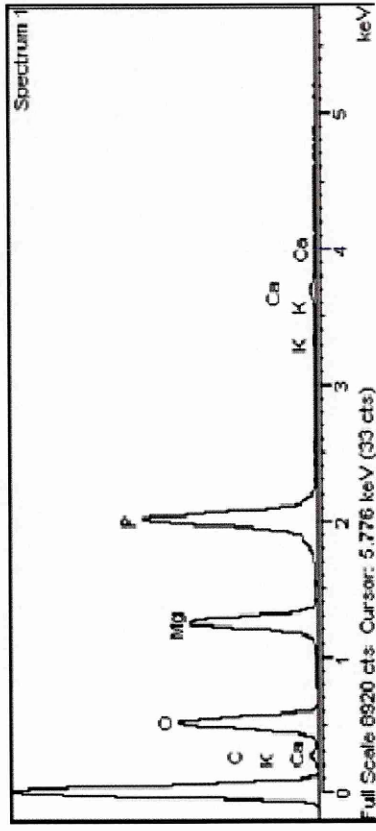
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :

C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	15.61	22.75
O K	52.18	57.09
Mg K	13.43	9.67
P K	17.84	10.08
K K	0.12	0.05
Ca K	0.83	0.36
Totals	100.00	



Experiment 20: FBR + Metallic mesh

08/02/2007 12:09:31

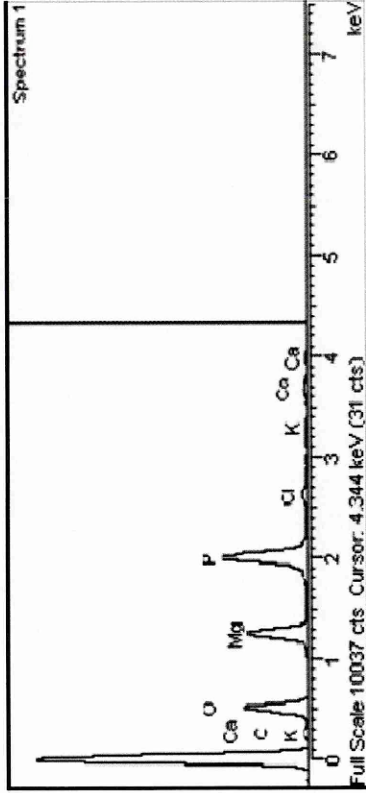
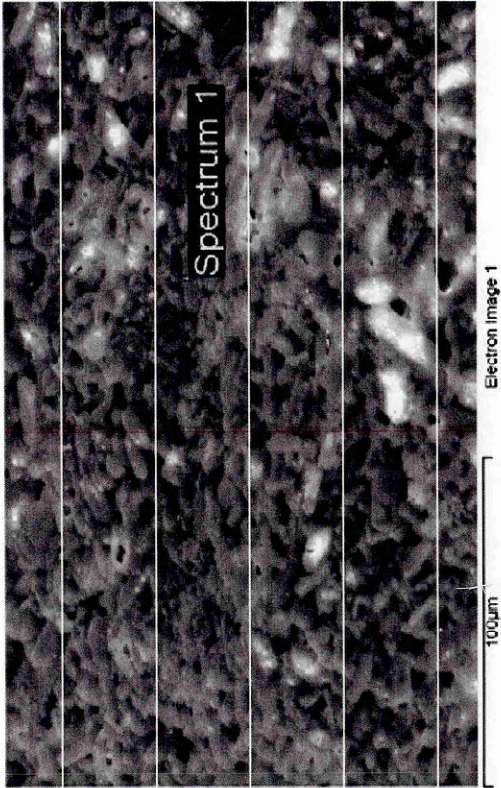
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 5

Standard :

- C CaCO3 1-Jun-1999 12:00 AM
- O SiO2 1-Jun-1999 12:00 AM
- Mg MgO 1-Jun-1999 12:00 AM
- P GaP 1-Jun-1999 12:00 AM
- Cl KCl 1-Jun-1999 12:00 AM
- K MAD-10 Feldspar 1-Jun-1999 12:00 AM
- Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	17.61	25.56
O K	50.27	54.79
Mg K	12.05	8.64
P K	17.04	9.59
Cl K	1.65	0.81
K K	0.16	0.07
Ca K	1.21	0.53
Totals	100.00	



08/02/2007 12:38:28

Experiment 20: Stirred tank + polyDADMAC

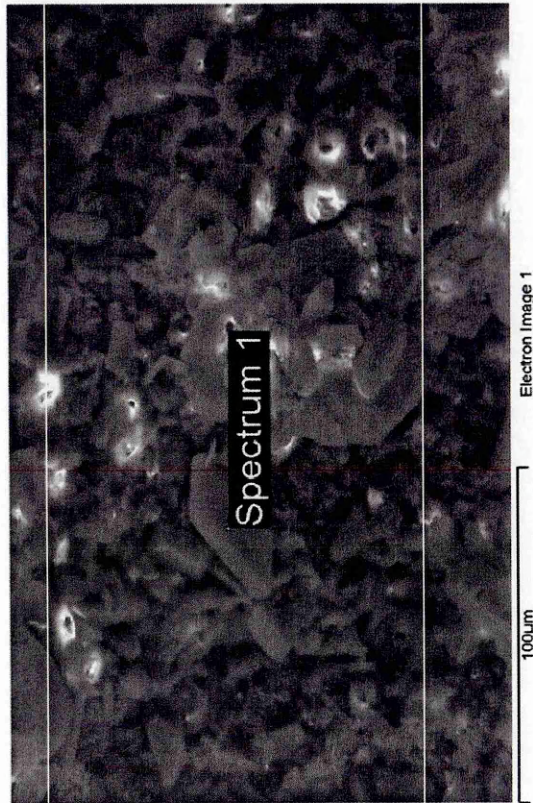
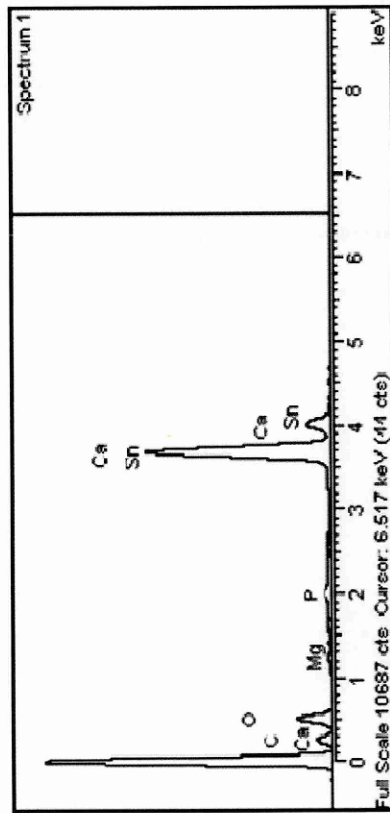
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :

C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Sn Sn 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
CK	10.23	17.40
OK	48.13	61.49
MgK	0.33	0.27
PK	0.71	0.47
CaK	39.61	20.20
SnL	1.00	0.17
Totals	100.00	



08/02/2007 12:39:21

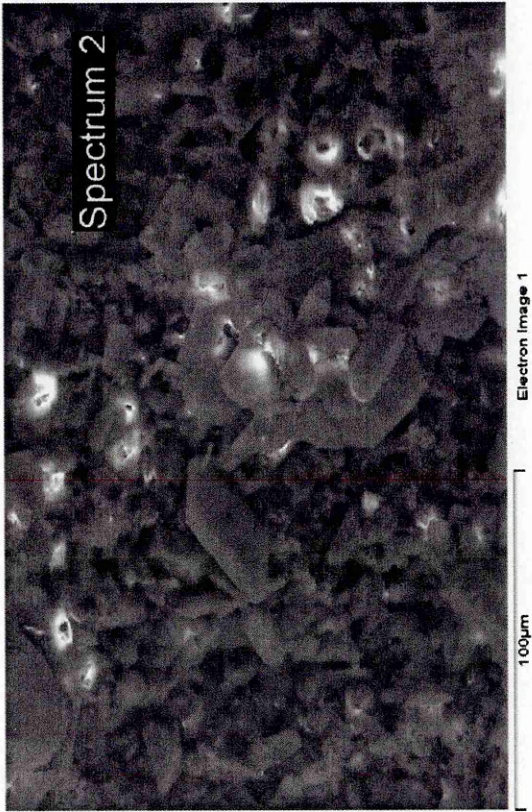
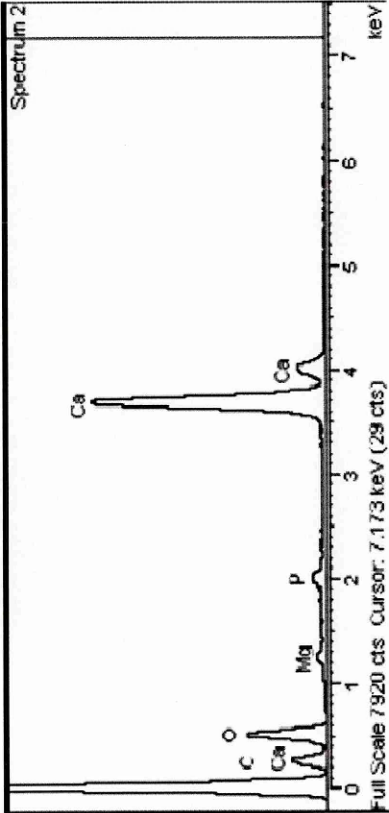
Experiment 20: Stirred tank + polyDADMAC

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 5

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	13.47	20.96
O K	54.61	63.82
Mg K	0.67	0.52
P K	0.88	0.53
Ca K	30.37	14.17
Totals	100.00	



08/02/2007 12:40:15

Experiment 20: Stirred tank + polyDADMAC

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :

C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	9.78	16.75
O K	47.29	60.85
Mg K	0.67	0.57
P K	0.79	0.53
Ca K	41.47	21.30
Totals	100.00	

