Cranfield University

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

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Kristell Sophie Le Corre

Understanding Struvite Crystallisation and Recovery

Supervisor: Professor Simon A. Parsons

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ABSTRACT

Struvite crystallisation from wastewater effluents is seen as an alternative to traditional biological and chemical phosphorus removal processes used widely in the wastewater treatment industry. It presents the advantage of not only removing phosphorus but also generating a compound that could be reused as a fertiliser. However the application of struvite crystallisation processes at full scale is not widespread due to the unknown economical value of the process and the product, the need of pH control, the necessity of long operational times to ensure quality of the product and the formation of crystal fines.

Preliminary crystallisation experiments were carried out at laboratory scale to provide a better understanding of nucleation and growth processes, and identify how basic parameters such as pH, mixing energy, water chemistry or presence of foreign ions affected struvite crystallisation. Particular attention was paid to the quality (*i.e.* size, shape and purity) of the crystal formed. The results revealed that the presence of calcium ions in solution could alter struvite purity and even inhibit its formation. pH was also identified as a parameter of major impact on struvite crystal quality. Indeed, pH could either influence struvite purity or affect size of crystals formed. Further investigations in a purposely built reactor also revealed that if struvite crystallisation is relatively simple to achieve, the control of struvite quality and more particularly crystal size is complex. Results at pilot scale showed that reactor operation and struvite surface charge could be a limitation to its agglomerative properties, hence to the formation of larger crystals.

To optimise struvite crystallisation and limit the problem of fines formation the present study has investigated two possible solutions: struvite fines recovery by coagulation or struvite crystallisation on seed materials. Struvite coagulation proved to be an efficient solution to remove and recover struvite fines rapidly through floc formation. Of the coagulant tested, polyDADMAC was the most effective resulting in the formation of flocs 10 times bigger than the initial size of crystals. With regards to crystallisation on seed materials, the results revealed that success of struvite attachment onto seeds in short contact times was only efficient when mixing energy in the reactor was limited. In that sense, the submersion of a metallic system in the reactor allowed excellent phosphorus removal and rapid struvite recovery in only 2 hours of operation.

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Without coffee, saucisson, crêpes, French cheese (the best!), Cider from Brittany (also the best!), Red Wine (especially Nuits Saint-Georges), pubs, Ben Harper and Oasis the results of this project would have been slightly different, I mean really different!!!!

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ABBREVIATIONS AND NOTATIONS

Abbreviations

AFM – Atomic Force Microscope
BNR – Biological Nutrient Removal
CaP – Calcium Phosphate
CEEP – Centre Européen des Polyphosphates
CSTR – Continuously Stirred Tank Reactor
EBPR – Enhanced Biological Phosphorus Removal
FBR – Fluidised Bed Reactor
HAP – Hydroxyapatite
MAP – Magnesium Ammonium Phosphate
MGD – Million Gallons Day
nN – nanonewton
p.e. – Population equivalents
polyDADMAC – polydiallyldimethylammonium chloride
RCA – Recycled Concrete Aggregates
rpm – Revolutions per minute
SEM-EDS – Scanning Electron Microscope coupled with Energy Dispersive Spectrophotometer
UWWTD – Urban Waste Water Treatment Directive
WWTP – Waste Water Treatment Plant
XRD – X-ray Diffraction

Notations

A – kinetic factor
a_i – Ionic activity
C – Concentration of a reactant
c* – Equilibrium solubility
C_0 – Initial concentration of a reactant
Ceq – Concentration of a reactant at equilibrium
Csp – Conditional solubility product

$d_{0.5}$ – 50 percentile equivalent diameter floc or particle size

G – Crystal growth rate

I – Ionic strength

J – rate of nucleation

k – Kinetic constant

k_g – Growth constant

k_H – rate of appearance of H^+ ions

k_{Mg} – rate of disappearance of Mg^{2+} ions

Kso – Activities solubility product

Ksp – Constant solubility product

pKso - Negative log of Kso

pKsp – Negative log of Ksp

Ra – Average surface roughness

T – absolute temperature

t_G – Growth time

t_{ind} – Induction time

t_N – Nucleation time

z^+, z^- – Valencies of the considered ions

γ – Interfacial tension

γ_i – Coefficient of ionic activity

ζ – Zeta-potential

λ - Wavelength

ρ – density

σ_g – Relative supersaturation

υ – Molecular volume

Ω – Supersaturation ratio

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 Project background

Phosphate mine rocks represent the main source of phosphorus commonly used by the fertiliser, detergent or insecticide industry (Steén, 2004). Nevertheless, reserves of phosphate naturally available are limited and the intensive exploitation of this resource could cause stock depletion in less than 100 years (Driver *et al.*, 1999). Alternative sources of phosphorus need then to be found. As a result, phosphorus recycling from wastewater effluents gained importance, especially since the European legislation reported pollution problems due to phosphorus release in effluents and imposed phosphorus removals to levels either below 1 or 2 $mg.L^{-1}$ (depending on the size of the sewage treatment work) in wastewater discharged to sensible areas such as lakes, rivers and reservoirs (UWWTD, 1991). Processes currently integrated in wastewater treatment plants to limit phosphorus discharge in effluents are precipitation with metal salt (Al and Fe or lime, Parsons and Berry, 2004) and biological processes (McGrath and Quinn, 2004). If both processes are efficient in removing phosphorus, the precipitates generated by those methods are not recyclable for direct reuse by the industry (de-Bashan and Bashan, 2004). The idea of removing and simultaneously recycling phosphorus as reusable and valuable compounds emerged then as an alternative to traditional phosphorus removal techniques (Morse *et al.*, 1998).

Primarily known by wastewater companies as a hard scale occurring at points of high turbulence along the treatment process (Figure 1.1) and resulting in major breakdowns and pipe blockages, magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$) commonly named struvite or MAP was later on identified as a premium fertiliser which exploitation could benefits to the wastewater treatment industry (Doyle and Parsons, 2002). In addition to represent a new approach to remove phosphorus from wastewater effluents, struvite crystallisation would also allow reduction of sludge volumes, hence sludge handling and disposal, when compared to traditional phosphorus removal techniques (*i.e.* biological and chemical, Shu *et al.*, 2006). This is all the more important since the legislation on sludge disposal became more stringent resulting in increases in sludge management costs (Fytili and Zabaniotou, 2006).

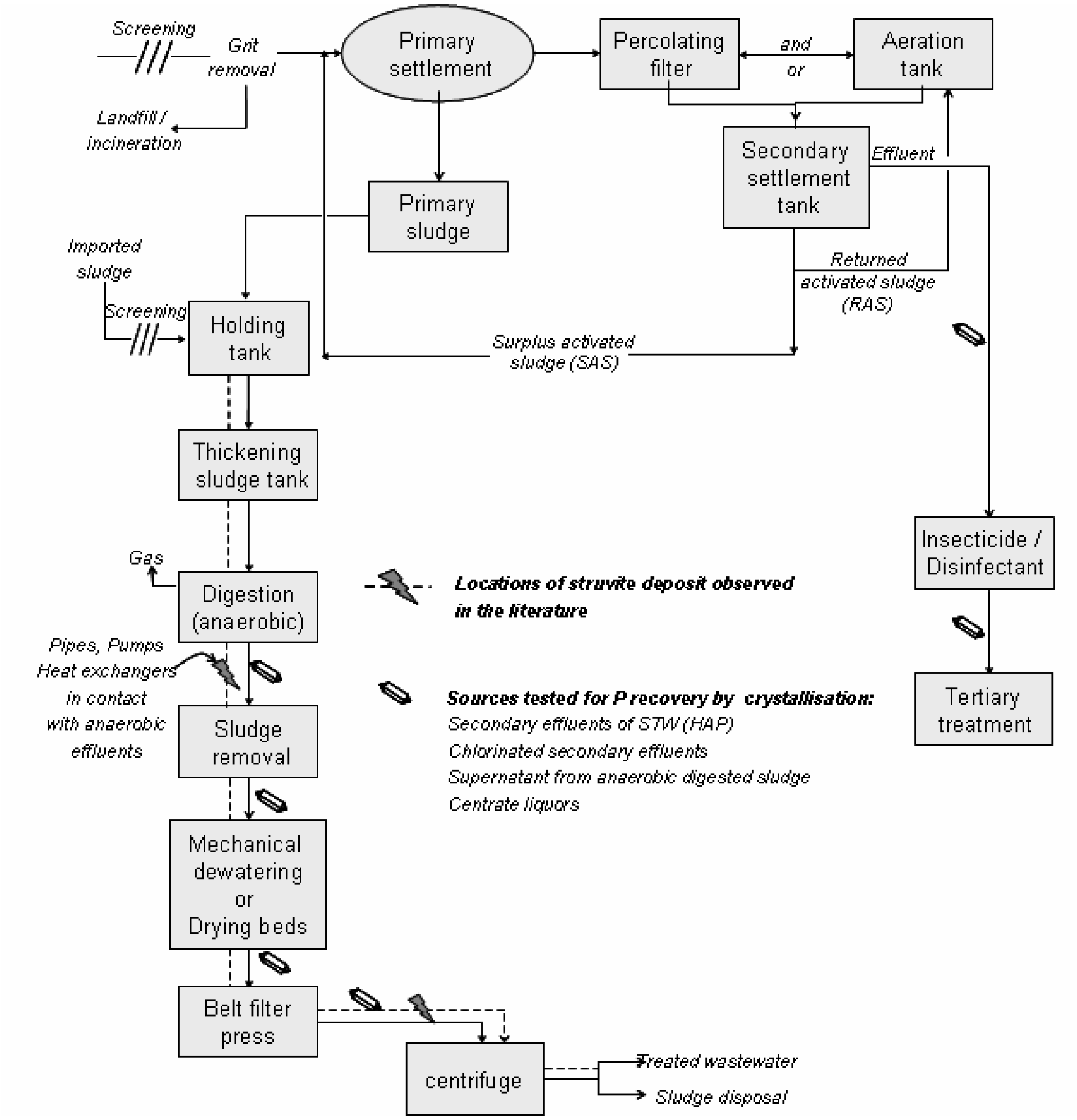

Figure 1.1. *Locations of struvite scale deposits in wastewater treatment plants and sources tested for its preferential crystallisation.*

The principles of struvite crystallisation have been then widely studied (Bouropoulos and Koutsoukos, 2000; Matynia *et al.*, 2006) and researchers have developed a multitude of processes, including selective ion exchange based reactors, fluidised bed reactors and stirred tank reactors (Liberti *et al.*, 2001; Cecchi *et al.*, 2003; Stratful *et al.*, 2004), to optimise phosphorus removal and recovery as struvite from wastewater effluents. Most of those processes mainly use anaerobically treated sludge liquors (Figure 1.1) and can achieve excellent phosphorus removal up to 94 % (Von Münch and Barr, 2001) as well as recovery with for example daily struvite productions of 500 to 550 kg achieved by Ueno and Fujii (2001) in a full scale reactor located in Japan.

However, this Japanese process is one of the rare full scale reactors in operation in a wastewater treatment plant. Indeed, most of the technologies tested to date remain experimental due to problems linked to the economical value of the process and the product formed, the need of an accurate pH control, and the formation of fines (Adnan *et al.*, 2003). Further more, the majority of the work carried out on struvite crystallisation mainly focused on the performance of crystallisation processes in removing and recovering phosphorus as struvite while little interest has been paid to the quality of the final product formed in terms of size, shape and purity. Consequently, further research on how parameters such as pH, supersaturation, presence of foreign ions and process operation known to affect struvite crystallisation, can affect struvite crystal characteristics, has to be investigated to improve struvite recovery rates and reuse.

1.2 Project development

The work presented in this thesis brought together research groups well recognised for their contributions in the phosphorus recovery area: the National History Museum (NHM), the Institute of Grassland and Environmental Research (IGER), Cranfield University and Severn Trent Water. The project initially looked at the impact of key physical and chemical parameters including magnesium dosing, calcium concentration, and pH on the success of struvite precipitation from synthetic liquors at laboratory, and subsequently at pilot scale in a specifically designed fluidised bed type reactor. Particular attention has been paid to the influence of operating conditions on the size, shape and purity of struvite crystals to facilitate struvite reuse as a good quality fertiliser.

1.3 Aims and objectives

The purpose of this thesis is to broaden the understanding of struvite crystallisation principles in order to improve struvite recovery from wastewater effluents in terms of quantity of product generated and characteristics (size, shape and purity) of the crystals formed.

Consequently, a series of objectives were identified:

- To assess at laboratory scale the impact of key parameters on struvite size, shape and purity.
- To develop a pilot scale reactor to evaluate the impact of operating conditions on the success of struvite crystallisation.
- To assess the effect of pH and crystal surface charge on struvite agglomerative properties.
- To develop a method to recover struvite fine crystals by coagulation.
- To look at forces of interaction between struvite and a range of seed materials typically used in the literature as active growth site to improve size of the recovered product.
- To evaluate the impact of seed material on crystal growth, and particularly assess the performance of a stainless steel structure as an innovative way of capturing struvite crystals, hence improving recovery rates.

1.4 Thesis plan

This thesis is presented in a paper format. All papers were written by the first author Kristell S. Le Corre and edited by Prof. Simon A. Parsons (supervisor). All experimental work was undertaken by the first author.

The principal objective of each paper and how they interconnect within the thesis is detailed in Figure 1.2. The work begins with a review of the literature on principles of struvite precipitation and crystallisation technologies studied to remove phosphorus and maximise its recovery from wastewater effluents (Chapter 2- submitted: Le Corre, K.S., Valsami-Jones, E., Hobbs, P. and Parsons, S.A., *Phosphorus removal and recovery from wastewater effluents by struvite crystallisation: a review. Critical Reviews in Environmental Science and Technology*).

Chapters 3 to 8 cover the technical content of the thesis. Chapter 3 investigates the influence of magnesium doses on kinetics of struvite precipitation. A kinetic model linking the pH of precipitation to magnesium concentrations in solution has been developed to predict the advancement of struvite crystallisation. (Chapter 3- submitted: Le Corre, K.S., Valsami-Jones, E., Hobbs, P. and Parsons, S.A. *Kinetics of struvite* *precipitation: effect of the magnesium dose on nucleation rates. Environmental Technology*)

Chapter 4 explores the effect of foreign ions, as calcium, on struvite crystallisation. Although foreign ions are known to affect struvite nucleation and induction times, this paper mainly focuses on the impact calcium ions can have on quality of crystals formed. (Chapter 4- Published in: Le Corre, K.S., Valsami-Jones, E., Hobbs, P. and Parsons, S.A. *Impact of calcium ions on crystal size, shape and purity. Journal of Crystal Growth (2005)*).

While chapter 3 and 4 related studies on struvite crystallisation principles at bench scale, chapter 5 looks at the influence of various parameters such as pH, foreign ions, and solution chemistry on struvite formation in a pilot scale reactor purposely designed at Cranfield University. (Chapter 5-submitted: Le Corre, K.S., Valsami-Jones, E., Hobbs, P. and Parsons, S.A. *Impact of reactor operation on success of struvite precipitation from synthetic liquors. Environmental Technology*)

Following theses first investigations at pilot scale, the process showed limitations with excess formation of small crystals also called fines. Chapter 6 gives details on the possible reason of the limited growth observed in the demonstrative reactor by investigating the agglomerative properties of struvite crystals. The feasibility of recovering struvite fines by coagulation and/or flocculation is also presented in this paper (Chapter 6-submitted: Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Jefferson, B. and Parsons, S.A. *Agglomeration of struvite crystals. Water Research*)

Chapter 7 and 8 looks at struvite crystallisation on seed material to improve crystal growth step.

The aim of Chapter 7 is to understand the importance of topographical and surface forces parameters on struvite crystallisation, and to investigate if force measurements can help to explain and predict the success of rapid struvite attachment onto seed materials (submitted: Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Boyd, R.D., Jefferson, B. and Parsons, S.A. *Influence of seed material characteristics on rapid struvite recovery. Water Research*).

Using findings resulting from Chapter 7, Chapter 8 looks at an innovative way of recovering struvite by submerging a metallic mesh system in pilot scale crystallisation reactor.(Submitted: Le Corre, K.S., Valsami-Jones, E., Hobbs, P., and Parsons, S.A. *Struvite crystallisation and recovery using a stainless steel structure as a seed material. Water Research*).

Chapter	Paper	Objective	Scale
2	*1*	*Literature review: Struvite crystallisation principles and recovering technologies*	-
3	*2*	*Kinetics of struvite precipitation*	*Bench and pilot*
4	*3*	*Impact of calcium ions on struvite crystal quality*	*Bench*
5	*4*	*Influence of process operation on success of struvite crystallisation*	*Pilot*
6	*5*	*Agglomeration of struvite crystals*	*Bench*
7	*6*	*Influence of seed materials characteristics on struvite crystallisation*	*Bench and pilot*
8	*7*	*Struvite crystallisation and recovery using a stainless steel structure as a seed material*	*Pilot*

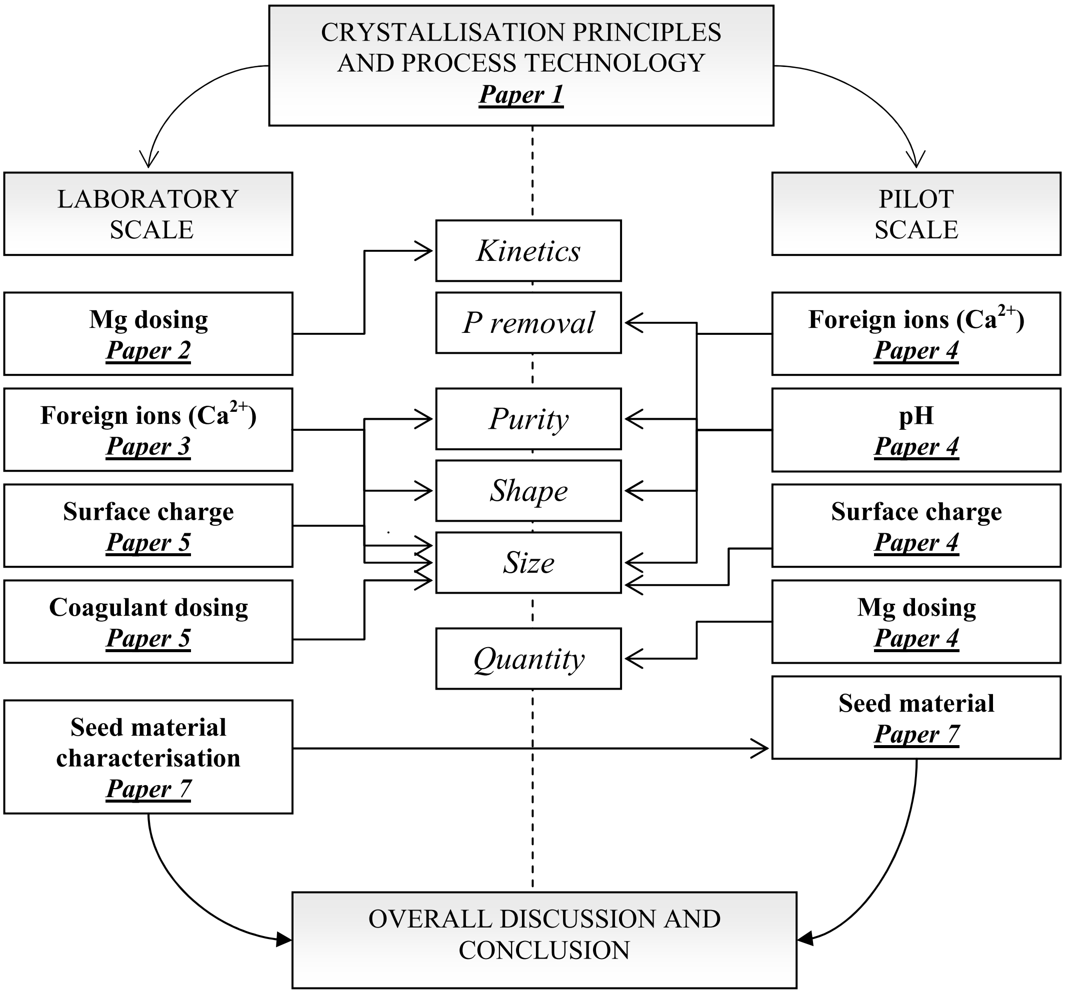

Figure 1.2. *Main objectives of each chapter and how they interconnect with each other within the thesis.*

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CHAPTER 2

PHOSPHORUS REMOVAL AND RECOVERY FROM WASTEWATER EFFLUENTS BY STRUVITE CRYSTALLISATION: A REVIEW

SUBMITTED TO:

Critical Reviews in Environmental Science and Technology, 2006.

2. PHOSPHORUS REMOVAL AND RECOVERY FROM WASTEWATER EFFLUENTS BY STRUVITE CRYSTALLISATION: A REVIEW

Kristell S. Le Corre[1], Eugenia Valsami-Jones[2], Phil Hobbs[3], Simon A. Parsons[1]

[1]School of Water Sciences, Cranfield University, Cranfield MK43 0AL, UK
[2] Department of Mineralogy, The Natural History Museum, Cromwell Road London, SW7 5BD, U.K
[3]Institute of Grassland and Environmental Research (IGER), North Wyke, Okehampton, Devon, EX20 2SB, UK

Abstract

The present review provides an understanding of principles of struvite crystallisation and examines the techniques and processes experimented to date by researchers at laboratory, pilot and full scale to maximise phosphorus removal and reuse as struvite from wastewater effluents. Struvite crystallisation is mainly known as a scale deposit causing concerns to wastewater companies. Indeed struvite naturally occurs under specific condition of pH and mixing energy in specific areas of wastewater treatment plants (e.g. pipes, heat exchangers) when concentrations in magnesium, phosphate and ammonium reach an equimolar ratio 1:1:1. However, thanks to struvite composition and its fertilising properties, the control of its precipitation could help to reduce levels of phosphorus rejected in effluents while simultaneously generating a valuable end by-product. A number of processes such as stirred tank reactors, air agitated and fluidised bed reactor have been then studied in that sense. Fluidised bed reactors emerged as one of the promising solution for removing and recovering phosphorus as struvite. Phosphorus removal can easily reach 70% and more, nevertheless the technique still needs improvement with regards to the control of the production quality and quantity to become fully applicable as a beneficial treatment for wastewater companies.

Keywords: phosphorus removal, struvite, crystallisation technologies, fertiliser

2.1 Introduction

Phosphorus (P) is one of the principal chemical elements on earth but doesn't exist in the form of a simple compound. It is combined with other elements (oxygen, hydrogen…) to form phosphates. Although P is essential for all living organisms, it is closely linked to problems of eutrophication. The eutrophication phenomena consists of the nutrient enrichment of surfaces waters, leading to an excessive increase of vegetation such as algae, which is responsible for turning water green in lakes, reservoirs, rivers, coastal waters and the marine environment in general (Burke *et al.*, 2004).

Phosphates represent the main source of P and are commonly used in fertilisers, detergents or insecticides. Morse *et al.* (1993) reported that the overdose of P in European Union (E.U.) countries water essentially comes from human sources in sewage and from live stock.

Since 1991, European legislation has approached this pollution problem by establishing a new directive (EC Urban Waste Water Treatment Directive 91/271/EEC, UWWTD, 1991). The removal of P in wastewater discharged to sensitive areas is now regulated and minimum P concentrations in effluents are imposed, depending on the size of discharge (Table 2.1).

Table 2.1. *Requirements of P concentration for discharges from urban waste water treatment plant (UWWTD, 1991)*

Population (population equivalents)	Phosphorus limit	Minimum percentage of reduction *
10 000-100 000 p.e.	2 mg. L^{-1}	80 %
More than 100 000 p.e.	1 mg.L^{-1}	80 %

** related to the load of the influent*

The legislative pressure has lead to more discussions on how to integrate P removal processes in wastewater treatment plants (CEEP, 1971- to present). The traditional P removal processes are based on phosphorus fixation in activated sludge either by a biological approach (biological nutrient removal, BNR) or chemical one (precipitation by metal salts). These processes are efficient in the sense that they can reduce the P concentration in wastewater effluents to less than 1 mg.L^{-1} (Booker *et al.*, 1999), but they lead to the accumulation of nutrients (P, N) in sludge, an increase of the sludge volumes, and contribute by reaction with magnesium and ammonium ions to the precipitation of magnesium ammonium phosphate hexahydrate most commonly known as struvite.

Struvite ($MgNH_4PO_4.6H_2O$) scale deposits are causing significant concern to wastewater treatment plants (Doyle *et al.*, 2003). The problem is not necessarily a new one as problems due to struvite spontaneous precipitation were first observed as a crust of crystalline material in 1937 in a multiple-stage sludge digestion system (Rawn *et al.*, 1937). Often perceived as a nuisance affecting the efficiency of treatment processes and causing maintenance problems, the control of struvite deposition has been widely investigated, including the dilution of struvite crystals with water effluents (Borgerding, 1972); preventive action by chemical dosing of iron salts (Mamais *et al.,* 1994) or addition of chemical inhibitor (Doyle *et al.*, 2003; Snoeyink and Jenkins, 1980).

In the past 10 years struvite precipitation though has gained interest as a route to phosphorus recovery (Doyle *et al.*, 2003). Its composition (nitrogen (N), phosphorus (P) and magnesium (Mg) ions in equal molar concentrations) makes it a potentially marketable product for the fertiliser industry, if its nucleation and the quality of crystals recovered can be controlled (Booker *et al.*, 1999). Researches in struvite formation are now widespread and include: prevention against scaling problems; alternative phosphorus removal and recovery from waste water effluents; and feasible exploitation to the benefit of wastewater companies and industries as a fertiliser.

Several studies have been carried out to assess potential methods to recover phosphorus as struvite at a bench and pilot scale, and few processes, integrated in treatment plants, already exist and are effective in Japan (Ueno and Fujii, 2001), The Netherlands (Giesen, 1999) and Italy (Cecchi *et al.*, 2003, Battistoni *et al.*, 2005a).

This review paper focuses on phosphorus removal and recovery by struvite crystallisation. It provides an understanding of principles of struvite crystallisation and reviews the techniques and processes experimented to date by researchers at laboratory, pilot and full scale to maximise phosphorus removal and reuse as struvite. Advantages and drawbacks of the different approaches presented here are analysed and discussed in order to identify research areas which require improvements to optimise struvite crystallisation from wastewater effluents and reuse as a fertiliser.

2.2 Struvite chemistry

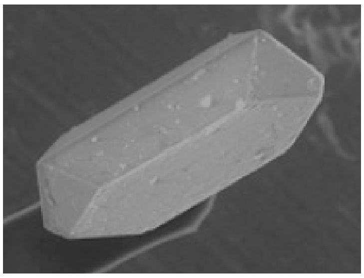
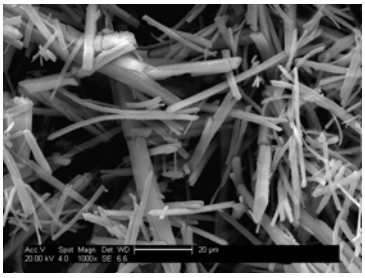
2.2.1 Struvite characteristics

Struvite is a mineral, which is composed of magnesium, ammonium, and phosphate in equal molar concentrations. It belongs to the group of the orthophosphates. The general formula for compounds of this group is:

> $NH_4\boldsymbol{M}PO_4$, $6H_2O$ where M correspond to a metal that can be either magnesium (Mg), cobalt (Co), potassium (K) or Nickel (Ni), (Bassett and Bedwell*,* 1933).

Struvite or magnesium ammonium phosphate hexahydrate crystallises as a white orthorhombic structure (*i.e.* straight prisms with a rectangular base). Table 2.2 summarises the main chemical and physical properties of struvite crystals.

Table 2.2. *Properties of struvite.*

Nature	Mineral salt
Chemical Name	Magnesium ammonium phosphate hexahydrate
Formula	$MgNH_4PO_4.\ 6H_2O$
Aspect	White glowing crystal, (Bassett and Bedwell, 1933).
Structure	Orthorhombic (space group $Pmn2_1$): regular PO_4^{3-} octahedra, distorted $Mg(H_2O)_6^{2+}$ octahedral, and NH_4 groups all held together by hydrogen bonding, (Abbona and Boistelle*,* 1979).
	 Dunn *et al.* (2004)  Le Corre *et al.* (2006b)
Molecular weight	245.43 $g.mol^{-1}$
Specific gravity	1.711 (ρ=1.711 $g.cm^{-3}$), (Borgerding, 1972)
Solubility	Low in water: 0.018g.100 ml^{-1} at 25°C in water High in acids: 0.033g.100 ml^{-1} at 25°C in 0.001 N HCl; 0.178g.100 ml^{-1} at 25 °C in 0.01 N HCl (Bridger *et al.*, 1961).
Solubility constant	$10^{-13.26}$ (Ohlinger *et al.*, 1998)

Struvite crystals occur spontaneously in various biological media. For instance, it has been found in rotting organic material such as guano deposits and cow manure, where it is produced through the microbiological combination of NH_4^+ ions of bacteria metabolisms with Mg and P already present in the media (Ben Omar *et al.*, 1994). It has also often been studied in the medical field as it can spontaneously form calculi in human kidneys (Coe *et al.*, 2005), and lately in soil sciences as a way to entrap nitrogen in compost (Jeong and Kim, 2001; Jeong and Hwang, 2005)

In the wastewater treatment area, struvite is well-known as a scale problem. In their study about digestion system published in 1937, Rawn *et al.* (1937) mentioned the occurrence of a "*crust of crystalline material*" in areas of a pipe that was carrying supernatants liquors and identified it as magnesium ammonium phosphate in a purity ratio of 96 %. Struvite as a source of scale deposits in wastewater treatment plants (WWTP) was then confirmed by Borgerding (1972) when it occurred on the walls of an anaerobic digestion system at the Hyperion treatment plant, Los-Angeles, 1963. This scale problem was first considered solved successfully as the struvite deposit was dissolved by an acidic treatment. Unfortunately it reappeared few years later and reduced significantly the diameter of pipes in the same plant. Since then, struvite as a scale agent had been the theme of several studies (Snoeyink and Jenkins 1980; Mohajit *et al.*, 1989; Doyle *et al.*, 2002), but most of the authors have considered struvite as a 'problem' to eliminate and not as a product which could be of economic interest.

2.2.2 Spontaneous precipitation of struvite in wastewater environments

Struvite precipitates in a 1:1:1 molar ratio following the general equation (with n= 0, 1, or 2):

$$Mg^{2+} + NH_4^+ + H_nPO_4^{3-n} + 6H_2O \rightarrow \mathbf{MgNH_4PO_4.6H_2O} + nH^+ \qquad (2.i)$$

The occurrence and development of struvite crystals follows two chemical stages: nucleation (crystal birth) and crystal growth (development of crystals until equilibrium), (Jones, 2002). Predicting or controlling these mechanisms is complex as it is controlled by a combination of factors including the crystal state of initial compounds, thermodynamic of liquid-solid equilibrium, phenomena of matter transfer between solid and liquid phases (Jones, 2002; Mullin, 1992), and kinetics of reaction (Ohlinger *et al.*,

1999) as well as several physico-chemical parameters such as: pH of the solution from which struvite may precipitate (Bouropoulos and Koutsoukos, 2000), supersaturation (Doyle *et al.*, 2002), mixing energy (Ohlinger *et al.*, 1999), temperature (Aage *et al.*, 1997) and presence of foreign ions (Le Corre *et al.*, 2005). To illustrate, according to equation (2.*i*), the reaction between magnesium, ammonium and phosphate ions causes the release of hydrogen ions in solution, and induces a drop of pH. In presence of an excess of phosphate ions, free hydrogen ions could then react preferentially with them and form orthophosphates ($H^{+} + PO_4^{3-} \rightarrow HPO_4$) rather than struvite.

As a result, spontaneous precipitation of struvite always occurs in specific areas of WWTP (Ohlinger *et al.*, 1999). As struvite solubility decreases when pHs become more basic, and decreases with increasing phosphate concentrations, most of struvite scales have been observed in areas of high turbulences (*i.e.* elbows, valves, propellers, pumps) and in parts of sludge treatment processes where phosphates concentrations are the highest that is to say in digested sludge and sludge liquors pipeline (Table 2.3).

Table 2.3. *Examples of locations of struvite deposits and relative damages caused.*

Authors	Location of deposit	Effects	Type of plant
Rawn *et al.* (1937)	Digestion sludge process: pipes carrying supernatants liquors	Accumulation in some places to the thickness of an inch (~ 2.5 cm)	Wastewater treatment plant, (USA)
Borgerding (1972)	Activated/digested sludge process: suction side of pump onto separating screen	310 mm diameter of the suction side reduced to 150mm	Hyperion waste water treatment plant, (USA)
Booram *et al.* (1975)	Items in contact with anaerobic liquids: pump impellers, pipes...	-	Livestock waste treatment and management plant, (U.S.A)
Mohajit *et al.* (1989)	In floating aerators, raw waste pumps, pipelines and outfall pipelines.	Accumulation: from 5.88 up to 14.44 mm in aerators from 8 up to 28mm in pipes carrying digester effluents	Pig waste treatment plant, (Singapore)
Ohlinger *et al.* (1998)	Accumulation on pipe walls from sludge basins supernatant system	Accumulation along 5.6 km of pipes.	Wastewater treatment plant, (USA)
Williams (1999)	Accumulation of struvite crystals in pipelines from the sludge holding tank to the centrifuges	Bore of pipes reduced from 100 to 50 mm	Wastewater treatment plant, (UK).
Doyle *et al.* (2000)	Pipes carrying centrate liquors	Pipe diameter reduction from 150 to 60 mm in 12 weeks.	Sludge destruction plant, (UK)
Battistoni *et al.* (2004)	Pipes carrying anaerobic supernatants.	Reduction of pipes diameter	Demonstrative Fluidised Bed Reactor plant, WWTP , (Italy)
Neethling and Benisch (2004)	Streaming pipes controlling polymer feed - flowmeters	2 months build up in a 3” rubber lined 90° elbow	WWTP, (USA)

The accumulation of struvite on walls of pipes can be very impressive with reductions in diameter up to 60 % (Doyle *et al.*, 2000). Several methods to control the formation of struvite have been then studied including the dilution of struvite crystals with water effluents (Borgerding, 1972); preventive action by chemical dosing of iron salts (Mamais *et al.*, 1994) or addition of chemical inhibitors (Parsons and Doyle, 2004). However, these methods are really expensive for wastewater companies due to a combination of chemical addition, manpower, and maintenance. To illustrate, Neethling and Benisch, (2004) reported that annual costs due to struvite scaling could range from \$2000 to \$10000 per MGD depending on the size of the treatment plant.

2.2.3 Notion of solubility and solubility product

2.2.3.1 Definition

As for other mineral salts, the chemistry of struvite is closely linked to the notion of solubility (Taylor *et al.,* 1963, Burns and Finlayson, 1982, Webb and Ho*,* 1992, Aage *et al.,* 1997).

The solubility of a chemical compound can be basically quantified as the maximum quantity (gram or mole) of solute dissolved in one litre of saturated solution under precise conditions of temperature, nature of solvent and nature of solute. It is generally expressed in gram per litre ($g.L^{-1}$) or mole per litre ($mol.L^{-1}$). The solubility is a function of temperature and pressure (Mullin, 1992), and every salts is characterised by its own solubility curve representing the concentration of the salt in a solvent versus temperature. Figure 2.1 represents the solubility curve for struvite determined by Borgerding in 1972.

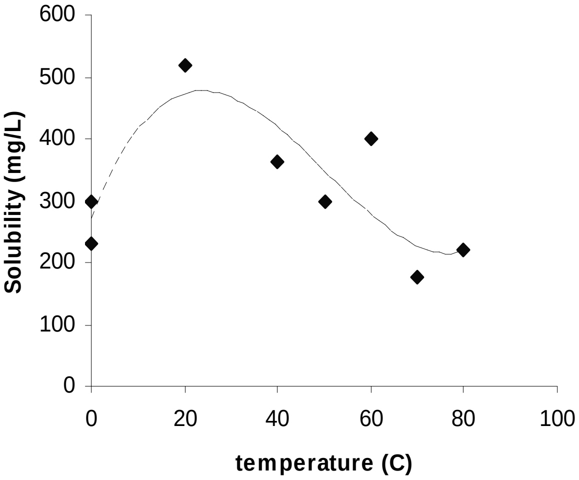


Figure 2.1. *Solubility curve of struvite adapted from Borgerding (1972).*

2.2.3.2 Solubility product

The solubility product is an equilibrium constant, which can be defined for every electrolyte solutions saturated in excess.

Given the general equation of dissolution of a salt in water:

$A_aB_{b(s)} \rightarrow aA^{z+}_{aq} + bB^{z-}_{aq}$

The constant solubility product K_{sp} can be expressed as:

$$\mathbf{K_{sp} = [A^{z+}]^a.[B^{z-}]^b} \qquad (2.ii)$$

where: - $[A^{z+}]$ and $[B^{z-}]$ are the total concentrations of ions in solution

-z^+, z^- are the valencies of the considered ions.

If we call c* the equilibrium solubility of each ion in the way that a=b=1, and $c^*=[A^{z+}]=[B^{z-}]$, then for a salt producing two ions, we have:

$K_{sp} = (c^*)^2$ or $c^* = K_{sp}^{\frac{1}{2}}$

Or more generally: $K_{sp} = (c^*)^{a+b}a^a b^b \leftrightarrow c^* = \left(\frac{K_{sp}}{a^a b^b}\right)^{\frac{1}{a+b}}$, (Mullin, 1992) (2.*iii*)

By applying equation (2.*ii*) and (2.*iii*) to struvite dissolution (2.*iv*), we have:

$$MgNH_4PO_4.6H_2O_{(s)} \rightarrow Mg^{2+} + NH_4^+ + PO_4^{3-} \qquad (2.iv)$$

$$\mathbf{K_{sp} = [Mg^{2+}].[NH_4^+].[PO_4^{3-}]} \text{ or } C^* = \left(\frac{Ksp}{1}\right)^{\frac{1}{3}} \qquad (2.v)$$

Equation (2.*v*) shows that if Mg^{2+}, NH_4^+, PO_4^{3-} concentrations are greater than the values of K_{sp}, then the solution is supersaturated with respect to struvite and precipitation will occur.

Several studies have been carried out to assess the solubility product of struvite, and numbers of K_{sp} values are available in the literature Table 2.4. These are usually expressed using its negative log, noted pK_{sp} for practical reasons.

Table 2.4. *pK_{sp} values and respective concentrations of ions required to reach them*

Authors	**K_{sp}**	**pK_{sp}**	**Mg^{2+} ($mg.L^{-1}$)**	**NH_4^+ ($mg.L^{-1}$)**	**PO_4^{3-} ($mg.L^{-1}$)**
Bube (1910)	$2.50.10^{-13}$	12.60	1.51	1.13	5.98
Taylor *et al.* (1963)	$7.10.10^{-14}$	13.15	0.99	0.74	3.93
Borgerding (1972)	$3.90.10^{-10}$	9.40	17.53	13.15	69.40
Burns and Finlayson (1982)	$7.50.10^{-14}$	13.12	1.01	0.76	4.01
Loewenthal *et al.* (1994)	$2.50.10^{-13}$	12.60	1.51	1.13	5.98
Buchanan *et al.* 1994	$4.32.10^{-13}$	12.36	1.81	1.36	7.18
Aage *et al.* (1997)	$1.15.10^{-13}$	12.94	1.17	0.87	4.62
Ohlinger *et al.* (1998)	$5.49.10^{-14}$	13.26	0.91	0.68	3.61

As the K_{sp} value is calculated from total molar concentrations of ions in solution its application to real treatment processes is compromised. Indeed, this constant takes no account of pH, ion activity, ionic strength and presence of foreign ions in the solution, hence it should be applied in limited cases (*e.g.* for very soluble salts in relatively pure solutions). Real sludge, or liquors separated from it, contains effectively several ions which can form other complexes than struvite by reaction with Mg^{2+}, NH_4^+, and PO_4^{3-}, reducing thus the precipitation potential of struvite (*e.g.* Ca^{2+} which can combine with phosphates).

Moreover, the pH of sludge varies according to the nature of the effluent treated whereas the K_{sp} value calculated is only accurate for a given pH value. Therefore the K_{sp} value can be expressed as an activity solubility product named K_{so} which takes into account the ionic strength (I) and the activity (a_i) of the ionic species. As pH, I and a_i are not considered in a Ksp calculation, the value generated by a K_{sp} is lower than the one generated by a K_{so} calculation. For struvite, K_{so} is calculated via the following formula:

$$\mathbf{K_{so}= a}_{Mg^{2+}} \times \mathbf{a}_{NH_4^+} \times \mathbf{a}_{PO_4^{3-}} \qquad (2.vi)$$

where: $\mathbf{a_i}$ is the activity of the i^th^ ion in solution defined as $\mathbf{a_i= \gamma_i.[C_i]}$

with γi representing the activity coefficient of the ionic specie ***i*** and $[C_i]$ its respective total concentration.

K_{so} can also be expressed as a pK_{so} value, such as $\mathbf{pK_{so}=-Log\ K_{so}}$.

Hence when the solutions are infinite diluted ($\gamma_i=1$), we have $K_{sp}=K_{so}$. This condition occurs in practise for concentrations of the ionic species up to 10^{-3} mol.L^{-1}, as Ai depends on all the other ions in solution.

The major difficulty in predicting struvite formation in media such as wastewater is that many ionic species (Ca^{2+}, K^+, CO_3^{2-}) can influence the production of struvite by reaction with Mg^{2+}, PO_4^{3-} and NH_4^+ ions. It is therefore necessary to know the total concentration of these ions which are available for a given pH to form struvite. For this, researchers use a series of chemical equilibriums to determine the activities of each ionic species in solution. The nature of the equations used, and their respective constants can vary from an author to another one and affect the K_{so} value derived.

For instance, Snoeyink and Jenkins (1980) used the following equations and constants to estimate ions concentrations in solution:

Ammonium:	$NH_4^+ \rightarrow NH_3 + H^+$	Log(Ka)=9.3
Phosphate:	$PO_4^{3-} + H^+ \rightarrow HPO_4^{2-}$	$Log(1/Ka_{,3})=12.3$
	$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^{2-}$	$Log(1/Ka_{,2})=7.2$
	$HPO_4^{2-} + H^+ \rightarrow H_3PO_4$	$Log(1/Ka_{,1})=2.1$
Magnesium:	$Mg^{2+} + OH^- \rightarrow Mg(OH)^-$	$Log(1/Kd_{,Mg})=2.7$

From them, they deduced:

$$\mathbf{K_{so} = a}_{Mg^{2+}} \times \mathbf{a}_{NH_4^+} \times \mathbf{a}_{PO_4^{3-}} \qquad (2.vii)$$

$$K_{so} = (\gamma_{Mg^{2+}}.[Mg^{2+}]).(\gamma_{NH_4^+}\ [NH_4^+])(\gamma_{PO_4^{3-}}\ [PO_4^{3-}])$$

Snoeyink and Jenkins (1980) also introduced the notion of conditional solubility product defined as:

$$Csp= C_{T,\ Mg^{2+}} \times C_{T,\ PO_4^{3-}} \times C_{T,\ NH_4^+} \qquad (2.viii)$$

where: $C_{T,\ Mg^{2+}} = \left(\frac{[Mg^{2+}]}{\alpha_{Mg^{2+}}}\right)$ is the total analytical concentration of magnesium (2.*ix*)

with α symbolising the ionisation fraction that can continue to form struvite

From (2.*vii*) and (2.*viii*) and (2.*iv*),

$$Csp=\left(\frac{Kso}{\alpha_{Mg^{2+}}\alpha_{NH_4^+}\alpha_{PO_4^{3-}} \times \gamma_{Mg^{2+}}\gamma_{NH_4^+}\gamma_{PO_4^{3-}}}\right)=\left(\frac{Ksp}{\alpha_{Mg^{2+}}\alpha_{NH_4^+}\alpha_{PO_4^{3-}}}\right) \qquad (2.x)$$

This conditional solubility product is a function of pH, so it is at its minimum when the product of the ionisation fractions is at its maximum. This minimum value corresponds also to a pH minimum usually called in the literature ***pH of minimum solubility*** (*e.g.* Snoeyink and Jenkins, 1980, pH_{mins}=10.7). This notion of conditional solubility product is interesting in the sense that it allows to know rapidly the crystallisation state of a solution (Table 2.5):

- if $Csp \leq C_{T,\,Mg} \times C_{T,\,PO4} \times C_{T,\,NH4,}$ the solution is oversaturated, and struvite should precipitate until equilibrium.
- if $Csp \geq C_{T,\,Mg} \times C_{T,\,PO4} \times C_{T,NH4,}$ the solution is highly undersaturated with respect to struvite, no precipitation will occur.
- if Csp=1, and the solution equilibrium is reached.

Table 2.5. *Comparison of Ksp and Csp value taken from the literature*

Authors	**Source**	**[Mg] mol.L^{-1}**	**[NH$_4$] mol.L^{-1}**	**[PO$_4$] mol.L^{-1}**	**pH**	**Csp**	**Ksp**	**Consequences**
Booram *et al.* (1975)	A.T.*	$1.97.10^{-3}$	$26.8.10^{-3}$	$2.63.10^{-3}$	7.5	$10^{-7.54}$	$10^{-6.87}$	Csp<<Ksp Struvite precipitation should take place
Snoeyink and Jenkins (1980)	R*	5.10^{-3}	5.10^{-3}	4.10^{-2}	5.5	10^{-4}	10^{-6}	Csp>>Ksp Undersaturated solution/ No precipitation
	D*	5.10^{-3}	1.10^{-1}	7.10^{-2}	7.5	$10^{-7.5}$	$10^{-4.5}$	Csp>Ksp Oversaturated solution
	D.D*	1.10^{-3}	$2.5.10^{-2}$	2.10^{-2}	7.5	$10^{-7.5}$	$10^{-6.3}$	Csp,<Ksp Supersaturation

* *A.T.: Anaerobically treated sludge, R: raw sludge, D: digested sludge, D.D: diluted digested sludge.*

2.2.4 Supersaturation

2.2.4.1 Definition

Supersaturation is the parameter governing any crystallisation process. It defines the state of a crystal compound in a solution. For example, given a solution A containing variable quantities of solute, three states are possible (Figure 2.2):

- undersaturated (in the undersaturated zone), meaning that crystals can dissolve when added to the solution. Crystallisation is thus impossible.
- metastable (in the metastable zone situated between the solubility curve [$A_1A_2A_3$] and the supersaturation curve [$B_1B_2B_3$]), meaning that the solution is saturated. Spontaneous nucleation can not occur, but growth can be induced by seed addition.
- oversaturated (in the labile or unstable zone), meaning that solute concentration exceeds the equilibrium value and causes spontaneous nucleation. Crystallisation can be rapid and abundant without any addition of foreign elements.

To crystallise a compound, the supersaturation need to be reached. It can be achieved by cooling the solution (A to C_1), by evaporating the solvent at constant temperature (A to C_3) or by combining these two methods (A to C_2).

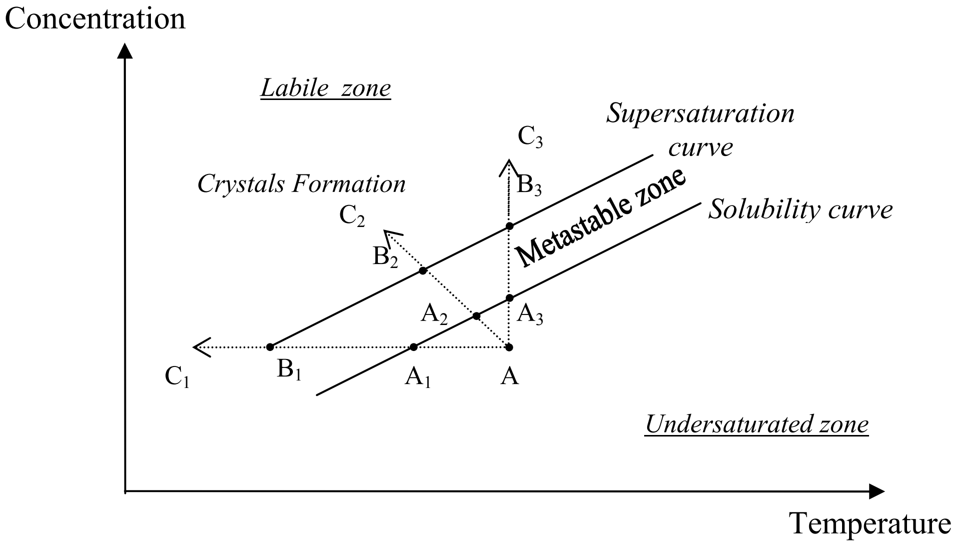


Figure 2.2. *States of a solution during the crystallisation process.*

The characteristics of the metastable zone (*i.e.* width, limits) will define the mode of crystallisation that will be optimum for the process. In fact, these characteristics are strongly linked to a parameter, called supersaturation ratio Ω. Ω can be defined in relation with the concentration driving force ΔC. ΔC= C-C* with C the concentration of the solution (e.g. C_1, C_2 or C_3), and C* is the equilibrium saturation at a given temperature (*e.g.* B_1, B_2, B_3). Thus $\Delta C/C^* = \Omega - 1 = \sigma$ where σ represents the relative supersaturation (Mullin, 1992).

But the application of this expression is limited, and can not be used for ionic systems as for struvite precipitation. Thus the more complex a solution is (*i.e.* wastewater where lots of ionic species are in solution) the more difficult the degree of supersaturation is to calculate and the characteristics of the metastable zone to establish.

2.2.4.2 Struvite supersaturation ratio

To describe the crystallisation state of a solution with respect to struvite, researchers use the notion of supersaturation Ω. Indeed, when Ω equals 1 the solution has reached equilibrium. Above this value, the solution is supersaturated, and struvite should precipitate until equilibrium, while below 1 the solution is undersaturated with respect to struvite, no precipitation will occur and dissolution could happen (Kofina and Koutsoukos, 2005).

Bouropoulos and Koutsoukos (2000) defined the supersaturation **Ω** as a representation of the driving force of the crystallisation. This latest is defined as the difference ***Δμ*** of the chemical potential of struvite in the supersaturated solution and its analogous value at equilibrium. To calculate the supersaturation they used the following expression:

$$\Omega = \left(\frac{a_{\mathrm{Mg}}^{2+} . a_{\mathrm{NH4}}^{+} . a_{\mathrm{PO4}}^{3-}}{\mathrm{K}_{\mathrm{so}}} \right) \qquad (2.xi)$$

where *a* represents the activity of the ionic species relative to struvite components in solution and Kso the struvite solubility product.

The activities of ionic species and the supersaturation **Ω** are determined by taking into account a series of chemical equilibrium characteristic of the system studied. Depending on the complexity of the system from which struvite may precipitate, the chemical equilibrium involved in ionic activities calculations can be numerous. Those parameters are then generally determined using iterative calculations with modeling software based on chemical equilibrium (Doyle and Parsons, 2002).

2.3 Mechanisms of struvite crystallisation

Crystal formation is a complex process of purification of a solute (liquid or solid) leading to the occurrence of a solid phase made of regular structures named crystals. Although it is a complex process which appeals to the crystals state of compounds, the thermodynamic of liquid/solid equilibrium, and phenomena of matter transfer between solid and liquid phases, the crystallisation operation is commonly used in the industry.
This chemical engineering process can be divided in two parts:

- *Nucleation:*
  It corresponds to the crystal birth into a liquid or a gaseous media. Ions combine together to form crystal embryos which are the first state of crystals. Nucleation is mostly governed by kinetics of reaction.

- *Crystal growth:*

  It corresponds to the development of crystals until the equilibrium is reached. The crystal growth determines the final size of crystal according to the crystallisation kinetics (rate of growth).

To crystallise a compound such as struvite, the supersaturation, as the driving force, need to be reached, in order to trigger off the first occurrence of crystals.

2.3.1 Struvite nucleation

2.3.1.1 Nucleation and nucleation rate

The nucleation process occurs in a solution when ions combine to form embryos (Mullin, 1992). As illustrated in Figure 2.3, there are two types of nucleation: the homogeneous primary process causes the spontaneous occurrence of crystals in highly purified or highly supersaturated solution, while the heterogeneous process induces crystals formation via foreign particles or impurities which function as foundation sites. For these reasons the heterogeneous process is thought to be the one causing struvite crystals formation in WWTP rather than homogeneous nucleation that needs specific and complex conditions of operation (*i.e.* highly pure and supersaturated solutions) (Ohlinger *et al.*, 1999)

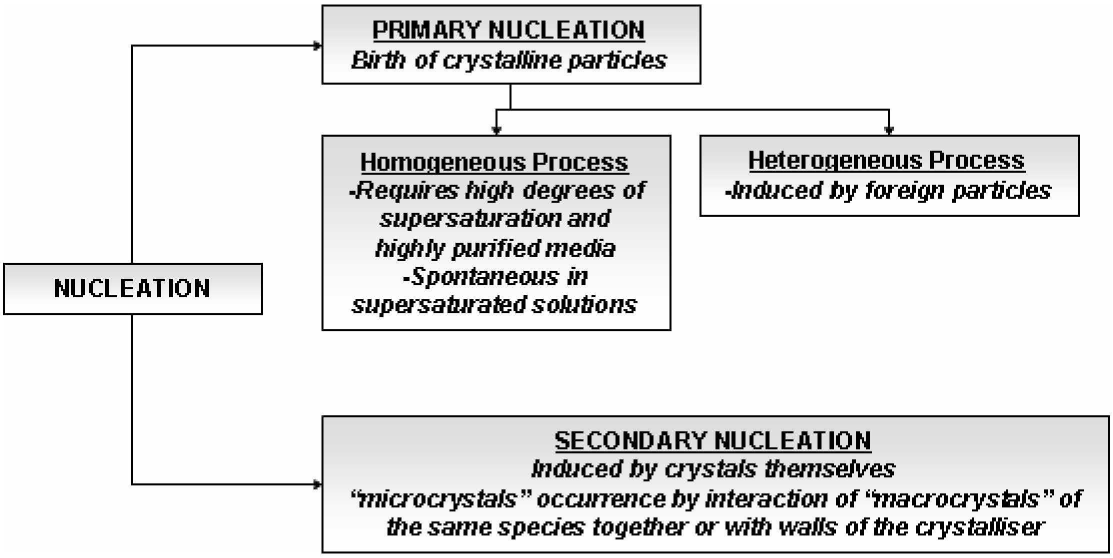


Figure 2.3. *The nucleation process.*

According to nucleation theory (Mullin, 1992; Jones, 2002), the rate of nucleation J or number of struvite nuclei formed per unit time (second) and unit volume (cm^3) follows the general equation:

$$J = A \exp\left[-\frac{16\pi\gamma^3 v^2}{3k^3T^3(\ln\Omega)^2} \right] \qquad (2.xii)$$

where A is a kinetic factor, k is the Boltzmann constant (1.38 J. K^{-1}), **Ω** is the supersaturation ratio, γ is the interfacial tension between a crystal and the solution ($mJ.m^{-2}$), v the molecular volume (cm^3), and T the absolute temperature (K).

As showed in the equation (2.*xii*), struvite nucleation rate is closely linked to the supersaturation level **Ω** of the solution in which crystals occurs, as well as on the kinetic factor A which is usually assumed to be 10^{17} $nuclei.cm^{-3}$ (Abbona and Boistelle*,* 1985; Bouropoulos and Koutsoukos, 2000)

Equation (*xii*) has been used to determine the interfacial tension (*i.e.* surface energy) γ of the struvite crystal formed. According to Abbona and Boistelle (1985) a rate of J = 1 $nucleus.cm^{-3}$ is characteristic of supersaturations at which nucleation takes place within 1 min. Using this value they obtained an interfacial tension for struvite of 50 $mJ.m^{-2}$.

Bouropoulos and Koutsoukos (2000) in their study of spontaneous struvite precipitation of struvite from aqueous solution obtained a similar value of the interfacial tension of struvite crystals, and analysed the dependence of rates of nucleation on supersaturation. They concluded that this dependence was of second order suggesting nucleation was controlled by surface diffusion mechanisms. Although they found the supersaturation to be the triggering factor of struvite nucleation they also revealed the great importance of the induction time on the crystallisation process.

2.3.1.2 Induction time

Ohlinger *et al.* (1999) defined the induction time as "the time period between blending of solutions containing precipitant constituents and the first measurable indication of the precipitants". The induction time can depend on the degree of supersaturation, the temperature and the presence of impurities in the solution.

Jones (2002) defined the induction time as:

$$t_{ind} = t_N + t_G \qquad (2.xiii)$$

where t_N represents the nucleation time and t_G is the growth time (time necessary to grow to a detectable crystal size).

It appears from this relation that the induction time depends on the different processes involved (nucleation and growth) but also on the kinetics induced by these processes (chemical reaction kinetics, mixing kinetics).

Experimentally speaking, the induction time can be determined via different methods such as light scintillation (Gunn and Murphy, 1972), turbidimetry and conductimetry (Söhnel and Mullin, 1982), absorbance measurements (Barrett and Parsons, 1998, Kabdaşli *et al.*, 2006a), or pH measurements (Bouropoulos and Koutsoukos, 2000).

Bouropoulos and Koutsoukos (2000) demonstrated that the induction time was inversely proportional to the supersaturation level **Ω**, making the supersaturation level one of the most influencing parameter on induction time. This is a general trend in studies that have assessed the variation in struvite induction time, but values can vary depending on condition of precipitation tested (Table 2.6).

Table 2.6. *Comparison of induction times reported from struvite precipitation in a molar ratio Mg:P:N 1:1:1*

Authors	**Precipitation method**	**Induction time measurement method**	**Supersaturation Ω**	**Induction time (t_{ind})**	**Agitation**
Abbona and Boistelle (1985)	Spontaneous precipitation ($MgSO_4.H_2O$ +$NH_4H_2PO_4$)	pH measurement	Ω=1.4 Ω=2.5 12<Ω<25	24 h 24 h 1 min	None
Ohlinger *et al.* (1999)	Spontaneous precipitation ($MgCl_2.7H_2O$ + $NH_4H_2PO_4$)	Visual observation of light scintillation	Ω=1.6 Ω=2.1 Ω=3.1	38min 1min 0.25 min	570 rpm
Bouropoulos and Koutsoukos (2000)	Spontaneous precipitation ($MgCl_2.7H_2O$ + $NH_4H_2PO_4$)	pH measurement	Ω=1.13 Ω=2.27 Ω=3.33	125 min 42 min 6 min	Constant agitation
Kabdaşli *et al.* (2004)	Spontaneous precipitation ($MgCl_2.6H_2O$ + $NH_4H_2PO_4$)	Light scattering, pH measurement, turbidity, absorbance and particle size measurement	Ω=2.346 Ω=3.209	14 min 3.5 min	Constant agitation
Kofina and Koutsoukos (2005)	Spontaneous precipitation (synthetic wastewater+ $MgSO_4$.7H2O+ $NH_4H_2PO_4$)	pH measurement	Ω=2.1 Ω=3.0	24.7 min 4.2	Constant agitation

The mixing speed can also influence the nucleation, but its impact on the induction time is reduced. To illustrate, Ohlinger *et al.* (1999) showed that for constant supersaturation levels (*e.g.* **Ω**= 2.1, 2.4, 2.7), a variation of mixing speed from 360 to 1060 rpm only reduced the induction time of about 10 seconds, suggesting that transport influences on struvite precipitation are less important than physico-chemical parameters. However, Abbona and Boistelle (1985) showed that in their system precipitating struvite without any agitation, the induction time at a **Ω**=2.5 was of 24 h. At a similar supersaturation ratio, but a 570 rpm mixing speed Ohlinger needed only 1 min (Table 2.6). To reach such an induction period in a static environment, Abbona and Boistelle (1985) needed extremely high supersaturation levels ranging between 12<**Ω**<25.

2.3.2 Crystal growth

Crystal growth is the step following nucleation, through which crystals embryos interact together or with impurities until they form crystals of detectable size (and beyond).

Growth rate is essentially controlled by processes of mass transfer and by surface integration mechanisms that means by kinetics involved by these processes. The mass transfer process corresponds to the transport of particles from the solution to the crystal surface by diffusion, convection or both; while the surface reaction process corresponds to the incorporation of material into the crystal lattice through mechanisms of surface integration.

From a theoretically point of view, crystal growth rate G can be expressed as a variation of the increasing size L versus time (t) (Jones, 2002). As for nucleation kinetics, the expression of struvite crystal growth rate following these theoretical principles is difficult to establish from experimental results, and is often correlated with practical parameters such as concentration and temperature using the following general power law derived from:

$$G=\frac{dL}{dt}\frac{(i.e\ \text{size variation})}{(i.e.\ \text{time variation})}=k_g\sigma^g \qquad (2.xiv)$$

where G represents the growth rate, k_g the growth constant and σ^g the relative supersaturation with g =1, for diffusion controlled growth, and g=1-2 or >2 for surface integration controlled growth.

Although nucleation seems to be the most important step in producing struvite crystals, it is obvious that mechanisms involved in crystal growth can not be neglected, as they are responsible of the final size and structure of the crystals, which are essential parameters in struvite recovery processes. For instance, Abbona and Boistelle (1979) demonstrated that for high growth kinetics crystals adopted a flat configuration with large {001} faces while for low growth kinetics "*stick-like crystals*" without {001} faces were formed.

2.3.3 Parameters affecting struvite crystallisation

Predicting and controlling nucleation and crystal growth is all the more complex as they depend on a combination of factors such as the initial crystal states of the compounds, phenomena of matter transfer between solid and liquid phases, thermodynamic and kinetics of reaction, as well as several physico-chemical parameters including: pH, supersaturation level **Ω**, mixing energy, temperature and the presence of foreign ions in the precipitating solution.

2.3.3.1 pH

The pH at which struvite may precipitate is one of the main factor influencing the crystallisation process as it is linked to the notion of solubility and supersaturation. It can then control the rate of precipitation and, as seen previously, the induction period. In WWTPs, struvite scaling occurs partly because of a pH increase as a result of CO_2 stripping ($HCO_3^- \rightarrow CO_2 \uparrow + OH^-$) (Neethling and Benisch, 2004).

Several authors have studied the effects of pH on struvite crystallisation, and it clearly appeared that it affects mostly the solubility constant. For instance, Borgerding (1972) reported that struvite solubility could decrease from around 3000 $mg.L^{-1}$ to less than 100 $mg.L^{-1}$ for pH rising from 5 to 7.5, while Buchanan *et al.* (1994) identified pH 9 as the pH of minimum solubility for struvite.

Furthermore, Booker *et al*. (1999) and Stratful *et al.* (2001) defined in their respective studies that it exists a pH range through which the precipitation rate of struvite is optimum. The data in Figure 2.4 illustrates this point. By plotting the molar removal of NH_4^+, Mg^{2+} and PO_4^{3-} by struvite crystallisation from initial solutions with an equimolar quantity of both N and P, and an excess of Mg, the removal of the different species is maximum within the pH range 8.5 to about 9.5 (Booker *et al.*, 1999).

According to equation (2.*i*), as struvite precipitates, it triggers a release of protons ions in solution. A change in pH occurs then in solution during the crystallisation process. The drop in pH is characteristic of the speed at which the first particles of struvite occurs, and is linked to the rate of struvite formation which can influence the quality of the crystals formed. It can thus be used as a good indicator of struvite nucleation (Bouropoulos and Koutsoukos, 2000; Kabdaşli *et al.*, 2004; Le Corre *et al.*, 2005).

A high initial pH can also be limiting in the sense that it causes the transformation of NH_4^+ ions into gaseous ammonia, reducing thus the nitrogen concentration and affecting the molar ratio Mg:N:P (minimum value 1:1:1) necessary to form struvite.

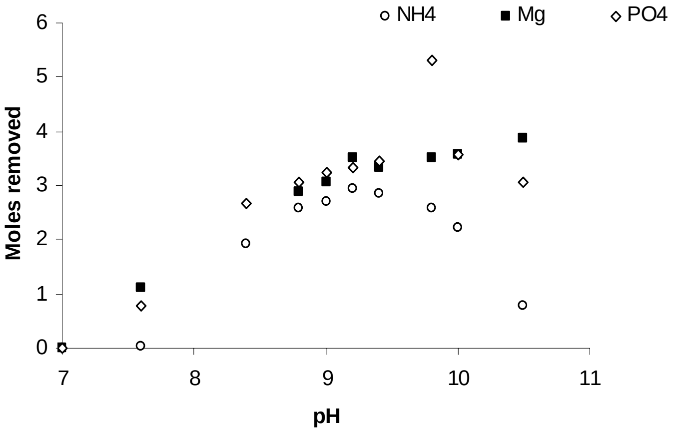


Figure 2.4. *Removal of Mg^{2+}, NH_4^+ and PO_4^{3-} by precipitation of struvite at various pH values, Booker et al., (1999).*

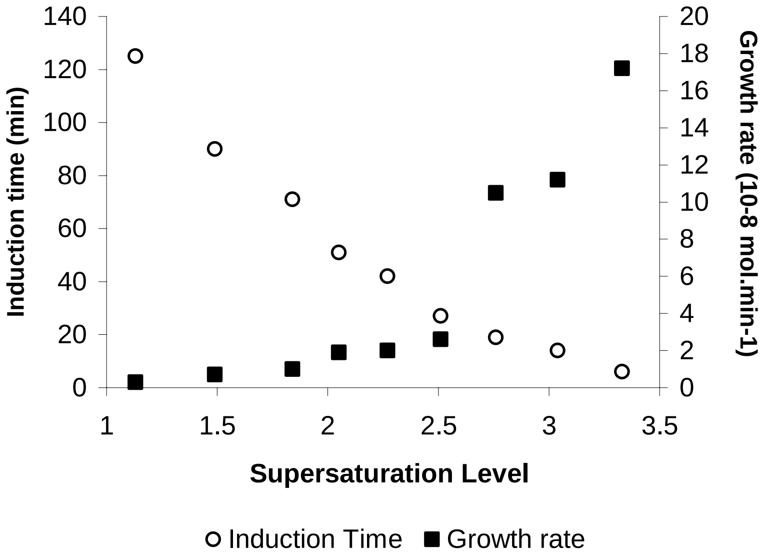
Solution pH also affects struvite crystal growth rate. Ohlinger *et al.* (1999) showed that the accumulation of struvite on stainless steel coupons in contact with supernatants of anaerobically digested sludge was influenced by the pH. An increase in pH caused an increase of supersaturation and a resultant increase in the growth rate. This was shown to be responsible for 30 % of the growth rate difference between low and moderate mixing area, and of 9 % of the growth rate between moderate and high mixing area.

Finally, pH can affect struvite crystal characteristics. Matynia *et al.* (2006) demonstrated that an increase of pH from 8 to 11 could decrease 5 times the mean crystal size of struvite formed in synthetic solutions. Le Corre *et al.* (2006a) have also showed that pH was responsible of change in struvite zeta-potential, hence influencing struvite agglomerative properties. They also indicated that in synthetic solutions at a pH 10.5 they formed $Mg_3(PO_4)_2.22H_2O$ rather than struvite. $Mg_3(PO_4)_2.22H_2O$ usually precipitates at pH 9 and above, and depending on limiting conditions could interfere with struvite precipitation (Tünay *et al.*, 1997).

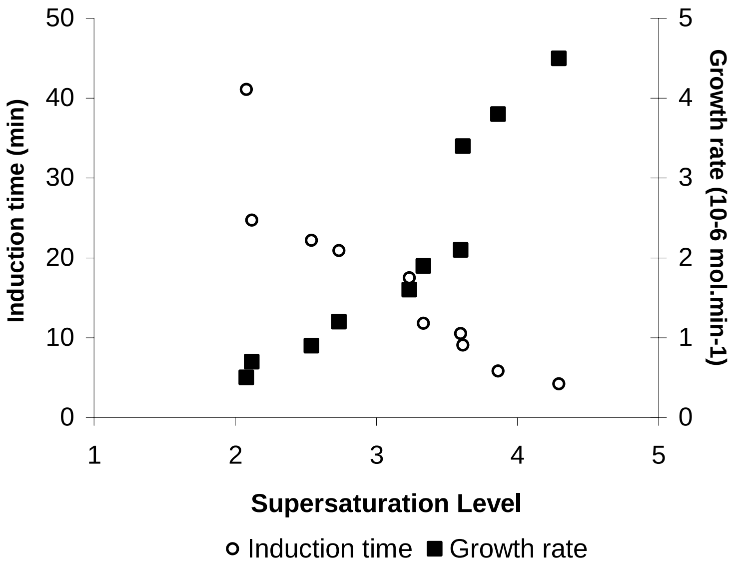
2.3.3.2 Supersaturation ratio

At a fixed pH, the supersaturation level of the solution affect the crystallisation process in terms of induction time and influence the rate at which the struvite crystals are produced. Bouropoulos and Koutsoukos, (2000) demonstrated that at a fixed pH of 8.5 struvite spontaneous precipitation was dependant on the solution supersaturation and struvite growth rate was following a power law $R_p=k_p.\sigma^n$ where σ is the relative supersaturation ($\sigma = \Omega^{1/3}$-1), n is the apparent order of the reaction, and k_p the constant of precipitation. They showed that an increase of Ω value from 1.13 to 3.33 shortened by around 20-fold the induction time whereas it increased more than 55 times the crystal growth rate (Figure 2.5).

Using the same methods but a different solvent (*i.e.* synthetic water instead of de-ionised water), Kofina and Koutsoukos (2005) confirmed these results by demonstrating a high order dependence of struvite crystallisation over the range of supersaturation (2.07 to 4.29) synonymous of surface diffusion mechanisms. However, as demonstrated on Figure 2.5, growth rate over this range of supersaturation were higher, and induction time shorter than for comparable supersaturation levels measured by Bouropoulos and Koutsoukos, (2000). This indicated an influence of the nature of solution in which struvite is precipitated as Kofina and Koutsoukos (2005) precipitated struvite by mixing $NH_4H_2PO_4$ and $MgSO_4.7H_20$ solutions into synthetic water composed of glucose, $NaHCO_3$, NaCl and $NaNO_3$ whereas Bouropoulos and Koutsoukos (2000) mixed solutions of $MgCl_2.7H_20$ and $NH_4H_2PO_4$ diluted in de-ionised water.



Adapted from Bouropoulos and Koutsoukos (2000)



Adapted from Kofina and Koutsoukos (2005)

Figure 2.5. *Effect of supersaturation ratio on the induction time, and growth rate of struvite at pH 8.50, 25° C.*

Doyle *et al.* (2002) illustrated the dependence of struvite growth rate on supersaturation level of the centrate liquors issued from sludge digesters. The accumulation of struvite on stainless steel coupons during 40 hours (Table 2.7) showed that at constant supersaturation level the growth rate reached up to 7 times its initial value from 8 h to 40 h of precipitation.

Table 2.7. *Scaling struvite rates on stainless steel coupons submerged in centrate liquors. Doyle et al. (2002).*

Supersaturation Ω	Scaling rate ($gm^2.h^{-1}$)		
	0-8h	**16-24h**	**32-40h**
1.7	0.4	2.6	2.8
2.2	1.2	1.9	3.8
5.3	1.2	3.9	5.4

2.3.3.3 Temperature

Although temperature has a lower impact on struvite precipitation than other parameters such as pH and supersaturation (Durrant *et al.*, 1999), it can affect struvite solubility and crystal morphology. Aage *et al.* (1997), and Burns and Finlayson (1982) showed the influence of the temperature on the solubility product of struvite (Figure 2.6). Struvite solubility product, determined with a radiochemical method, increased from $0.3.10^{-14}$ to $3.73.10^{-14}$ between 10 ºC and 50 ºC in Aage *et al.* (1997) study. Burns and Finlayson, (1982) obtained a similar trend using pH and concentrations measurements, but here the increase in solubility was from $0.7.10^{-14}$ to $1.45.10^{-14}$ at 25 ºC and 45 ºC respectively. As the solubility product is linked to the supersaturation state of the solution in which crystals may occur, the precipitation of struvite is more difficult to obtain at high temperatures. This may explain why the temperature range between 25 and 35 ºC, is usually used by authors to study struvite precipitation either from synthetic solutions or real anaerobic digested liquors.

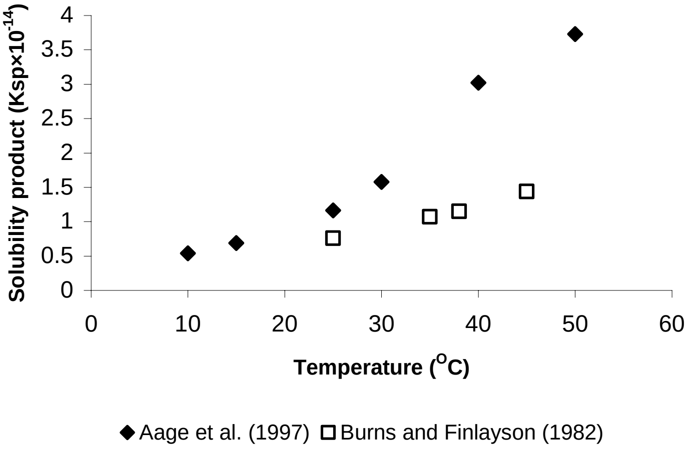


Figure 2.6. *Evolution of struvite solubility product (pK_{sp}) on temperature according to Aage and Burns data (Aage et al., 1997; Burns and Finlayson, 1982).*

Temperature is also known to affect crystal growth as it affects the relative rates of diffusion and surface integration. High temperature of crystallisation usually leads to diffusion controlled growths, while low ones lead to surface integration controlled growths (Jones, 2002). Moreover the rate of crystal growth often increases at high temperature, and can affect crystal size shape and type. Boistelle *et al.* (1983) effectively noticed a change between struvite crystals obtained at 25° C and crystals obtained at 37° C. While at 25° C struvite crystal were found "*rectangular and prismatic*", at 37° C they were mainly "*square and thick*". This was later on confirmed by Babić-Ivančić *et al.* (2002) who explained that for an identical range of concentrations, struvite crystals adopted a denditric form in a wider zone at 37° C than at 25° C. They also indicated that for high magnesium concentrations, high temperature could affect the nature of crystal formed, with for example struvite transforming faster into newberyite ($MgHPO_4.3H_2O$) than at lower temperature.

2.3.3.4 Mixing energy or turbulence

Mixing energy (or turbulence) can also influence the precipitation of struvite. In areas of high turbulence, CO_2 liberation can cause an increase of pH in the solution favouring thus the occurrence of struvite crystals.

For constant thermodynamics conditions, Ohlinger *et al.* (1999) showed that different mixing energy could influence struvite crystal size and shape as (in area of low turbulence where struvite was precipitating) the crystals formed were more elongated than in area of high mixing speeds suggesting transport limitation of struvite growth. He demonstrated that lowest growth rates (*i.e.* 1.8 $g.m^{-2}.d^{-1}$) occurred in quiescent zone of the process where struvite was precipitating, while the highest ones (*i.e.* 22.4 $g.m^{-2}.d^{-1}$) were always found in high mixing environments.

In struvite crystallisation reactors, the mixing energy is known to affect size of crystals formed. Indeed, high mixing speeds can accelerate nucleation rate hence limit crystal growth, and is also known to increase crystal breakage (Durrant *et al.*, 1999).

2.3.3.5 Presence of foreign ions

Impurities in solution are also known to affect the growth rates of crystalline compounds due to blocking of sites where crystals could formed, inhibiting the increase of crystal size (Jones, 2002). Although few authors have studied the influence of foreign ions on struvite crystallisation, it is known that the presence of calcium or carbonates ions in the media affects negatively the growth rate and can lengthen the induction time preceding the first occurrence of crystals (Koutsoukos *et al.,* 2003). In wastewater effluents where calcium levels can be relatively high (Table 2.8), calcium ions can interact with phosphate or carbonate ions to form calcium phosphates (commonly as hydroxyapatite) or calcium carbonates according to equation (*xv*) and (*xvi*) (Le Corre *et al.*, 2005).

$$5Ca^{2+} + 3PO_4^{3-} + H_2O \rightarrow Ca_5(PO_4)_3OH + H^+ \qquad (2.xv)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad (2.xvi)$$

Table 2.8. *Average levels of magnesium and calcium in settle sludge liquors of different WWTP in United Kingdom. (Adapted from Parsons et al., 2001).*

	Magnesium (mg.L^{-1})	Calcium (mg.L^{-1})	Molar ratio Mg:Ca
Barston	46	257	1:3.4
Coleshill	19	94	1:3
Mansfield	52	123	1:1.4
Milcote	34	165	1:3
Owestry	31	185	1:3.6
Spernal	53	321	1:3.7
Wanlip	41	188	1:2.8

Le Corre *et al.* (2005) demonstrated that for molar ratios Mg:Ca 1:1 and above, struvite formation was limited and even inhibited by the formation of an amorphous calcium phosphate. Kabdaşli *et al.* (2006a) also showed that the presence of sodium, calcium, sulphate and carbonate-bicarbonates ions had an impact on either induction time or struvite crystal morphology and sizes. To illustrate, for identical supersaturation ratios, an increase of concentrations in sulphate from 12.5 mM to 25 mM, increased the induction time from 1 min 59 to 4 min 25s.

2.4 Phosphorus removal and recycling as struvite

2.4.1 Phosphorus removal from wastewater

2.4.1.1 Current treatments

Unlike nitrogen, the phosphorus contained in wastewater effluents has to be transformed into a solid form to be removed (Heinzmann, 2004). Traditional phosphorus removal processes work then by fixing the phosphorus into the sludge:

- either chemically by precipitation of soluble phosphorus with aluminium or iron salts into insoluble phosphates compounds. Separation of the precipitates is then achieved by sedimentation, filtration or flotation. (Parsons and Berry, 2004)
- or biologically (*i.e.* BNR, EBPR) using the ability of some micro-organisms to accumulate phosphates as polyphosphates for their own metabolism (Mulkerrins *et al.*, 2004, Driver *et al.*, 1999),

These processes are efficient in the sense that they can reduce phosphorus concentrations in wastewater treated to less than 1 mg.L^{-1} (Booker *et al.*, 1999, Tebutt, 1998), but they present some disadvantages, among them:

⇒ the accumulation of nutrients (P, N) in the resulting sludge (Parsons and Doyle, 2004),

⇒ an important sludge production especially when using chemical processes where P is removed by the formation of P-rich sludge (*i.e.* iron phosphates and iron hydroxides precipitation) leading to significant increases in sludge management costs (Woods *et al.*, 1999).

⇒ the reaction of phosphorus with soluble magnesium and ammonium ions leading to the spontaneous accumulation of struvite in pipelines, and different items of the process. Indeed, previous studies have reported large increases of soluble Mg levels in effluents treated with iron metal salts, raised the potential to spontaneously form struvite (Mamais *et al.*, 1994, Laridi *et al.*, 2005).

Finally, if both processes are efficient in removing phosphorus, the phosphorus precipitates generated by these methods are not recyclable for reuse by the industry (de-Bashan and Bashan, 2004)

2.4.1.2 The crystallisation solution

Another approach to remove phosphorus from wastewater effluents is the crystallisation of reusable compounds such as calcium phosphate or struvite ($MgNH_4PO_4.6H_2O$), (Doyle and Parsons, 2002). This has gained particular interest since both struvite and calcium phosphates have been identified as marketable fertilisers (Gaterell *et al.*, 2000) although their application remains principally experimental due to problems linked to the economical value of the process and the product formed, the need of an accurate pH control, and the formation of fines (Adnan *et al.*, 2003a/b).

Several laboratory and pilot scale studies have been carried out to assess the potential of such methods in removing and recovering phosphorus as a reusable product, and a few of them have been tested at full scale in The Netherlands (Giesen, 1999) and Italy (Battistoni *et al.*, 2005a/b) (Table 2.9). However Japan is the only country where complete P removal and recovery from anaerobically digested sludge liquors as struvite has been implemented and the resulting production sold to fertiliser companies (Gaterell *et al.*, 2000; Ueno and Fujii, 2001)

The recovery technologies currently tested are based on the crystallisation of phosphorus as hydroxyapatite (HAP) or struvite (MAP) and the majority uses sludge liquors generated from anaerobic digesters as their influent (Table 2.9). The technologies can be classified in three main categories:

⇒ Selective ion exchange (*i.e.* RIM-NUT® process, Liberti *et al.*, 1986).

⇒ Precipitation in a stirred reactor (Laridi *et al.*, 2005; Stratful *et al.,* 2004; Mangin and Klein, 2004; Seco *et al.*, 2004)

⇒ Precipitation in fluidised bed reactors or air-agitated reactors, which operating principles are the base of a majority of processes experimentally trialled (Von Münch and Barr, 2001, Ueno and Fujii, 2001, Battistoni *et al.*, 2005a/b)

FBRs are the most studied processes for struvite crystallisation. According to Mangin and Klein (2004), FBR are mainly chosen because solid and liquid retention times are not systematically similar. Their design can be integrated as an additional process step to most wastewater treatment works, as they can be continuously feed with liquors, while the solid product can be sequentially harvested.

Table 2.9. Crystallisation technologies for P recovery

References	Process/Technology	Scale	Source	P removal	P recovered form
Liberti *et al.* (1986)	Selective ion exchange, RIM-NUT Process®	Full scale	Chlorinated secondary effluents	≥ 90%	MAP
Fujimoto *et al.* (1991)	Aeration, stirring and crystallisation in a stirred reactor.	Bench and pilot	Supernatant from anaerobic digester	60 to 70%	MAP
Brett *et al.* (1997).	▪CSIR Fluidised bed crystallisation column seeded with quartz sand	Bench	Anaerobic digester supernatant, pond effluents, abattoir wastes	90%	MAP/HAP
	▪Kurita fixed bed seeded with phosphate rock grains (Kurita Water Industries Ltd, 1984)	Full scale	Secondary effluent of STW	Up to 90%	HAP
Giesen (1999).	DHV Crystalactor®	Full scale	Supernatant from anaerobic sludge	-	CaP
Battistoni *et al.* (2000)	FBR, seeded with sand.	Bench	Anaerobic supernatants after belt press.	62 to 81%	MAP, or mixed MAP/HAP
Jaffer (2000)	Aerated reactor	Bench	Centrifuge liquors	Up to 97%	MAP
Ohlinger *et al.* (2000)	FBR seeded with struvite crystals	Pilot scale	Sludge lagoon supernatant	> 80%	MAP
Ueno and Fujii (2001)	FBR	Full scale	Dewatered liquors from anaerobic sludge digestion	≥ 90%	MAP
Von Münch and Barr (2001)	Air agitated column reactor	Pilot scale	Centrate from anaerobically digested sludge	94%	MAP
Suzuki *et al.* (2002)	Aeration column	Pilot scale	Swine waste water	65%	MAP/HAP
Wu and Bishop (2003)	2L beakers seeded with sand or struvite	Bench	Centrate from sludge dewatering centrifuge	Between 65 and 70%	MAP
Adnan *et al.* (2003a/b)	FBR	Pilot scale	Synthetic liquors	90%	MAP
Cecchi *et al.* (2003)	FBR seeded with silica	Full scale	Anaerobic supernatant	Average of 62%	MAP/HAP
Jaffer and Pearce (2004)	Air-agitated reactor	Full scale	Centrifuge liquors	60-80%	MAP
Ishikawa *et al.* (2004)	FBR seeded with struvite crystals	Full scale	Centrate from dewatering system	≥ 90%	MAP
Seco *et al.* (2004)	Stirred reactor	Pilot	Supernatant from sludge digestion	90%	MAP/CaP
Mangin and Klein, (2004)	Stirred reactor	Pilot	Synthetic liquors	> 60%	MAP
Laridi *et al.* (2005)	Stirred reactor	Pilot	Pre treated swine wastewater	Up to 98%	MAP
Battistoni et *al.* (2005b)	FBR	Full scale	Anaerobic supernatants after belt press.	64-69%	MAP/HAP

**MAP: magnesium ammonium phosphate; HAP: Hydroxyaptite; CaP: Calcium phosphate*

2.4.2 Design and description of processes used for struvite crystallisation

2.4.2.1 Selective ion exchange processes

2.4.2.1.1 The RIM-NUT® Technology

This type of process consists of a three stage combined ion exchange and precipitation process. Secondary effluents from an activated sludge sedimentation tank enter a combined resin columns system made of 2 cationic and 2 anionic columns (Figure 2.7). The cationic resins (R_c), filled with natural zeolite, remove ammonium ions following the general equation: $R_cNa+NH_4^+ \rightarrow R_cNH_4+Na^+$ while the anionic resins (R_a), filled with a basic resin, remove PO_4^{3-} ions according to the general equation: $2R_aCl+HPO_4^{2-} \rightarrow R_{a2}HPO_4+2Cl^-$.

The resultant enriched phosphate and ammonium effluents are mixed and enter a reactor where struvite is precipitated by addition of NaOH, $MgCl_2$, HPO_3 to reach the required molar ratio Mg:P:N of 1:1:1, (Liberti *et al.*, 1986).

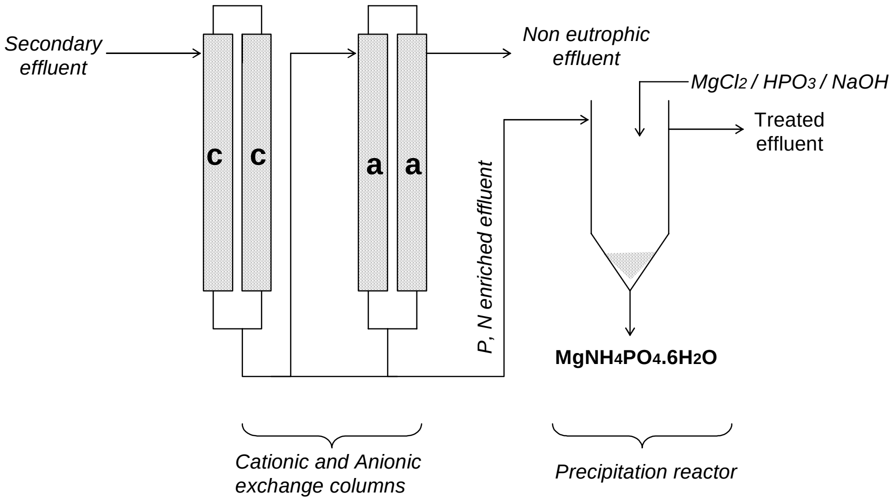


Figure 2.7. *The RIM-NUT process (adapted from Liberti et al., 1995)*

2.4.2.1.2 Advantages and drawbacks

The RIM NUT® process uses chemical dosing to precipitate struvite from enriched P and N effluents. No additional sludge is produced and P removal of 90 % can be achieved. The downside of this process is the competition by NO_3^{2-}, HCO^{3-} and SO_4^{2-}. Indeed, according to Petruzzelli *et al.* (2004), the efficiency of the process used by Liberti *et al.* (2001) was limited by the lack of phosphate ions selectivity of the anion resin and they have undertaken research of new phosphate sorbents to remedy this problem.

Furthermore, a monitoring of P and N concentration in the enriched effluent is also required to dose the chemicals in the precipitation reactor. And finally the ions exchange process require extra time to recover the struvite and needs regular regenerations of the resin (*i.e.* a regeneration cycle with NaCl is required every 3 hours, Brett *et al.,* 1997) due to the fouling by solids present in regenerated effluents. The combination of all this factors are known to affect the economics of the process (Petruzzelli *et al.*, 2004)

2.4.2.2 Stirred reactors

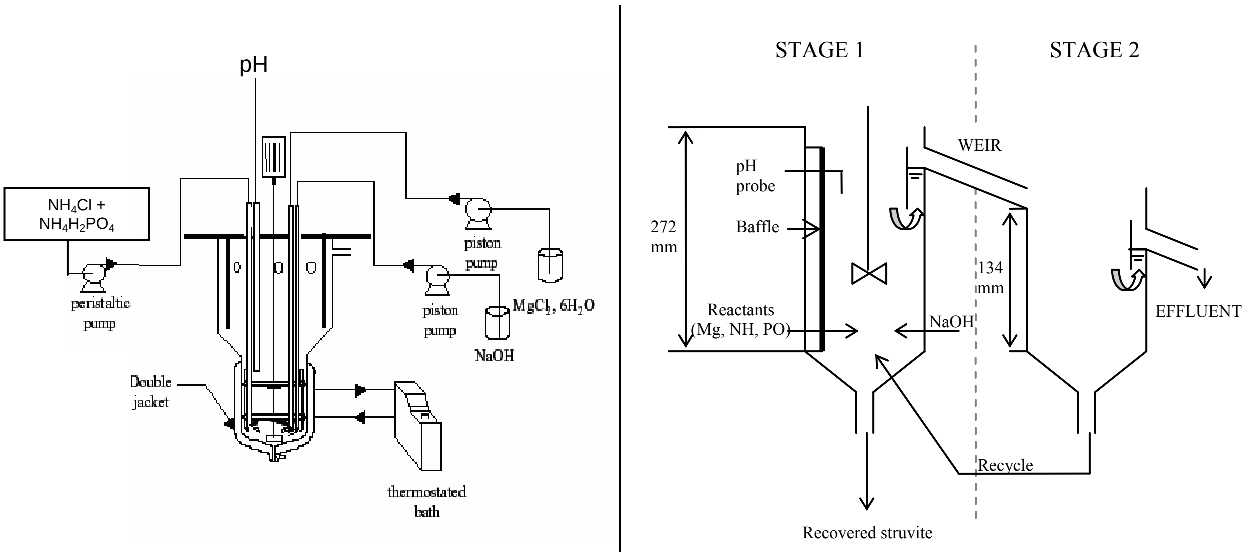
2.4.2.2.1 Operation principles

In these types of processes, struvite is crystallised in the reactor by addition of chemicals, usually $MgCl_2$, to reach the minimum molar ratio Mg:P 1:1. The pH required to set off the nucleation is typically adjusted by NaOH addition, while a propeller is used to mix the solutions and favour the occurrence of struvite crystals. A settling zone has to be integrated to the reactor to maintain particles in it (Mangin and Klein, 2004).

To date only a few studies have studied the efficiency of mechanically stirred reactors for struvite crystallisation (Reggy *et al.*, 2002; Yoshino *et al.*; 2003, Stratful *et al.*, 2004). One pilot scale process and a laboratory scale one are illustrated in Figure 2.8.

The first stirred reactor presented here (Figure 2.8) has been designed and developed at pilot scale at the "Laboratoire d'Automatique et de Génie des Procédés" in Lyon (Regy *et al.,* 2002). Its capacity in removing phosphorus from synthetic liquors as struvite has been assessed with and without seed material (sand or struvite pellets). Seco *et al.* (2004) used a similar reactor to assess the effects of pH and Mg:N:P molar ratios on struvite precipitation from supernatants of digested sludge.

In this reactor type, the crystallisation takes place in the bottom part of the reactor. The reacting solutions, a phosphate solution made by dilution of NH_4Cl+$NH_4H_2PO_4$+NaOH in drinking water, $MgCl_2$ and NaOH for the experiments on synthetic liquors (Regy *et al.,* 2002), or digested sludge supernatant (Seco *et al.*, 2004) were mechanically agitated and the pH adjusted with sodium hydroxide to values around 9. The upper part of the reactor, or settling zone, was enlarged to keep the solid particles in the reactor.



V=20.55 L

Adapted from Regy *et al.*, (2002)

V_{stage1}=1.4 L / V_{stage2}=1.0 L

Adapted from Stratful *et al.*, (2004)

Figure 2.8. *Pilot stirred reactor for struvite crystallisation.*

The second process, a continuously stirred tank reactor (CSTR) (Figure 2.8), tested at laboratory-scale by Stratful *et al.* (2004) combined a CSTR and a second tank used for recycling of fines. Struvite was precipitated from solutions of $MgSO_4.7H_2O$, NH_4Cl and NH_2HPO_4. pH was adjusted in the CSTR to values between 8 and 9 by addition of NaOH. The second reactor was used to test the influence on crystal growth of recycling fine struvite particles issued from the main reactor.

2.4.2.2.2. Advantages and drawbacks

Mechanically stirred reactors conception is simple and P removal efficiencies are relatively high. Regy *et al.* (2002) achieved P removals over 60 % for precipitation from synthetic liquors, whereas Seco *et al.* (2004) reached up to 90% from anaerobic digestion supernatant. However, in the Seco *et al.* (2004) example the removal percentage was higher due to the presence of calcium in the liquors leading to the co-precipitation of P as struvite (76.9%) and calcium phosphate (23.1%). In their laboratory scale CSTR, Stratful *et al.* (2004) achieved magnesium removals ranging from 76 % to 88 % depending on stirring speed and pHs of precipitation used. Both processes achieved reasonable struvite mean crystal size of 300 μm and 425 μm for respectively Regy *et al.* (2002) and Stratful *et al.* (2004). Improvement of crystal growth by seeding with sand or struvite in this type of reactor is difficult due to high mixing speed necessary to fluidise the seed (Regy *et al.*, 2002).

The main advantage of this type of processes is their simplicity of operation when compared to other processes such as ion exchange and fluidised bed reactors (Stratful *et al.*, 2004). One of the main problems of their application at full scale would be the fouling of the impeller when used in continuous mode. Furthermore, growth limitation and production of large quantities of fines can be observed due to high mixing speed necessary to homogenise the solution and keep particles in suspension (Regy *et al.*, 2002).

2.4.2.3 Fluidised bed reactors and air agitated reactor

2.4.2.3.1 Process principles

Processes most commonly used to crystallise struvite from wastewater are fluidized bed reactors FBR or air agitated reactors. In such processes, struvite particles can precipitate spontaneously from supernatants following the addition of chemicals to reach the molar ratio Mg:P:N 1:1:1. Once the nucleation of the first particle starts, the growth takes place either by interaction of small struvite particles together that is to say agglomeration (air agitated reactors), or by contact on seed materials (*e.g.* sand or struvite) constituting the initial bed of particles (FBR). Suspension of particle is controlled by either liquid flowrates (Cecchi *et al.*, 2003) or an up-flow circulation of air (Suzuki *et al.,* 2002; Jaffer, 2000), so that the particles in the reactor are in continuous motion, and behaves like a dense fluid.

Methods using air agitated or fluidized bed reactor to recover phosphorus as struvite crystals have been widely investigated and a selection of them is presented in table 10a and 10b. Feed solutions, typically centrate liquors and anaerobic digested sludge, enter in the reacting zone from the bottom of the reactor. Depending on the reactors configuration, influent flowrates can vary from 0.004 to 0.3 $m^3 \cdot h^{-1}$ (Table 10a and 10b). When used, upward airflows allow a uniform fluidisation of particles to avoid growing struvite particles from settling down. Airflows can also help to reach the pH value (*i.e.* 8-9) necessary for struvite crystallization (Battistoni *et al.*, 2004 and 2005a). However pH is often adjusted by NaOH addition (Table 10a and 10b). The velocity of the flow (as well as the pressure in the reactor) decreases from the column to the upper section allowing the evacuation of the treated effluent at the top of the reactor, while struvite particles (and seed) are fluidized and grow in the column section. Removal of phosphorus achieved by these types of processes can vary from 60 % up to 94 % (Table 9). The solid phase is partly or totally recovered from the reactor when particles reached a reasonable size for reuse, this mean that such reactors work in batch for the solids phase and continuously for the liquid phase (Mangin and Klein, 2004). Solid retention times are usually in the order of day with for example 3 to 14 days for Shimamura *et al.* (2003) to achieve particle size between 0.41 to 1.43 mM or 6 to 17 days for Adnan et *al.* (2003a/b) to reach size of struvite crystals up to 3.5 mm. In that latest case, size of particles was enhanced by agglomeration phenomena. But size of struvite particles is also strongly dependant on the utilisation of seed materials. To illustrate, Von Münch and Barr (2001) (Table 10a) who used 500 g of crushed struvite crystal to seed their agitated reactor achieved an average size of particles of 110 µm whereas Battistoni, (2004) observed an increase of sand grains from 0.9 mm to 1.4 mm by struvite (and hydroxyapatite) growth onto them.

Table 2.10a. *Struvite crystallisation in fluidised bed or air agitated reactors.*

References	**Process**	**Method**	**Shape**	**Influent**	**Seed material**	**Dimensions**			**Bed height, volume or mass**	**Flow rates**	**pH adjustment**	**Size (mm) of recovered product**	**Fines**	**RT (days)**
						***H (m)**	***D (m) ***	**V (m^{-3})**						
Battistoni, *et al*. (1997)	Bench scale FBR	Batch	Glass column	Anaerobic supernatants	quartz	0.42	0.058	1.1.10^{-3}	*H_c=0.15 m *H_x=0.30 m	0.11<Up flowrate <0.3 m^3.h^{-1}	Air aeration 8.3-8.6	-	Yes (8.7 up to 24.5%)	
	Stripper		Tank					5.10^{-3}		Air flow rate=0.9 m^3.h^{-1}				
Battistoni *et al.* (2000)	FBR	Batch	Column connected to an expansion tank	Anaerobic supernatants	quartz sand (0.21 to 0.35mm)	1	0.09	6.36.10^{-3}	*H_c =0.4m *H_x =1 m	4 to 19 L.h^{-1}	Air aeration 8.1-8.9	0.4	yes	
	Stripping tank+ stripping device		Tank +column			-	-	18.10^{-3} + 3.10^{-3}		15<Airflow rate< 19 L.h^{-1}				
Ohlinger *et al.* (2000)	Pilot scale	Batch and continuous	Acrylic plastic column	Sludge lagoon supernatant	struvite	1	0.0635	3.17.10^{-3}	*H_c =0.31 m	Influent flowrate= 3.2 to 20 L.h^{-1}	Medium bubble aeration	1.7	-	
	Stripping tank+ stripping device				(0.6 to 1.18mm)				100% expanded	upflow velocity =11 cm.s^{-1}	(+0.1N NaOH when necessary)			
	pH adjustment tank		high density polyethylene plastic			0.30 x 0.30		9.10^{-3} or 19.10^{-3}						
Ueno and Fujii (2001)	FBR (full scale)	continuous	Column + precipitation portion	Dewatering filtrate from anaerobic sludge digestion	granulated struvite	9	1.43 3.6	-	-	filtrate flow rate= 650 m^3.d^{-1}	$Mg(OH)_2$ 8.2-8.8	0.5 to 1.0	Yes	10
Von Münch and Barr (2001)	Air agitated reactor	continuous	Reaction zone + Settling zone	Anaerobic digested liquors	crushed struvite		0.3 0.6	143L	-	Air~7L.min^{-1} Feed: 0.3-2L.min^{-1}	8.5-9 with Alkali	Range from 0.025-0.215 $D_{0.5}$= 0.11	loss of fines	5
Shimamura *et al.* (2003)	Air agitated tank coupled with fines recycle tank	continuous	Column with enlarged section	Anaerobic wastewaters	struvite fines	-	-	-	-	Raw water in main tank = 1.1 to 6.7 m^3.d^{-1} Raw water in sub tank = 0.11-0.32 m^3.d^{-}	NaOH	0.41-1.43	Yes	3-14 days

**H_c: High of the compressed bed, H_x: High of the expanded bed, RT: solids retention time, calc: calculated, H: height, D: diameter, V: volume, $D_{0.5}$: mean crystal size, calc: calculated, NM: not mentioned*

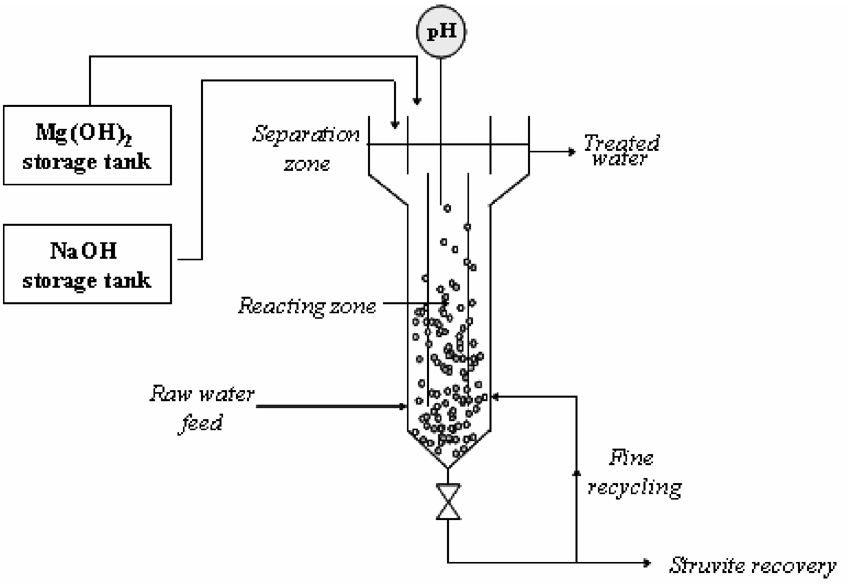
***Table 2.10b.** Review of struvite crystallisation in fluidised bed reactors.*

References	Process	Method	Shape	Influent	Seed material	Dimensions			Bed height, volume or mass	Flow rates	pH adjustment	Size (mm) of recovered product	Fines	Solid RT (days)
						*H (m)	*D (m) *	V (m^{-3})						
Adnan *et al.* (2003a/b)	FBR (pilot scale)	continuous	4 sections plastic polyvinyl reactor:	synthetic water $MgCl_2.6H_2O$ + $(NH_4)H_2PO_4$ $+NH_4Cl$	-	5	0.04-0.20	$28.3.10^{-3}$		up flow rate=0.16 to 0.22 $m^3.h^{-1}$	NaOH	3.5		6 to 17
Ishikawa *et al.* (2004)	2-tank FBR (full scale), main reactor	continuous	Reaction zone+settling portion	Centrate from dewatering system	Struvite fines (0.3mm)	1.8	0.80 for the settling portion	0.904 (calc.)	*H_x ~2	Circulated water (+ $MgOH_2$) = 0.5 to 2.5 $m^3.h^{-1}$ raw water = 0.5-0.8 $m^3.h^{-1}$	8	0.4	Yes $D_{0.5}$= 0.1mM	3-4
			Air lift pump				0.65			Upward Air flow				
	Sub reaction Tank		Reaction portion (including settling zone)	Centrate from dewatering system	Struvite fines (0.1mm)	2.4	0.25	0.117 (calc.)	-	raw water flowrate=0.06 to 0.15 $m^3.h^{-1}$		0.3	yes	
			Air lift pipe				0.4			Circulated water = 0.06 to 0.18 $m^3.h^{-1}$				
Cecchi *et al.* (2003)	FBR (full scale)	continuous	column enlarged at the top:	anaerobic supernatants	Silica pellets	4.4		1.41		feed flow rate= 1 or 1.5 $m^3.h^{-1}$	air stripping	> 0.1 to 0.5	-	-
			column section			4	0.6				8.3 or higher			
			enlarged section			0.4	1.2							
Jaffer and Pierce (2004)	Aerated reactor	continuous	Reaction zone + Settling zone	Centrate liquors	Recycled struvite	*NM**	*NM**	5.8 + 6.8 or 13.6	-	Air= 60-140 $L.s^{-1}$	7.5-9 with air and NaOH	0.3 maximum	*NM**	*NM**
Battistoni, 2004, Battistoni *et al.* (2005a)	Full scale FBR Stripping tank+ stripping device	Continuous	Column coupled to a Dortmund apparatus to avoid was out of fines	Anaerobic supernatants	Sand seeded (0.09mm) Or auto-nucleated	-	-	1	475 kg		Air stripping	1.4	yes	-
Suzuki *et al.* (2005)	Aerated reactor	continuous	Aeration column in a reaction tank	Swine wastewaters	None or Metallic surface	3.64	1.50	4.32	-	Air=15.6 $m^3.h^{-1}$ Swine wastewater = 4.0 $m^3.d^{-1}$	Air stripping	-	*NM**	30

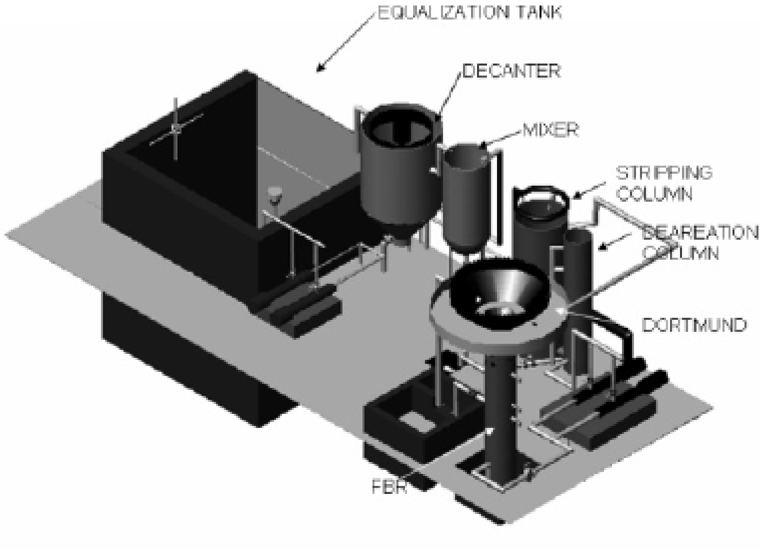
**H_c: High of the compressed bed, H_x: High of the expanded bed, RT: solids retention time, calc: calculated, H: height, D: diameter, V: volume, $D_{0.5}$: mean crystal size, calc: calculated, NM: not mentioned*

2.4.2.3.2 Examples of two typical FBR and Air agitated designs

Good illustrations of this type of reactors are the processes used at full scale by Ueno and Fujii (2001) for Unitika Ltd, Japan and by Battistoni (2004) (Figure 2.9).



-A- Air agitated reactor
Adapted from Ueno and Fujii (2001)



-B- FBR seeded with sand
Courtesy of Battistoni (2004)

Figure 2.9. *Example of full scale Fluidised Bed type reactors*

The process reported by Ueno and Fujii (2001) (Figure 2.9-*A*-) consists of an air agitated column. Digested sludge liquors enter at the bottom of the reactor. $Mg(OH)_2$

and NaOH are respectively added in the reactor to reach a minimum 1:1 Mg:P molar ratio and adjust the pH to values ranging from 8.2 to 8.8. Struvite particles are kept in suspension by an upward airflow and grow up to sizes between 0.5 and 1.0 mm in 10 days. They are periodically separated from fines. Fines particles are recycled and returned to the reactor to act as seed material, while the larger particles are dried before being sold as a raw material for the fertiliser industry. Minimum P removals of 90 % obtained, and the good quality of the struvite generated make of this process the only full scale process economically reliable.

The process experimented at full scale by Battistoni (2004) (Figure 2.9-*B*-) used anaerobic supernatant from Treviso WWTP (Italy). Before entering the FBR, supernatant are pre-treated to remove suspended solids and stored in an equalisation tank to insure continuous feeding of the FBR. The influent is stripped with air then transferred into a de-aeration column before entering the FBR filled with sand grains (Battistoni, 2004). pHs of operation vary from 8.3 to 8.7. P removals achieved were of 61 % average in this configuration and sand particles increased in size from 0.09 mm to 0.14 mm. This process has also been recently tested without application of seed material by auto-nucleation of struvite, achieving in that configuration removals up to 86 % and particles reaching 0.20 to 0.30 mm (Battistoni *et al.*, 2005a).

2.4.2.3.3 Limitation of FBR and air agitated processes, areas of improvement

The size of particle is an essential parameter to control for practical reasons and its implications for any future reuse of struvite as a fertiliser. One of the solutions to produce larger struvite particles in a FBR is the utilisation of a seed material so that struvite can form agglomerates with seeds. This method has proved to be efficient with particle sizes ranging from 0.1mm (Cecchi *et al.,* 2003) up to 1.7 mm (Ohlinger *et al.*, 2000). However, the operation of such processes requires high flow rates and/or significant mixing energy to insure the bed of seeds is continuously fluidised. This energy consideration, as well as raw material costs, could become a limit to their application by wastewater companies (Battistoni *et al.*, 2005a). The utilisation of a metallic support as a seed material to capture struvite crystals could be one of the solution to remedy this energy consideration while facilitating struvite recovery (Suzuki *et al.*, 2005). Furthermore, as seen in table 2.10a and 2.10b, processes often encountered problems due to the production of fines. Excess fine production is undesired as it usually leads to loss of particles in treated effluent due to the high mixing energy needed to maintain the growing particles in suspension (Mangin and Klein 2004, Battistoni *et al.*, 2005b). The few studies have looked at problems of fine productions have partly limited the problem by recycling fines as a fresh seed material to grow struvite on (Ueno and Fujii, 2001; Shimamura *et al.*, 2003).

For an effective and continuous P recovery as struvite, the characteristics of the influent used have to be monitored and adjusted when necessary. Indeed, to date the purity of the product precipitated is not always guaranteed, due to competition between calcite, struvite and hydroxyapatite crystallisation (Battistoni, 2004). Selectivity of the process toward struvite will depend on the levels of compounds known to interfere with the nucleation and growth of struvite crystals, thus on quantity of chemicals needed to reach the minimum ratio Mg:N:P 1:1:1 necessary for struvite to occur and/or counterbalance levels of foreign ions. To illustrate, as seen in table 8 ratios magnesium to calcium in the UK can vary from 1:1.4 to 1: 3.7 depending on the location, which according to Le Corre *et al.* (2005) study would mean that the utilisation of this kind of liquors for P recovery by crystallisation would favour calcium phosphates precipitation if no magnesium dosing was applied.

2.5 Interests in controlling and recovering phosphorus as struvite

2.5.1 Environmental impact

2.5.1.1 Pollution reduction

The eutrophication of water in aquatic ecosystems is a condition where high nutrient removal (P and N) stimulates algae growth and leads to fish deaths and loss of water resources. In their study on removing phosphorus from wastewater effluent, Pretty *et al.* (2003) mentioned that the costs generated by this form of pollution to the water industry in the UK is estimated to $ 77 million per annum. As seen previously, in most of experimental studies on P removal from wastewater sludge by struvite crystallisation, the results showed relatively high efficiencies (never less than 60 %) and would then limits problems linked to eutrophication. At the same time struvite crystallisation offers the advantage of being able to remove nitrogen simultaneously to P (Table 2.11).

Table 2.11. *Example of nitrogen removal by struvite precipitation.*

References	Source	Ammonium removal (ratio 1:1:1
Maekawa *et al.* (1995)	Swine wastewater	More than 90%
Priestley *et al.* (1997)	BPR anaerobic digested effluents	98%
Altinbaş *et al.* (2002)	Anaerobically pre-treated wastewater	from 68 to 72%
Kim *et al.* (2004)	Slurry type swine wastewater	Up to 99% depending on the ratios
Tünay *et al.* (1997)	Synthetic samples	Over 85%
	Industrial wastewater	Never less than 50%, mostly above 75%
Miles and Ellis, (1998)	Anaerobically treated swine waste	93%
	Waste activated sludge	51%
Uludag-Demirer *et al.* 2005	Anaerobically digested dairy manure	>95%
Kabdaşli *et al.* (2006b)	Human urine	Up to 95%

2.5.1.2 Sludge reduction

Sludge disposal and production is effectively a major problem for water companies, especially since the application of the 91/271/EEC directive (UWWTD, 1991). It was effectively predicted in 2002 that the application of the directive would cause an increase in sewage sludge production from 7 to 9.4 million tonnes per year by 2005 in the European Union (Steén, 2004), and from 1.1 to 1.5 million tonnes in the UK by 2005/2006 (Bruce and Evans, 2002). Woods *et al.* (1999) and Woods e*t al.* (2000) showed that sludge mass could be reduced by 8 to 31% by implementing phosphorus recovery by crystallisation.

2.5.1.3 Use as a fertiliser

The agronomic properties of struvite as a fertiliser have been widely discussed. It represents a highly effective source of nutrients (P, N an Mg) for plants (Li and Zhao, 2003) and was found to be as efficient as mono calcium phosphates (MCP) (Johnston and Richards, 2003). Its low solubility in water (0.018g/100ml at 25°C-Bridger *et al.,* 1961), also presents the advantage to prolong the release of nutrients during the growing season (Gatterell *et al.*, 2000) without danger of burning roots of crops treated (Ries *et al.,* 1969). To date, struvite has only been commercialised in Japan as a fertiliser for growing rice and vegetables (Ueno and Fujii, 2001). Shu *et al.* (2006) gave the reasons as to why struvite is not widely applied as a fertiliser to its limited availability to farmers, and the lack of communication on its applicability and benefits.

2.5.2 Economics

As seen previously phosphorus recovery from wastewater effluent as struvite presents various interests: it can help to solve and prevent scaling problems in WWTPs, it reduces pollution linked to excess discharge of nutrient (N and P) in wastewater effluents, while its potential reuse as a fertiliser could benefits to wastewater companies (Doyle and Parsons, 2002). However, the success of the implementation of struvite crystallisation processes to WWTPs depends on their economical sustainability. For this reasons the main challenge is to make P recovery as struvite cost effective by taking into account costs of production (*i.e.* chemicals, maintenance, and energy) and assessing the value of struvite on the market of fertilising products.

Costs of struvite production mainly depends on amounts, hence costs, of chemicals to be injected in the process (Jaffer et al., 2002; Von Münch and Barr, 2001), and the energy required to ensure mixing during the crystallisation (Battistoni *et al.*, 2005a) (Table 2.12). Most studies use relatively high amounts of $MgCl_2$ to reach the appropriate Mg:N:P molar ratio, and NaOH to adjust the pH of precipitation. To illustrate, Jaffer *et al.* (2002) estimated that the sodium hydroxide addition needed to reach an appropriate pH for struvite crystallisation in their pilot scale reactor (*i.e.* influent flowrate of 400 $m^{-3}.d^{-1}$) was responsible of 97 % of the chemical expenses. This corresponded to important costs ranging from 205€ to 75088€ per year. In their pilot scale investigations, Battistoni (2004) used air stripping as a way to adjust the pH of struvite precipitation. This could be an option to reduce costs linked to NaOH additions. Moreover, some studies have looked at alternative ways to reduce costs associated with Mg dosing by for example using $Mg(OH)_2$, which is cheaper than $MgCl_2$ and simultaneously helps to increase the pH (Von Münch and Barr, 2001). Shin and Lee (1997) also indicated that brine or seawater could be used as an alternative source of magnesium and managed to reach 95 % of P removal with seawater compared to 97 % removal with $MgCl_2$. If the costs due to chemical addition would be reduced by this way, the seawater or brine transport could cause further costs and this solution could be then out of interest except for WWTPs located next to the sea.

Another way of reducing costs of struvite production would be to limit the energy consumption needed for pumping and mixing of solutions. One option would be to favour auto-nucleation of struvite over seeded crystallisation with materials such as sand. Indeed, Battistoni *et al.* (2005a) indicated that operative costs of struvite production could be reduced from 0.28€.m^{-3} to 0.19€.m^{-3} when using the auto-nucleation method rather than seeded crystallisation. Indeed, costs of seeded crystallisation are higher due to purchase costs of the raw seed material and mainly to greater airflows needed to fluidise the particles.

Table 2.12 – *Economics of struvite crystallisation*

Reference	Type of reactor	Influent flowrate (m^3.d^{-1})	Cost of chemicals or energy	Estimated income generated by struvite production	Global profits
Jaffer *et al.*, 2002	Air agitated reactor	400	NaOH: 205-75088 € per year.	23.6-29.6 k€ per year*	-
Von Münch and Barr, 2001	Air agitated reactor	0.43-2.88	-		-7800€ to 89400€ per year**
Ueno and Fujii, 2001	FBR	650	-	45.6-506. k€ per year*	-
Battistoni *et al.*, 2005 a	FBR Autonucleation	24-48	Energy+ reagents: 0.19€ per m^3 of supernatant treated	-	-
	FBR seeded with silica	24-48	Energy+ reagents: 0.28€ per m3 of supernatant treate	-	-

* *based on struvite selling price in Japan (250 €.t^{-1})*

** *based on struvite estimated selling price in Australia (180-300 €.t^{-1})*

The profitability of a struvite crystallisation process will obviously be dependant on profits generated from struvite sales. As the application of struvite at full scale is still limited, the estimation of its economical value as a fertiliser is difficult to assess as it should be influenced by rates of production and the regional demand for such a product (Gaterell *et al.,* 2000). However, in Japan struvite has already been sold as a fertiliser at a cost of nearly 250€.t^{-1} (Köhler, 2004). Based on this value, Jaffer *et al.* (2002) estimated that the income generated from the selling of their struvite production could vary from 23600€ to 29600€. Von Munch and Barr, 2001 estimated that the selling price of struvite achievable in Australia could range from 180€ to 300€ per tonne, which for Oxley Creek WWTP (Australia) would result in profits ranging from -7800€ to +89400€ a year.

The fertiliser industry currently uses phosphate rock, valued at 31 to 39€ per tonne in 1999, to generate phosphate fertilisers (Driver *et al.*, 1999). Compared to the economical value of struvite demonstrated above and to costs of struvite production ranging from 109€.t^{-1} in Australia to 359€.t^{-1} in Japan (Doyle and Parsons, 2002), fertiliser production from phosphates rock seems to be still more interesting. However if the recovery of P as a fertiliser does not seem to be yet of direct economic interest, it could become a real challenge given that it could help to reduce handling costs of sludge disposal as it can reduce significantly sludge volumes. To illustrate, Shu *et al.* (2006) estimated that for WWTPs treating 100 m^{-3}.d^{-1}, 1000 m^{-3}.d^{-1} and 55000 m^{-3}.d^{-1} of wastewaters, savings generated on sludge handling and disposal by struvite crystallisation could reach respectively 0.68 €.d^{-1}, 6.92 €.d^{-1} and 374€.d^{-1}. Furthermore, savings on costs due to struvite scaling in WWTPs would also be non negligible as Neethling and Benisch (2004) demonstrated that annual cost due to spontaneous precipitation in WWTP in the united states could range between 1560 and 7800€.

Finally the implementation of a sustainable process for P reuse and recycling and the profitability of struvite recovery as a fertiliser will rely on the way how potential customers will perceive struvite as a new fertiliser (Von Sothen, 2004).

2.6 Summary

- Struvite ($MgNH_4PO_4.6H_2O$) crystallisation occurs spontaneously in WWTPs as stable white orthorhombic crystals. Struvite forms in a Mg:N:P molar ratio 1:1:1 under specific conditions (including supersaturation, pH, temperature, mixing energy and presence of foreign ions) and because of these generates problems of scale deposits in specific areas such as pipes and recirculation pumps.

- The formation of struvite is governed by two mechanisms: nucleation and crystal growth. The majority published works on the principles of struvite formation focused on the influence of supersaturation ratio and pH on the crystallisation, as these parameters were found to be the most influent on struvite crystallisation. Indeed they control the induction period preceding the first release of struvite crystals, and also reduce crystal growth rate, while other parameters such as presence of foreign ions, mixing energy, and temperature mainly affect struvite crystal growth and crystal quality.

- The control or prevention of struvite formation by chemical dosing was the first approach considered by researchers to solve problem of scale deposits in WWTPs. Nevertheless, the opportunity to deliberately form struvite before it occurs in WWTP and causes several maintenance problems became a real challenge as struvite can help to remove phosphorus from wastewater effluents and recover it as a fertiliser.

- This paper has reviewed the techniques and processes experimented to date by researchers at laboratory, pilot and full scale to maximise phosphorus removal and reuse as struvite. Struvite crystallisation from digested sludge liquors by means of fluidised bed reactors directly integrated in WWTP lines are the most common processes studied with success. However, if good phosphorus removals are always insured, the technique still needs improvements with regards o quality and quantity of the product formed to be applicable as an economically valuable route to recover phosphorus.

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CHAPTER 3

KINETICS OF STRUVITE PRECIPITATION: EFFECT OF THE MAGNESIUM DOSE ON NUCLEATION RATES

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3. KINETICS OF STRUVITE PRECIPITATION: EFFECT OF THE MAGNESIUM DOSE ON NUCLEATION RATES

Kristell S. Le Corre[1], Eugenia Valsami-Jones[2], Phil Hobbs[3], Simon A. Parsons[1]

[1]School of Water Sciences, Cranfield University, Cranfield MK43 0AL, UK
[2] Department of Mineralogy, The Natural History Museum, Cromwell Road London, SW7 5BD, U.K
[3]Institute of Grassland and Environmental Research (IGER), North Wyke, Okehampton, Devon, EX20 2SB, UK

Abstract

The formation of white deposits in specific areas of wastewater treatment plants is generally the consequence of the spontaneous formation of a mineral called struvite. Struvite formed when the levels of phosphate, ammonium and magnesium naturally available in wastewater effluents reach a minimum molar ratio 1:1:1 under specific conditions of pH, temperature and mixing energy. Originally regard as a phenomenon to control or eliminate, struvite was lately identified as an alternative way of removing and recovering P from wastewater effluents and generates a product identified as an excellent slow release fertiliser. Chemical and physical principles of struvite precipitation and the development of crystallisation technologies have been then widely investigated. However, little interest has been given to kinetics of struvite precipitation. In the present work the kinetics of struvite formation have been investigated at both laboratory and pilot scale in synthetic solutions containing Mg^{2+}, NH_4^+, and PO_4^{3-} ions in a molar ratio 1:2:2 at room temperature. These different tests have used pH measurements to assess the impact of water chemistry on induction times, and more precisely the influence of magnesium levels on kinetic rates. Experimental results and kinetic calculations revealed that the control of the magnesium dose initially present in solution is decisive of the speed at which struvite nucleates.

Keywords: struvite; nucleation and growth; kinetics; magnesium dose

3.1 Introduction

Phosphorus (P) removal from wastewater effluents has become a real driver, especially since 1991 when the European legislation made compulsory the removal of phosphorus from wastewater discharged in sensitive areas and imposed minimum P concentrations in wastewater effluents to limit problems of eutrophication (UWWTD, 1991). As a result of this strict legislation, numbers of new P removal processes have been developed and include biological removal technologies (BNR, EBPR), chemical precipitation by metal salts and lately crystallisation of P as either calcium phosphate or struvite (Mulkerrins, 2004 Parsons and Berry, 2004). If the two first methods have been largely applied, the two others remain principally at an experimental stage. However the removal of phosphorus from wastewater effluents by struvite crystallisation is a promising solution as conversely to the other methods it presents the advantage of generating a fully recyclable product which sales could benefit to wastewater companies. Indeed, researchers have identified struvite ($MgNH_4PO_4.6H_2O$) as a slow release fertiliser highly effective for foliar and soil application and as efficient as traditional mono calcium phosphates (MCP) (Gatterell *et al.*, 2000; Johnston and Richards, 2003).

Struvite occurs spontaneously in solution when the content in Mg^{2+}, NH_4^+ and PO_4^{3-} reaches a 1:1:1 molar ratio under specific conditions of pH, temperature, mixing energy and presence of foreign ions (Doyle and Parsons, 2002). If conditions affecting success of P removal and recovery as struvite and their consequences on thermodynamics of precipitation have been widely investigated (Ohlinger *et al.*, 1998; Michalowski and Pietrzyk, 2005), knowledge on kinetics of struvite precipitation, that is to say on rates at which struvite occurs, is still limited (Nelson *et al.*, 2003). Struvite crystallisation kinetics can be divided in two major steps: the nucleation and crystal growth (Jones, 2002). The rate at which struvite precipitates corresponds to the lapse of time taken for the first particles to occur more commonly known as induction time (Bouropoulos and Koutsoukos*,* 2000, Kabdaşli *et al.*, 2004). Struvite induction time is known to depend on the nucleation process involved in struvite crystal formation and on a multitude of parameters including supersaturation levels, mixing energy and presence of foreign ions (Nelson *et al.*, 2003, Ohlinger *et al.*, 1999 and Kabdaşli *et al.*, 2006). Controlling precisely the effects of all these parameters seems then fundamental in the success of struvite crystallisation.

In the present work the influence of magnesium ions on kinetics of struvite crystallisation in synthetic liquors has been investigated. Initially used to estimate the magnesium impact on struvite induction time of struvite crystallisation, pH measurements have then been used to assess kinetic rates of struvite precipitation.

3.2. Material and methods

3.2.1 Laboratory scale investigations

Struvite was precipitated from volumes of stock solutions of magnesium chloride hexahydrate ($MgCl_2.6H_2O$/ Fisher Analytical Reagent Grade, UK) and ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$/ Fisher Analytical Reagent Grade, UK) diluted in deionised (DI) water into 250 mL flasks so that the final concentration of Mg after mixing ranged from 1.2 mM to 3.5 mM, the molar ratio Mg:N:P always equalled 1:2:2 and Mg remained here as the limiting factors over struvite crystallisation. Prior to mixing, the diluted solutions were adjusted to pH 9, by addition of sodium hydroxide (NaOH 0.01 N and 2 N / Fisher Analytical Reagent Grade, UK). The two solutions were then simultaneously mixed together in a 600 mL beaker, and the pH was measured periodically over 25 minutes. At the end of each test, the precipitate was filtered through 0.2 µm pore size Whatman membranes (Fisher scientific, UK) dried at room temperature. The recovered product was characterised via XRD (Powder X-ray Diffractometer D5005, Siemens, Germany) and SEM (Scanning Electron Microscope XL 30 SFEG, Philips, The Netherlands). All experiments were carried out at room temperature and repeated 3 times.

3.2.2 Pilot scale investigations

A pilot scale crystallisation reactor has been designed and developed at Cranfield University (Figure 3.1) to study struvite nucleation and growth on both synthetic and real liquors. The process was composed of a 10 L reactor with three side sampling ports and a drain valve. A peristaltic pump injected simultaneously solutions of ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$ / Fisher Analytical Reagent Grade) and magnesium chloride hexahydrate ($MgCl_2.6H_2O$ / Fisher analytical Reagent Grade) prepared by the dissolution of the corresponding solid compounds in deionised (DI) water.

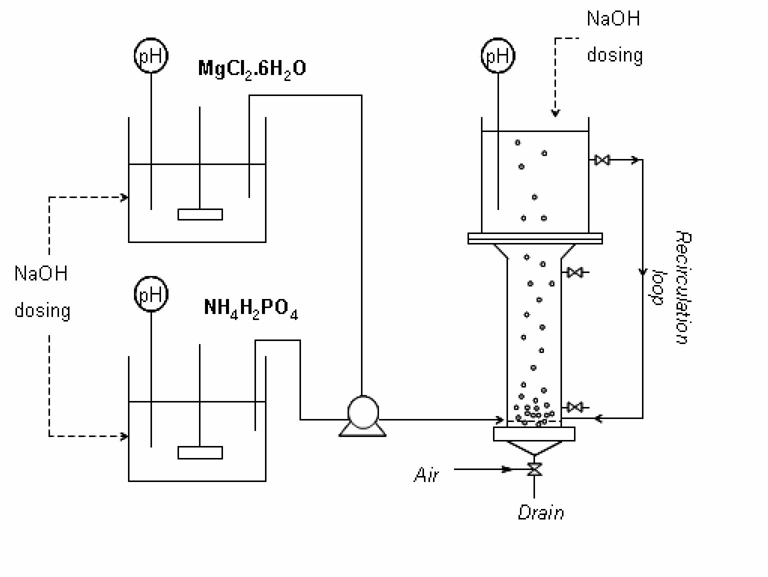


***Figure 3.1**. Pilot scale unit*

Prior to mixing in the reactor, each solution was adjusted to pH 9 with sodium hydroxide (NaOH 2N/ Fisher analytical reagent grade) in stirred buckets. Both solutions were transferred in the reactor up to 9 L so that the final molar ratio Mg:N:P always equalled 1:2:2. A pH probe introduced in the reacting zone controlled the pH during the crystallisation process. The pH was recorded in the column shaped zone of the reactor every minute, over 1 hour of experiments. An upward air-flow and a liquid recirculation were used and adjusted (10 to 5 $L.min^{-1}$ for air, and 1.5 to 1.35 $L.min^{-1}$ for liquid) to ensure the mixing and growth of the particles formed so that they are kept in suspension during the experiment. Struvite crystal harvesting was achieved through a drain valve situated at the bottom of the reactor. All standard experiments were conducted at room temperature over 60 minutes and repeated 3 times.

3.2.3 Kinetics of struvite formation

As struvite precipitates it releases hydrogen ions in solution causing a drop in pH, directly linked to rate of struvite formation and to the consumption of magnesium ions reacting to form struvite.

In the system studied here, struvite formed according to the following equation:

$$\mathbf{Mg^{2+} + NH_4^{+} + H_2PO_4^{-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + 2H^{+}} \qquad (3.i)$$

From equation (3.*i*), the rate of struvite occurrence can then be expressed as:

$$\frac{d[MgNH_4PO_4.H_2O]}{dt} = \frac{1}{2}\frac{d[H^+]}{dt} = -\frac{d[Mg^{2+}]}{dt} = -\frac{d[NH_4^+]}{dt} = -\frac{d[H_nPO_4^{3-n}]}{dt} = Kr \qquad (3.ii)$$

where: K is the reaction kinetic constant and r is the rate of crystallisation in mol.L^{-1}.s^{-1}.

The rate of disappearance of Mg^2 (k$_{Mg}$)$^+$ ions can then be defined as:

$$-\frac{d[Mg^{2+}]}{dt} = k_{Mg}[Mg^{2+}] \text{ or } -\frac{d[Mg^{2+}]}{[Mg^{2+}]} = k_{Mg}dt \qquad (3.iii)$$

And the rate of appearance (k$_H$) of H$^+$ ions is:

$$\frac{1}{2}\frac{d[H^+]}{dt} = k_H[H^+] \leftrightarrow \frac{1}{2}\frac{d[H^+]}{[H^+]} = k_H dt \qquad (3.iv)$$

In the current work, mixing speed as well as Mg:NH$_4$:PO$_4$ ratios were kept constant and the initial pH set to 9 to leave Mg as the only limiting parameter in the formation of struvite. Consequently, the rate of disappearance of Mg^{2+} ions equalled the rate of appearance of H$^+$, so combining equation (3.*iii*) and (3.*iv*) lead to the following expression

$$-\frac{d[Mg^{2+}]}{[Mg^{2+}]} = \frac{1}{2}\frac{d[H^+]}{[H^+]} \qquad (3.v)$$

By integrating equation (3.*v*) between the initial time (t=0) and the final time (t= 25min or 60 min at pilot scale), it was then possible to link the magnesium concentration to the pH value recorded over time as by definition pH=-Log [H$^+$] as followed:

$$-\int_0^t \frac{d[Mg^{2+}]}{[Mg^{2+}]} = \frac{1}{2}\int_0^t \frac{d[H^+]}{[H^+]}$$

$$Ln\,[Mg^{2+}]^t = Ln\,[Mg^{2+}]_0 - \frac{1}{2}Ln\left(\frac{[H^+]^t}{[H^+]^o}\right)$$

$$\mathrm{Ln}\ [Mg^{2+}]^{t} = \mathrm{Ln}\ [Mg^{2+}]_{0} - \frac{1}{2}\mathrm{Ln}\left(\frac{10^{-pHt}}{10^{-pHo}}\right)$$

$$[Mg^{2+}]^{t} = \mathrm{Exp}\left(\mathrm{Ln}[Mg^{2+}]_{0} - \frac{1}{2}\left(\frac{10^{-pH_t}}{10^{-pH_0}}\right)\right) \qquad (3.vi)$$

This expression was then used to estimate the evolution of magnesium concentration over time using the different pH values recorded during the various laboratory and pilot scale experiments. The kinetic constants of struvite formation were then assessed by fitting a first order kinetic model to the different set of data as according to previous studies struvite kinetics of reaction were found to follow this model (Nelson *et al.*, 2003, and Quintana *et al.*, 2005). For pilot scale tests only the concentrations calculated in the initial stage of reaction where used to fit the model to compare them to lab-scale experiments and ensure constant determined corresponded to nucleation kinetics. The linear form of the modified expression of a first-order kinetics model given by Nelson *et al.* (2003) has been used here. The form of the rate expression is:

$$\mathrm{Ln}(C-C_{eq}) = -kt + \mathrm{Ln}(c-C_0) \qquad (3.vii)$$

where: C is the concentration of the reactant concentration at a moment t, Ceq the reactant concentration at equilibrium, C_0 the initial reactant concentration, and k the kinetic constant.

In the present study, if the rate of Mg^{2+} reaction follows this model, a plot of Ln([Mg]-[Mg_{eq}]) versus time should be linear with a slope of –k.

3.3 Results and discussion

3.3.1 Induction time

Initial experiments at both laboratory and pilot scale used changes in solution pH to indicate the start and rate of struvite nucleation, hence to determine induction time for different initial magnesium concentrations. The effects of varying the concentration of Mg ions in solution on struvite precipitation are showed in Figure 3.2A and 3.2B. The plots of tangents to pH curves obtained for both laboratory and pilot scale experiments illustrate that when the concentration in the limiting ions increased, the rate at which the pH drops increases indicating a strong influence of the Mg dose on the reaction kinetics.

In his study of struvite crystallisation kinetics, Nkansah (2003) also concluded that rates at which struvite precipitation reached a steady state were closely linked to the concentration of mere solutions in Mg from which it was precipitated, with for example induction times decreasing from 150 to 15 seconds for respective Mg concentrations increasing from 2.337 to 5.827 mM in molar ratios Mg:N:P 1:2:2.

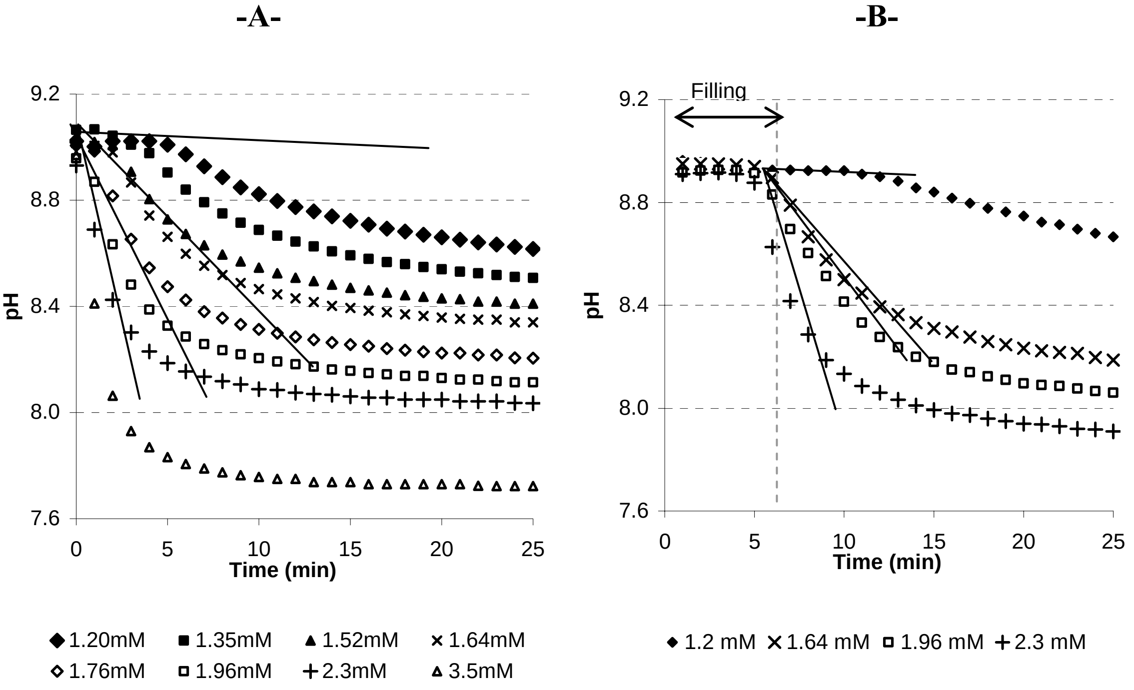


__Figure 3.2.__ Average pH versus time for various initial magnesium concentrations at lab-scale (A) and Pilot scale (B). (Deviation of pH measurement ≤ 0.05 for all experiments (A) and (B).

Determination of the period of time preceding the occurrence of first crystals at laboratory scale showed that an increase in initial magnesium concentration from 1.2 mM to 2.3 mM resulted in an approximately 10 fold reduction of the induction time (Table 3.1). These results are in accordance with previous studies that have demonstrated that the induction time for struvite crystallisation was mainly reaction controlled (*i.e.* pH and supersaturation dependant) (Ohlinger *et al*., 1999). For instance, Bouropoulos and Koutsoukos, (2000) also demonstrated the dependence of the induction time on solution supersaturation, hence Mg dose. For precipitation tests in synthetic solutions ($MgCl_2.7H_2O$ + $NH_2H_2PO_4$) at pH 8.5 they reported similar trends as for an increase of Mg from 2.75 mM to 4 mM, the relative induction period decreased from 125 min to 6 min. However, times taken for struvite crystals to occur in the current system seemed higher than that observed by Bouropoulos and Koutsoukos, (2000).

These variations can be attributed to the difference in pH of precipitation and conditions of precipitation (i.e. composition of synthetic solutions, mixing energy, temperature and agitation). Indeed Nelson *et al.* (2003) illustrated the effects of pH on struvite precipitation rates in anaerobic swine lagoon effluents by showing that rate constants varied significantly from 3.7 h^{-1} to 12.3 h^{-1} between pH 8.4 and 9.

Table 3.1. *Struvite induction time at bench and pilot scale*

	Induction time in beakers (min)		**Induction times in reactor (min)**	
	Eye visible	**Estimated from pH graphs**	**Eye visible**	**Estimated from pH graphs**
1.2 mM	5	5	12	12
1.64 mM	2	1.75	6.8	7
1.96 mM	< 1	0.75	6.7	7
2.3 mM	< 0.5	< 0.5	6	6

At pilot scale, induction times were less affected by variations in magnesium concentrations than for laboratory tests (Table 3.1). For example, at the Mg concentration of 1.2 mM, the solution became cloudy after 12 minutes of reactor operation, while at 2.3 mM the first particles were visible only 6 minutes after the filling up start.

From the previous observations it is clear that the intensity of the drop in pH is linked to the concentration in magnesium initially present in solution and is characteristic of the speed at which the first crystals of struvite occurs, consequently to the rate of struvite formation. Finding a relationship between pH and Mg concentration against time could then help to predict kinetics of struvite precipitation and determine rate constants of struvite formation under specific condition of precipitation.

3.3.2 Rate of nucleation and kinetics of precipitation

Equation (3.*vi*) has been used to assess the evolution of the magnesium concentration versus time from the different pH measurements showed in Figure 3.2A and 3.2B.

Based on the literature (Nelson *et al.*, 2003, and Quintana *et al.*, 2005), the struvite formation reaction has been assumed to obey a first-order kinetic model with respect to Mg and H ions.

Figure 3.3 illustrates plots of Ln ($[Mg^{2+}]-[Mg^{2+}]_{eq}$) versus time for the different experimental conditions tested at laboratory scale. The different plots revealed that calculated Mg concentrations fitted well to a first kinetic order model as correlation coefficients (R^2) ranged from 0.92 to 0.99 over the range of initial Mg concentrations tested.

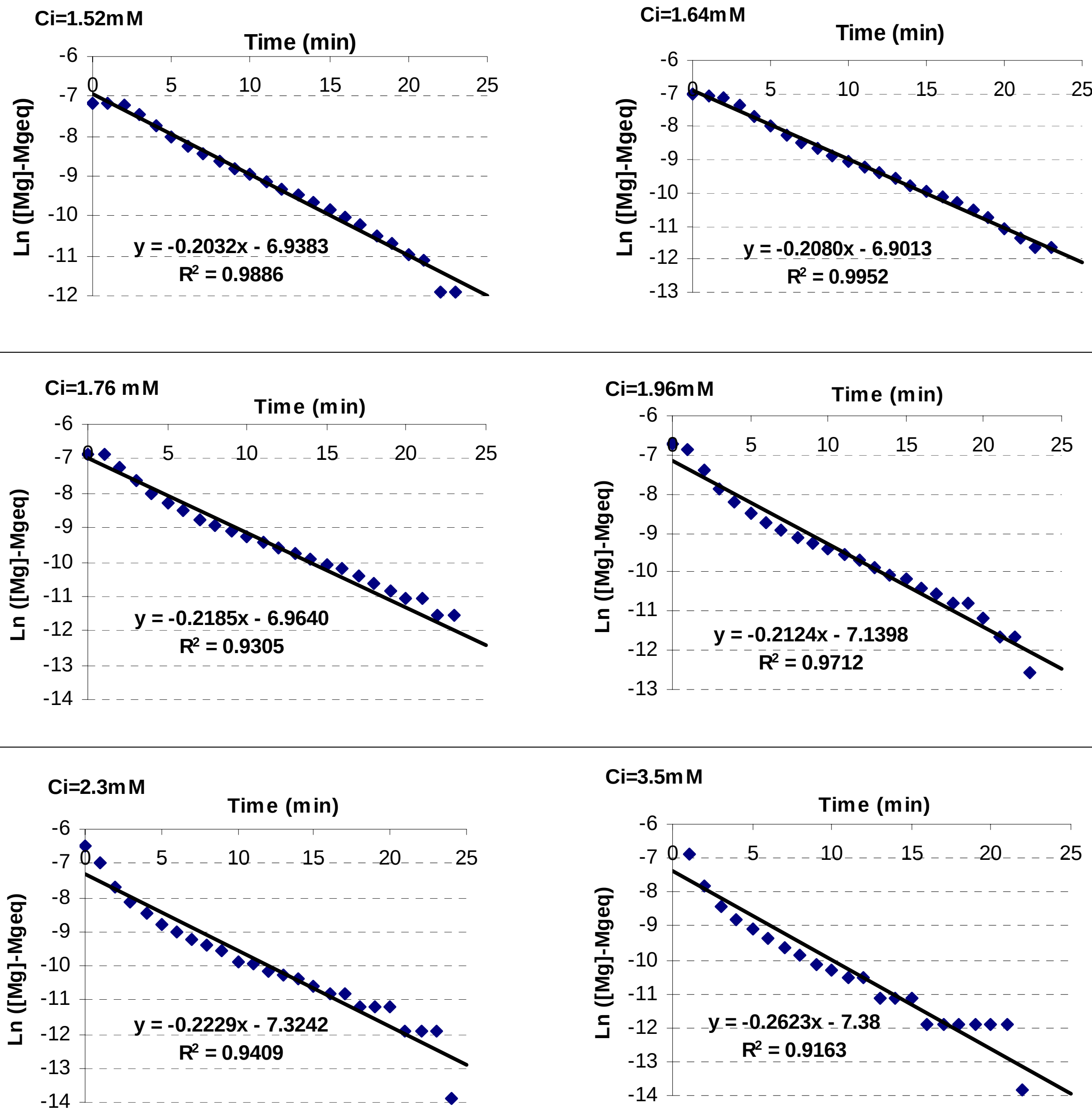


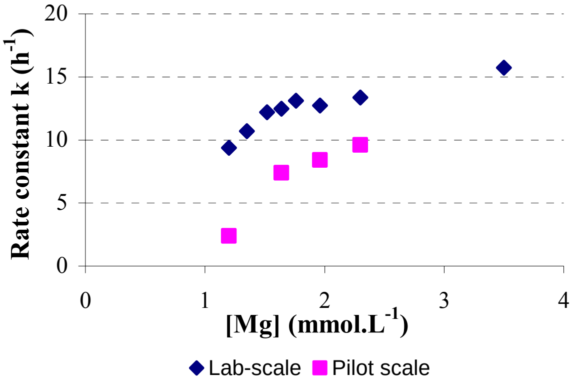
Figure 3.3. *Fit of calculated* Mg^{2+} *concentrations to the linear form of the first-order kinetic model.*

At pilot scale, good correlations of the magnesium concentration calculated to the first-order kinetic model were also obtained with R^2 values 0.92 to 0.98 over the range of initial Mg concentrations tested (*i.e.* 1.2mM, 1.64mM, 2.3mM and 3.5mM). The rate constants (obtained from each plot are reported in Table 3.2).

Kinetic constants seem to follow a trend in that the higher the initial Mg concentration, the higher the rate constant and so the faster the nucleation. To illustrate, kinetics constants obtain at laboratory scale ranged from 9.7 to 15.7 h^{-1} for Mg increasing from 1.2 to 3.5 mM, while at pilot scale kinetic constants range from 2.4 to 9.6 h^{-1} between 1.2 and 2.3 mM.

Table 3.2. *Rate constants calculated for struvite solutions of various initial Mg concentrations*

Initial [Mg] (mM)	Lab scale k (h^{-1})	Pilot scale k (h^{-1})
1.2	9.4	2.4
1.35	10.7	
1.52	12.2	
1.64	12.5	7.4
1.76	13.1	
1.96	12.7	8.4
2.3	13.4	9.6
3.5	15.7	



Comparison of the laboratory and the pilot tests for similar initial concentrations showed that rate constants at pilot scale were significantly lower than those determined at laboratory-scale, especially for low concentrations in Mg. For an Mg concentration of 1.2 mM at both laboratory and pilot scale, constant kinetics were respectively 9.2 h^{-1} and 2.4 h^{-1} while at an Mg concentration of 2.3mM constant kinetics were 13.4 h^{-1} and 9.6 h^{-1} (Table 3.2). Nelson *et al.* (2003) reported for anaerobic swine lagoon that lower kinetics constants are influenced by the time taken for the crystallisation to start, or induction time. As induction times observed for precipitation tests in the reactor were significantly longer than at lab scale (Table 3.1), this would explain the lower rate constants determined at pilot scale. Furthermore, although previous studies have minimised the influence of mixing energy on nucleation kinetics (Ohlinger *et al.*, 1999), mixing energy in small volumes of solution such as during jar tests are thought to be higher than in the 10 L reactor agitated with air, hence playing a speed-up role in nucleation kinetics.

When compared to rate constants observed in the literature, the values obtained here are in the range of the one reported for struvite precipitation in real liquors. For example, in their study of struvite kinetics using sludge lagoon supernatants in a pilot fluidised bed reactor, Ohlinger *et al.* (2000) determined a rate constant of 4.2 h^{-1} (based on decrease in orthophosphate concentration) at a precipitation pH of 8.3, whereas Nelson *et al.* (2003) found at laboratory scale a rate constant of 3.7 h^{-1} for struvite precipitated in a similar media at pH 8.4, and initial Mg concentrations varying from 0.8 to 1.2 mM. Constant rates determined by Nkansah (2003) for identical conditions of precipitation as the one presented here (*i.e.* Mg:N:P molar ratio 1:2:2/ identical stock solutions, mixing apparatus and speed) were similar to the one calculated here at the same Mg concentrations. To illustrate, for initial Mg concentrations of 2.3 mM and 3.5 mM the constant determined here were respectively of 13.4 and 15.7 h^{-1} while Nkansah values were respectively of 11.3 and 13.3 h^{-1}.

Furthermore, by applying equation (3.*vi*) used here to predict the evolution of Mg concentration with time to the set of pH data reported by Nkansah (2003), the results confirmed the use of a first-order kinetics model to describe struvite nucleation kinetics and indicated an excellent correlation between the concentration calculated at equilibrium and actual concentrations in Mg he measured at equilibrium by Inductively Coupled Plasma Emission Spectroscopy (Table 3.3). To illustrate for an initial Mg concentration in Mg of 2.3 mM the present model predicted an equilibrium concentration of 0.916 mM while Nkansah (2003) measured an equilibrium concentration of 0.922 mM.

***Table 3.3**. Comparison between equilibrium concentrations measured by Nkansah (2003), and the corresponding concentrations predicted.*

	Nkansah, (2003)	**Current work**	
Initial [Mg] (mM)	Measured [Mg] at equilibrium (ICP analyses/ mM)	[Mg] calculated with the current model (equation7)	Error (%)
1.2	0.666	0.683	2.5
2.3	0.922	0.916	0.7
3.5	1.010	1.009	0.1

3.4 Conclusion

The result presented here showed that pH measurement can be used for the prediction of the kinetic of struvite precipitation. The drop in pH typically observed during struvite precipitation reflects effectively rates at which struvite crystals nucleate. The magnesium concentration as expected has a major impact on struvite kinetics, with higher concentrations leading to shorter induction times, hence faster rates of nucleation leading to production of fine crystals. The present paper also showed that pH measurements correlated well with magnesium concentrations, especially at laboratory scale. However, investigations at both laboratory and pilot scale demonstrated that struvite nucleation in synthetic liquors corresponded to a first order kinetic model as observed in previous studies, confirming then the reliability of investigating kinetics from pH measurements.

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CHAPTER 4

IMPACT OF CALCIUM ON STRUVITE CRYSTAL SIZE, SHAPE AND PURITY

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4. IMPACT OF CALCIUM ON STRUVITE CRYSTAL SIZE, SHAPE AND PURITY

Kristell S. Le Corre[1], Eugenia Valsami-Jones[2], Phil Hobbs[3], Simon A. Parsons[1]

[1]School of Water Sciences, Cranfield University, Cranfield MK43 0AL, UK
[2] Department of Mineralogy, The Natural History Museum, Cromwell Road London, SW7 5BD, U.K
[3]Institute of Grassland and Environmental Research (IGER), North Wyke, Okehampton, Devon, EX20 2SB, UK

Abstract

Struvite precipitation occurs spontaneously in wastewater treatment plants under conditions that are influenced by many factors including concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} ions, pH, temperature and mixing energy. These parameters are often difficult to control and as a result struvite generates problems of scale deposits in areas such as pipes and recirculation pumps. At the same time, struvite is considered as a potentially marketable product as an alternative fertiliser. For those two reasons, it has become important to study the principles of struvite precipitation, and to assess the parameters controlling struvite crystallisation. In the present work the influence of Ca^{2+} ions on the precipitation of struvite was investigated in aqueous solutions containing Mg^{2+}, NH_4^+ and PO_4^{3-} ions in a molar ratio 1:2:2 at room temperature and constant pH. Different laboratory experiments have been used to assess the effects of Ca^{2+} ions on size, shape, and purity of the crystals formed. Tools used include particle size analysis, X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDS). The experimental results showed that the presence of calcium in the media can affect significantly struvite crystal growth, and the characteristics of the crystal produced.

Keywords: struvite, precipitation, crystal size and morphology, calcium.

4.1 Introduction

Struvite or magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$) scale deposits are causing considerable concern to wastewater treatment operators (Doyle and Parsons, 2002; Doyle *et al.*, 2003). The problem is not necessarily a new one as problems due to struvite spontaneous precipitation were first reported as *a crust of crystalline material* in 1937 in a multiple-stage sludge digestion system (Rawn *et al.*, 1937). Often perceived as a nuisance affecting the efficiency of treatment processes and causing maintenance problems (Mohajit *et al.*, 1989), the control of struvite deposition has been widely investigated, including the dilution of struvite crystals with water effluents (Borgerding, 1972); preventive action by chemical dosing of iron salts (Mamais *et al.*, 1994) or addition of chemical inhibitors (Doyle *et al.*, 2003; Snoeyink and Jenkins, 1980). In the past 10 years struvite precipitation has gained interest as a route to phosphorus recovery (Doyle and Parsons, 2002). Its composition (nitrogen (N), phosphorus (P) and magnesium (Mg) ions in equal molar concentrations) makes it a potentially marketable product for the fertiliser industry, if the properties of the final product can be controlled (Booker *et al.*, 1999).

4.1.1 Struvite formation

Struvite usually precipitates as stable white orthorhombic crystals in a 1:1:1 molar ratio according to equation (4.*i*) (with n= 0, 1, and 2, as a function of pH) (Abbona and Boistelle, 1985):

$$Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + nH^+ \qquad (4.i)$$

The occurrence and development of struvite crystals follow two chemical stages: nucleation (crystal birth) and crystal growth (enlargement of crystals until equilibrium) (Jones, 2002).

Predicting or controlling these stages is complex as it is controlled by a combination of factors including thermodynamic of liquid-solid equilibrium, phenomena of matter transfer between solid and liquid phases (Jones, 2002; Mullin 1992), and kinetics of reaction (Ohlinger *et al.*, 1999) as well as several physico-chemical parameters such as: pH of the solution from which struvite may precipitate, supersaturation, mixing energy, temperature and presence of foreign ions.

The influence of pH and supersaturation on the precipitation rate and crystal characteristics of struvite has been demonstrated by a number of authors (Abbona and Boistelle, 1985; Ohlinger *et al.*, 1999; Bouropoulos and Koutsoukos, 2000; Stratful *et al.*, 2001; Kofina and Koutsoukos, 2003), but as yet little interest has been paid to the influence of foreign ions on struvite nucleation and crystallisation.

Theoretically speaking, impurities in solution from which a compound may precipitate can affect the growth rate of crystals due to blocking of active growth sites inhibiting the increase of crystal size (Jones, 2002). In the case of struvite crystallisation from wastewater sludge, foreign compounds are numerous (amongst them potassium, chloride, calcium, carbonates, zinc) and could perturb, be absorbed on crystal surfaces and retard struvite formation, hence phosphorus binding (Koutsoukos *et al.*, 2003).

Indeed for a struvite precipitation process to be successful and economically valuable at full scale, particular attention has to be paid to the properties and quantity of the final product formed. That is to say purity and size of crystal recovered has to be controlled for a reuse as fertiliser: the strength of the granule formed has to be sufficient enough for practical reason (collection, transport and land filling) while purity is essential for environmental reasons.

4.1.2 Influence of calcium and carbonate ions

The way calcium and carbonate ions could affect struvite nucleation and growth is particularly of interest as their levels in wastewater effluent are relatively high. The study published by Parsons *et al.* (2001) mentioned magnesium to calcium ratio (Mg:Ca) ranging from 1:1.4 to 1:3.7 in settled sludge liquors from various wastewater treatment plant in the UK (Parsons *et al.*, 2001). While it is also not unusual to find carbonates (CO_3^{2-}) concentrations, (measured in terms of alkalinity, *i.e.* mg.L^{-1} as $CaCO_3$) above 200 mg.L^{-1} in various streams of sewage treatment works (Jaffer *et al.*, 2002).

Although few authors have studied the influence of calcium and carbonates on struvite crystallisation, it has been showed previously that the presence of calcium (Ca^{2+}) or carbonates (CO_3^{2-}) ions in the media where struvite precipitates can lengthen the induction time preceding the first occurrence of crystals and affect negatively the growth rate (Bouropoulos and Koutsoukos, 2000; Koutsoukos *et al.*, 2003; Kofina and

Koutsoukos, 2004). Ca^{2+} ions interact effectively with phosphate or carbonate ions to form calcium phosphates (in wastewater systems commonly a poorly crystallised hydroxyapatite) or calcium carbonate according to the following equations:

$$5Ca^{2+} + 3\,PO_4^{3-} + H_2O \rightarrow Ca_5(PO_4)_3OH + H^+ \qquad (4.ii)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad (4.iii)$$

The presence of Ca^{2+} ions can influence struvite formation, either by competing for phosphate ions or by interfering with the crystallisation of struvite. In the latter case, the characteristics of struvite crystals formed are likely to be affected; but this has never been assessed. The main objective of this paper is thus to explore how Ca^{2+} ions can affect struvite crystals nucleation and growth, and discuss the impact this has on the quality of the recovered product.

4.2 Materials and methods

A series of experiments have been undertaken to assess the impact of Ca^{2+} ions on struvite crystallisation using absorbance measurements, particle size analysis and the characterisation of struvite crystals formed through X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDS).

For all the experiments reported here struvite was precipitated from mixed solutions of magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$) and ammonium phosphate ($NH_4H_2PO_4$). Stock solutions of magnesium chloride hexahydrate ($MgCl_2.6H_2O$ / BDH AnalaR) 0.05 M and ammonium phosphate ($NH_4H_2PO_4$ / Sigma ACS Reagent) 0.2 M were prepared by dissolving the corresponding crystalline compounds in ultra-pure water (Purelab Ultra, Elga). Each stock solution was then filtered through a 0.22 µm paper filter to eliminate the presence of impurities, and stored at room temperature. All the experiments mentioned in the present paper have been undertaken at room temperature.

4.2.1 pH and absorbance experiments

Initial experiments used changes in solution pH to indicate the start and rate of nucleation. Experiments at various initial Mg concentrations were carried out to determine an initial Mg concentration for which the induction period is reasonable and the nature of the crystal formed acceptable.

Struvite was precipitated from volumes of stock solutions $MgCl_2 \cdot 6H_2O$ and $NH_4H_2PO_4$ diluted in 250 mL flasks so that the final concentration of Mg after mixing ranged from 1.2 mM to 3.5 mM and the molar ratio of magnesium, nitrogen and phosphorus (Mg:N:P) always equal 1:2:2. Prior to mixing, the diluted solutions were adjusted to pH 9, by addition of sodium hydroxide (analytical reagent grade) 0.01 N and 2 N and then the two solutions were simultaneously mixed together in a 600 mL beaker, and the pH was measured periodically over 25 minutes. At the end of each test, the precipitate was filtered through 0.22 μm filters, dried at room temperature and then characterised via XRD (Powder X-ray Diffractometer D5005, Siemens, Germany) and SEM-EDS (Scanning Electron Microscope XL 30 SFEG, Philips, The Netherlands).

The influence of Ca^{2+} ions on absorbance during struvite crystallisation was investigated at constant initial Mg concentration ($[Mg^{2+}]$ =1.64 mM) and at a wavelength of 385 nm.

Ca^{2+} ions were added in the Mg chloride solution as Ca chloride dihydrate 0.4M ($CaCl_2 \cdot 2H_2O$ / Fisher Chemicals) and carbonates ions were added in the ammonium phosphate solution as sodium hydrogen carbonate 0.4M ($NaHCO_3$ / AnalaR Fisher Chemicals) to provide alkalinity so that the solutions were better analogues to real media (*i.e.* wastewater effluents/sludge liquors). The molar ratios $Mg:Ca:CO_3$ investigated were 2:1:1, 1:1:1 and 1:2:2.

4.2.2 Particle sizing experiments and crystal characterisation

The effects of Ca^{2+} ions on struvite crystal size, shape and purity were then investigated using particle size analysis, SEM and XRD. Here a Mastersizer 2000 combined with a Hydro 2000MU (Malvern instruments) was used to follow changes in particle size distribution during struvite crystallisation in presence of Ca ions. Struvite was precipitated in a 1 L beaker from equal volumes (400 mL) of $MgCl_2 \cdot 6H_2O$ and $NH_4H_2PO_4$ so that the Mg concentration in the final solution was 1.64 mM and the ratio of Mg:N:P was 1:2:2. Prior to mixing, various volumes of $CaCl_2 \cdot 2H_2O$ 0.4 M were added to the Mg chloride solution, and equal volumes of $NaHCO_3$ 0.4 M were added in the ammonium phosphate solution. Then each solution was pH adjusted to 9 by addition of NaOH. Ratios Mg:Ca:CO_3 experimented were 2:1:1, 1:1:1 and 1:2:2. The particle size distribution was automatically recorded as the experiment progressed.

At the end of each experiment, the samples were filtered through 0.22 µm filters, dried at room temperature and analysed with XRD and SEM-EDS.

4.3 Results and discussion

4.3.1 pH

Struvite crystallisation is governed by the combination of key parameters amongst which are the pH, the initial concentration of the ionic species in solution, the mixing speed and the presence of foreign ions. In order to assess the impact of Ca ions on the quality, that is to say here size, morphology and purity, of struvite crystals, it was necessary to limit the impact of the other parameters on crystal formation. Experiments were undertaken at room temperature and at a constant mixing speed. Solutions were made to a standard recipe with the molar ratio Mg:N:P (1:2:2) leaving the concentration of Mg as the limiting parameter.

The initial experiments undertaken used pH as an indicator of struvite nucleation. As struvite precipitates, it triggers a release of protons ions in solution and hence a change in pH occurs during the nucleation process. The drop in pH is characteristic of the speed at which the first crystals of struvite occurs, and is linked to the rate of struvite formation which can influence the quality of the crystals formed.

The first series of tests measured changes of pH with time for a range of Mg concentrations. It was seen that as expected increasing the concentration of the limiting Mg ions leads to an increase in the change in pH and a reduction in induction time (Figure 4.1). XRD and SEM were used to characterise the purity and morphology of the produced crystals. Little difference in purity was observed but the morphology of the crystals was influenced by the initial concentration of Mg in solution. When the Mg concentration increases up to 1.64mM, the characteristics of struvite crystals is better, that is to say that the typical orthorhombic shape of struvite is more frequent and their size is bigger. However, beyond 1.64mM further increases in Mg concentrations lead to the formation of fines. From these experiments the Mg concentration of 1.64 mM was chosen as a good compromise between induction period and quality of the resulting product.

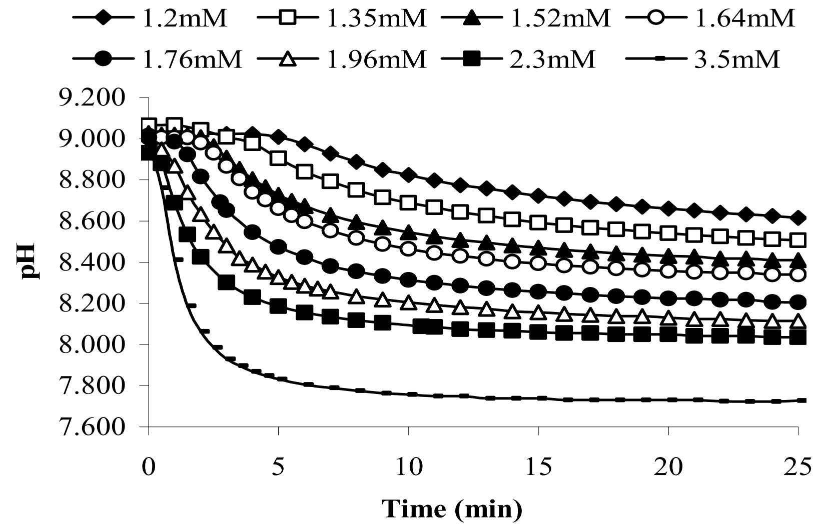


***Figure 4.1.** Evolution of pH during struvite crystallisation for different initial Mg concentration*

4.3.2 Effects of Ca ions on absorbance during struvite crystallisation

In addition to pH, absorbance measurements have often been used to follow nucleation and growth (Barrett and Parsons, 1998). The absorbance measurement corresponds to the quantity of energy absorbed (or transmitted) by the matter, and hence following the evolution of the absorbance of a solution at a specific wavelength, we can see the advancement of the crystallisation process and hence the evolution of the particle growth.

Here we have investigated the effect that Mg:Ca ratio has on struvite nucleation and growth. Without any Ca the absorbance increases quickly (less than 2 minutes) due to the nucleation of struvite particles, before reaching a maximum stable value (around 0.170) corresponding to crystal growth and sedimentation stages (Figure 4.2). By adding Ca at a molar ratio of Mg:Ca 2:1, we observe an increase in absorbance values, probably due to the formation of Ca carbonate or phosphate but we also notice an increase in the induction time from 2 minutes to more than 3 minutes. At the higher molar ratios Mg:Ca 1:1, and 1:2, the turbidity of the solution just after mixing is high due to the preferential reaction of Ca ions with carbonate or phosphate ions making it difficult to extract data on the formation of struvite crystals.

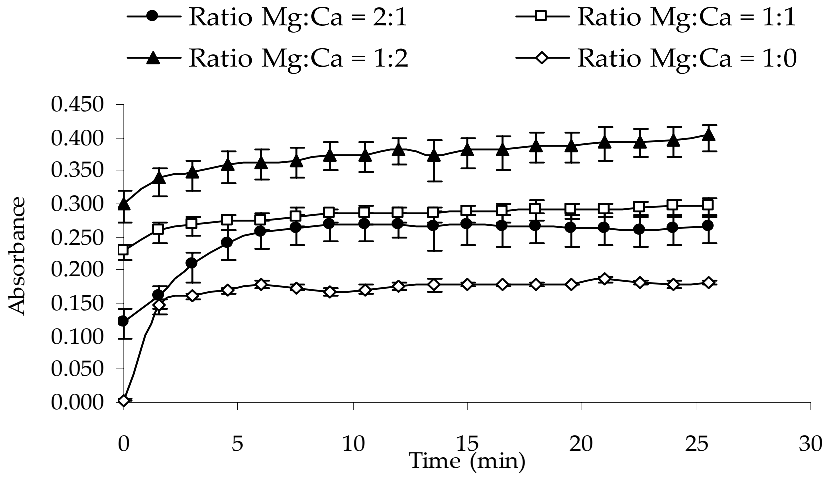


Figure 4.2. *Influence of increasing addition of Ca on absorbance measurements during struvite crystallisation.*

At a molar ratio Mg:Ca 2:1, it appears that an instantaneous precipitation occurs in the early stage of the reaction causing the initial turbidity of the solution, but the time taken to reach constant absorbance values is not as quick as it was during the first experiment without Ca. Despite this first reaction, some particles continue thus to nucleate. As phosphate ions are present in this case in large excess comparing to calcium, even if the totality of Ca ions react preferentially with phosphates to form calcium phosphate, the minimum 1:1:1 Mg:N:P ratio necessary for struvite to occur is still available, this would explain that struvite nucleation is possible. At this level, calcium ions could thus affect the rate of growth and the induction time as Koutsoukos *et al.* (2003) mentioned it in their work (Koutsoukos *et al.*, 2003). At higher molar ratios Mg:Ca 1:1, and 1:2, the results are more difficult to interpret as although the turbidity of the solution just after mixing is high due to the preferential reaction of Ca ions with carbonate or phosphate ions, making it difficult to extract data from absorbance measure on the formation of struvite crystals. To understand what happens in those cases in terms of crystal formation and/or characteristics of the compound generated, analysis of the recovered product was necessary. To clarify these first statements the following experiments concerning particle sizing and crystal characterisation were carried out.

4.3.3 Particle sizing experiments and crystals characterisation

To determine the influence of Ca^{2+} ions at higher concentrations, and to investigate their effect on the struvite crystal properties, it was decided to undertake a series of experiments using particle sizing, XRD and SEM-EDS. Particle size measurements were performed continuously at constant mixing speed during the precipitation process and the particle size was recorded over periodic intervals. Again changes in particle size were followed for a range of Mg:Ca ratios. As a reference the change in particle size in a solution without added Ca was measured and the data obtained showed a monomodal particle size distribution for all the distributions, with a mean size rising to constant values comprised between 13.416 and 15.157 μm after 5 minutes of experiment (Figure 4.3, Figure 4.4).

The effects of Ca concentration on the evolution of struvite particle size are showed here by plotting the particle size distribution at the beginning (T=5 min) and the end (T=20 min) of the experiment. An increase of the Ca concentration in relation to the Mg concentration results in a decrease of the mean size measured after 5 minutes run: maximum peaks are recorded between 2.15 μm to 2.429 μm for the ratio 2:1, 2.745 μm to 3.101 μm for the ratio 1:1 and 3.958 μm to 4.472 μm for the ratio 1:2. After 20 minutes run, the results are different. The distribution in presence of Ca^{2+} ions at low concentration (ratio Mg:Ca 2:1) appears with a maximum peak corresponding to a mean size of particle lower than for the run without Ca. At higher Ca concentrations (ratios 1:1, and 1:2), the data showed a rise in the population of particles with higher mean size (Figure 4.4) than for the results without Ca addition. This may indicate an agglomeration of the particles so that the percentage of individual particles decreases compared to the agglomerates. SEM pictures taken of dried samples recovered at the end of each trial helped to explain this supposition.

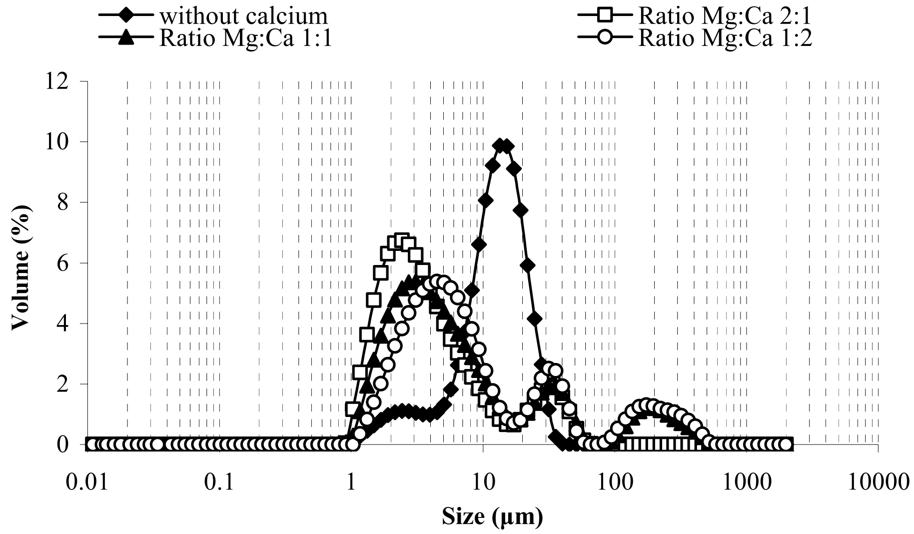


Figure 4.3. *Particle size distribution five minutes after the mix of the solutions for different molar ratio Mg:Ca.(V_{mixing}=2500 rpm).*

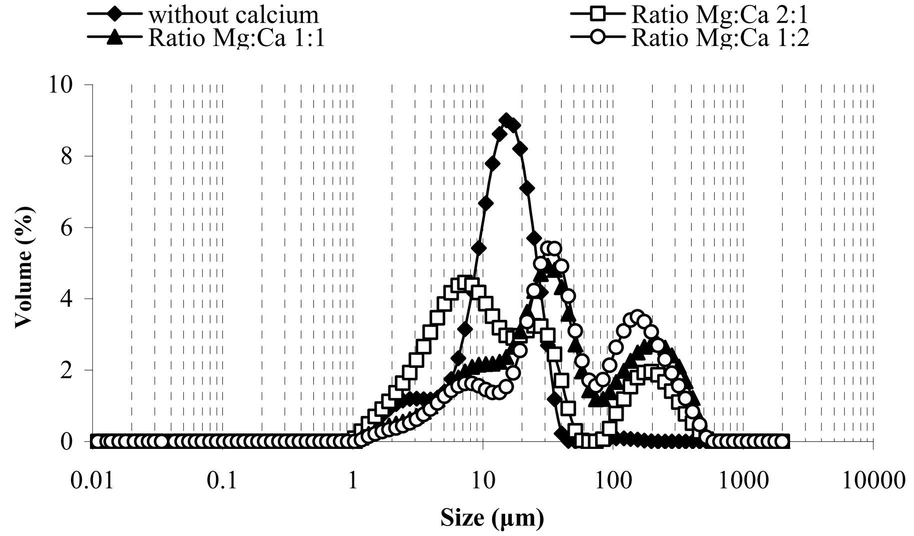


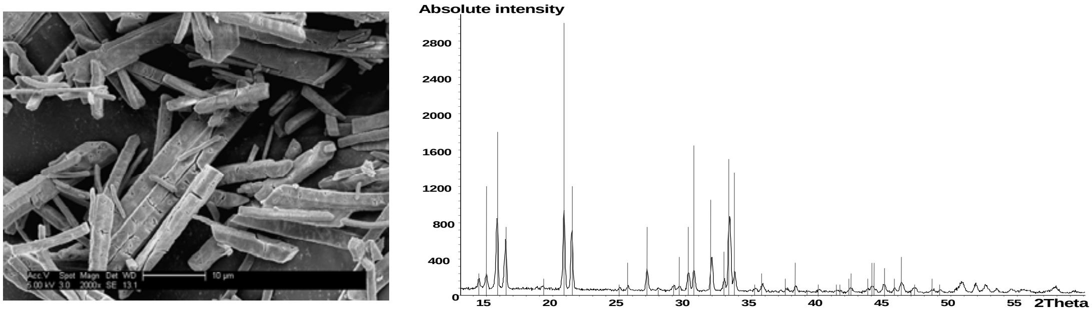
Figure 4.4. *Particle size distribution 20 minutes after the mix of the solutions for different molar ratio Mg:Ca (V_{mixing}=2500 rpm).*

Firstly, the XRD pattern generated from the sample without Ca matched with the database model for struvite (i.e. position and intensity of the peaks, Figure 4.5, sample 1), identifying the precipitate to be struvite (PCPDFWIN database). But as Ca concentration increases (Mg:Ca 2:1, Figure 4.5, sample 2), XRD results showed a more noisy pattern with reduction in peak size and definition. At higher Ca concentrations the analysis revealed only background noise, indicating that there was no macro crystalline compound present in the samples (Figure 4.5, XRDs of samples 3 and 4). SEM confirmed the results of the particle size experiments and XRD analysis in that the formation of struvite crystals (Figure 4.5, picture sample 1) is affected by the presence of Ca^{2+} ions. At a low calcium concentration in solution, we can still distinguish the shape of struvite particle but covered by a precipitate (Figure 4.5, picture sample 2) whilst a rise to higher Ca concentration inhibits the occurrence of struvite crystals and leads to the formation an amorphous matter (Figure 4.5, pictures sample 3 and 4), probably a calcium phosphate compound. To identify the elemental composition of this amorphous matter, energy dispersive spectrometry has been used on specific area localised on the SEM pictures.

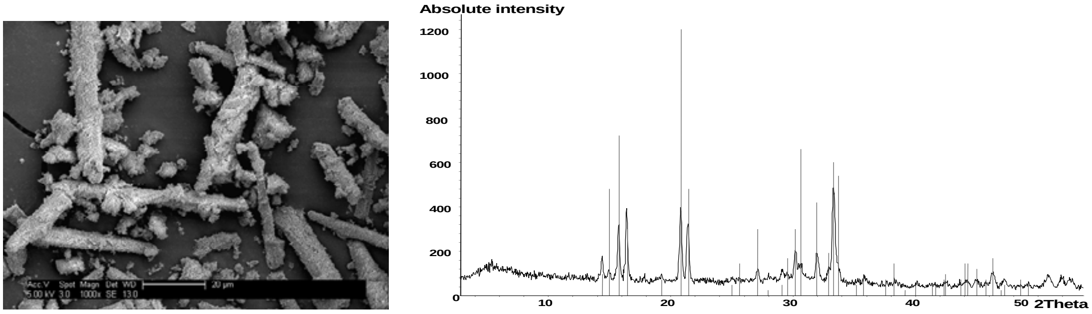
As expected for samples without Ca, EDS spectrum (Figure 4.6, Sample1) showed highest peaks were obtained for Mg, P and O (*i.e.* major elements composing struvite in mass percentage), confirming the purity of the crystal formed as no traces of other compounds have been found. At a Mg:Ca ratio of 2:1, EDS performed on struvite like crystals covered with an amorphous substance, showed the presence of a distinctive peak for Ca while peaks for Mg and P were quasi unchanged (Figure 4.6, Sample 2 A). We can say that at this level another phase precipitates on struvite crystal surfaces and around, hence starting to interact with its formation. It is more than just calcium which is absorbed on the surface of struvite crystals. An EDS analysis performed on an amorphous part next to the crystal like shape in the same sample (Figure 4.6, Sample 2 B) revealed a higher peak for Ca and an important peak for phosphorus when compared to the magnesium one. The formation of this precipitate at the surface of crystals would thus explain the multitude of background noises observed previously on the XRD patterns (Figure 4.5, sample 2) while struvite peaks are still identifiable.

At Mg:Ca 1:1 and above (Figure 4.6, samples 3 and 4), the EDS spectrum of this amorphous matter reinforce the first hypothesis that the precipitate formed at this stage is due to the formation of an amorphous calcium phosphate. Indeed both spectra show prominent peaks for phosphorus and calcium when compared to magnesium. From a first point of view, we could have identified it as either an amorphous calcium phosphate or another calcium phase (*i.e.* calcium carbonate or calcium hydroxide), but in the latter case XRD pattern for samples 2 to 4 would have showed them on Figure 4.5, as they are crystalline substances. This confirms thus that the chemical nature of this matter is easily assimilated as an amorphous calcium phosphate.

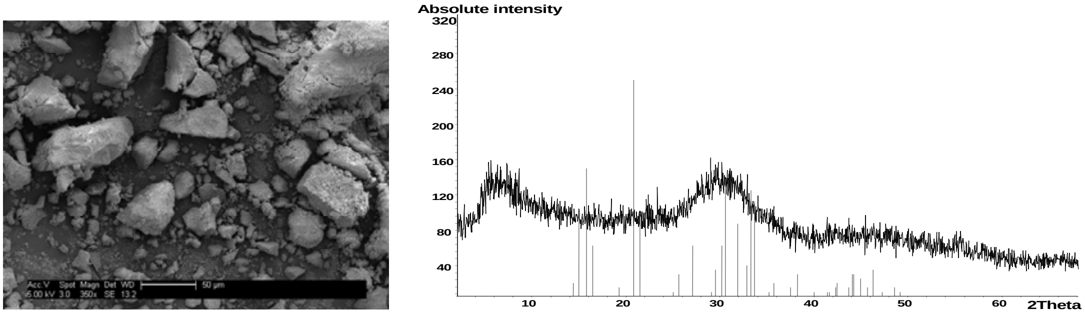
- *Sample 1:* [Mg]= 1.64mM, Ratio Mg:Ca=1:0



- *Sample 2:* [Mg]= 1.64mM, Ratio Mg:Ca=2:1



- *Sample 3:* [Mg]= 1.64mM, Ratio Mg:Ca=1:1



- *Sample 4:* [Mg]= 1.64mM, Ratio Mg:Ca=1:2

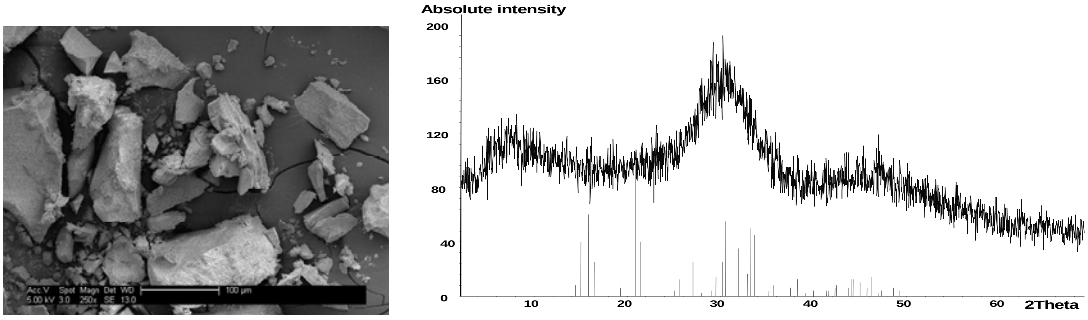
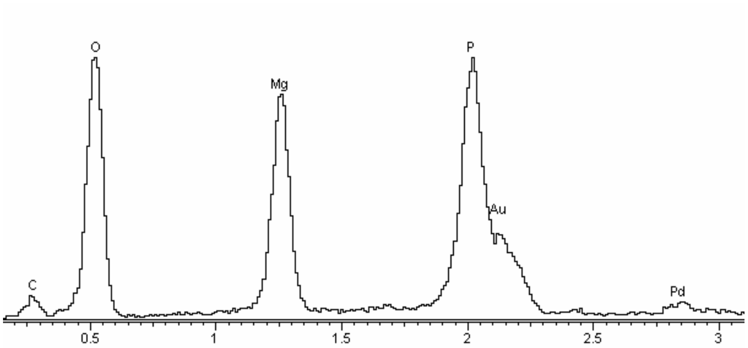
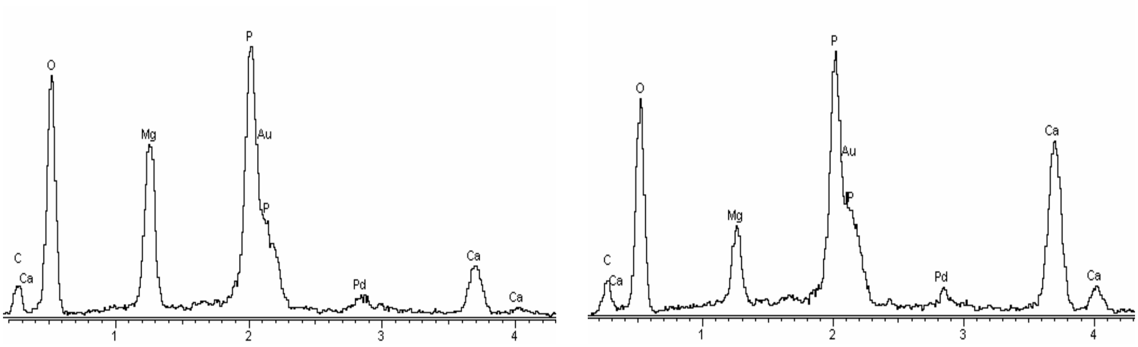


Figure 4.5. *Impact of growing amounts of Ca^{2+} ions on struvite crystal morphology and purity. SEM pictures and their respective X-ray Diffractograms*

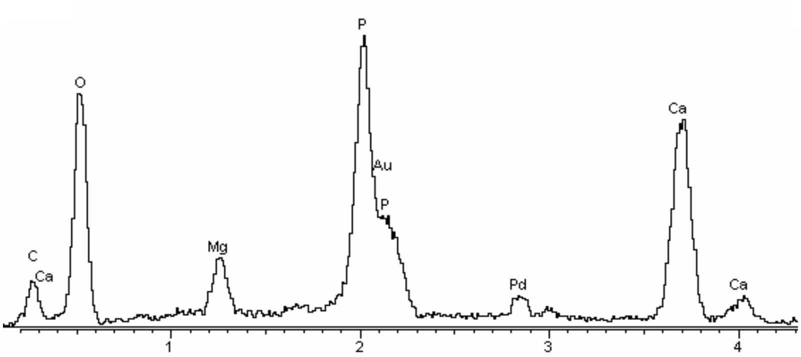


Sample 1: [Mg]= 1.64mM / Ratio Mg:Ca=1:0

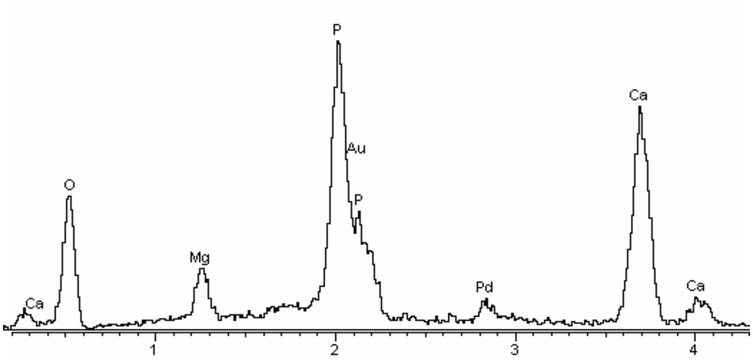


Sample 2: [Mg]= 1.64mM / Ratio Mg:Ca=2:1

A B



Sample 3: [Mg]= 1.64mM / Ratio Mg:Ca=1:1



Sample 4: [Mg]= 1.64mM / Ratio Mg:Ca=1:2

Figure 4.6. *Impact of growing amounts of Ca^{2+} ions on struvite crystallisation. Elemental surface analysis by EDS.*

4.4 Conclusion

The impact of Mg and Ca solution concentrations on struvite crystallisation has been investigated using a range of analytical tools including pH, absorbance, particle size, XRD and SEM-EDS.

It has been shown that the presence of Ca ions in solution has a significant impact on struvite crystallisation in terms of size shape and purity of the product recovered. In the present study, it has been found that increasing the calcium concentration reduces the crystal size and inhibits the struvite growth, or affects struvite crystallisation and leads to the formation of an amorphous substance rather than crystalline struvite.

At molar ratios Mg:Ca~1:1 and above, no more crystalline compound is formed but a substance identified as an amorphous calcium phosphate.

As Ca ions levels in sludge liquors are high in relation with Mg levels, Ca impact on struvite crystal morphology will have to be considered in the future in order to improve the recovery and reuse as a fertiliser.

Further works will thus focus on the extrapolation of these laboratory results using a reactor which has been designed and is currently being used to study struvite nucleation and growth at larger scale.

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CHAPTER 5

IMPACT OF REACTOR OPERATION ON SUCCESS OF STRUVITE PRECIPITATION FROM SYNTHETIC LIQUORS

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5. IMPACT OF REACTOR OPERATION ON SUCCESS OF STRUVITE PRECIPITATION FROM SYNTHETIC LIQUORS

K.S. Le Corre[1], E. Valsami-Jones[2], P. Hobbs[3], S. A. Parsons[1]

1 School of Water Sciences, Cranfield University, Cranfield MK43 0AL, UK
*Tel: +44 (0)1234 754841, Fax: +44 (0)1234 751671
E-mail address: s.a.parsons@cranfield.ac.uk
2 Department of Mineralogy, The Natural History Museum, Cromwell Road London, SW7 5BD, U.K
3 Institute of Grassland and Environmental Research (IGER), North Wyke, Okehampton, Devon, EX20 2SB, UK

Abstract

A pilot scale reactor was designed and developed to study struvite crystallisation principles. The present work focuses on the possible impact of reactor's operating parameters on struvite characteristics, and evaluates the performances of the process in removing phosphorus. Struvite precipitation from synthetic liquors was investigated under various situations including: pH and magnesium doses variations, addition of foreign ions as calcium and increasing retention times. If under any conditions tested good phosphorus removals were achieved, small differences in pH, magnesium and calcium doses, or retention times were found to have significant effects on struvite crystals characteristics and/or production. For instance, an increase of pH from 10.0 to 10.5 favoured the formation of $Mg_3(PO_4)_2$.22H2O rather than struvite. And for molar ratios Mg:Ca above 1:1, calcium ions competed with magnesium to form an amorphous calcium phosphate, hence inhibiting struvite formation. With regards to crystal growth, the process showed some limitations. Indeed, large amounts of fines were produced, and crystal rarely grew over 100 µm under optimum conditions. Based on those observations, zeta-potential measurements of struvite crystals were investigated. Results revealed highly negative zeta-potential values after any set of experiments, limiting then struvite tendency to grow through agglomeration.

Keywords: Phosphorus removal, struvite production, particle size, morphology, zeta-potential

5.1 Introduction

The simultaneous reduction of natural phosphorus resources available for the phosphate industry, and the increasing awareness of pollution problems such as eutrophication due to phosphorus release in wastewater effluents (UWWTD 1991, Shu *et al.*, 2006), have led to research into new processes to remove and recover phosphorus from effluents.
Traditional phosphorus removal processes work by fixing the phosphorus into the sludge:

- either chemically by precipitation of soluble phosphorus with aluminium or iron salts into insoluble phosphates compounds (Donnert and Salecker, 2001);
- or biologically (*i.e.*: BNR, EBPR) using the ability of some micro-organisms to accumulate phosphates as polyphosphates for their own metabolism Mulkerrins *et al.*, 2004).

Both processes are efficient as they are capable of reducing phosphorus concentration in treated effluents below 1 $mg.L^{-1}$ as stated by the European legislation (Booker *et al.*, 1999). However they lead to the accumulation of phosphorus in the sludge as well as an increase in sludge volumes (Wood *et al.*, 1999).
An approach to remedy those problems and help removing phosphorus from wastewater effluents consists in its crystallisation as struvite ($MgNH_4PO_4.6H_2O$) (Doyle and Parsons, 2002). Although known as a scaling agent which affects treatment processes as it leads to operational failures associated to build-up in sludge pipes, centrifuge, heat exchangers, flow-meters (Doyle and Parsons, 2004; Neethling and Benisch, 2004), struvite crystallisation, if controlled, represents a promising solution for phosphorus removal and recycling from wastewater effluents. Indeed, as a slow release fertiliser, struvite was proved to be a good source of phosphorus for crops, almost equal in efficiency to mono calcium phosphates, MCP (Johnston and Richards, 2003). Furthermore, struvite crystallisation presents other major advantages in that it can help to reduce volumes of sludge generated by conventional P-removal processes from 5 % up to 49% depending on the treatment configuration (Woods *et al.*, 2000), hence reducing sludge handling costs (Woods *et al.*, 2000; Doyle and Parsons 2002; Shu *et al.*, 2006), and should limit chemical costs typically high when compared to metal salt precipitation (Shu *et al.*, 2006).

In the past ten years, research groups have developed several processes at laboratory or pilot scale, and few at full scale, to study and improve struvite crystallisation from wastewater effluents (Ueno and Fujii, 2001; Wu and Bishop, 2004; Battistoni *et al.*, 2005; Suzuki *et al.*, 2005). The processes can be divided in two categories:

- Those which generate struvite particles in stirred or air agitated reactors where crystal growth occurs by interaction of struvite nuclei together (Fujimoto *et al.*, 1991; Jaffer and Pierce, 2004)
- Those which form struvite by crystallisation on seed materials in fluidised bed reactors (FBR) or air agitated reactors. As with the stirred reactors, crystallisation is initiated through chemical addition (*i.e.*: to reach the minimum ratio Mg:N:P 1:1:1 needed) and pH adjustment but growth is achieved by interaction of nuclei with seeds such as sand or preformed struvite crystals (Battistoni *et al.*, 1998; Ohlinger *et al.*, 2000).

Although widely studied either at laboratory or pilot scale, struvite crystallisation in a specific reactor located alongside sludge treatment processes remains exceptional at full scale (Ueno and Fujii, 2001). If most of the time good phosphorus, as well as nitrogen, removals are achieved (*i.e.* up to 90% P removal, Ishikawa *et al.* (2004) and up to 95% NH_4-N removal, Uludag-Demirer *et al.* (2005)), such processes still need improvements especially concerning the control of the quality (size, morphology and purity) and quantity of struvite generated.

The success of struvite crystallisation is governed by various parameters. Among the ones known to be particularly influent are pH, magnesium concentration, presence of foreign ions, retention time and presence of seed materials (Le Corre *et al.*, 2005; Matynia *et al.*, 2006; Wang *et al.*, 2006). A better understanding on how those parameters can influence the quality of the recovered product is then necessary to maximise phosphorus removal and recovery as struvite.

In the present work, the influence of magnesium concentration, pH, presence of calcium ions and retention time on struvite crystallisation from synthetic liquors was investigated at pilot scale. Experiments particularly focused on how such operating factors could affect purity, size, morphology, and quantity of crystal formed but also the impact they have on phosphorus removal. Zeta-potentials of struvite particles were also measured to investigate if this parameter could be an explanation to overproductions of fine particles. Finally, based on the results achieved, a map of operating conditions which affect (or not) struvite characteristics and PO_4-P removal was developed in order to identify a set of conditions under which struvite crystallisation was for this system optimised.

5.2 Material and methods

5.2.1 Process design and running configurations

A pilot scale crystallisation reactor was designed and developed at Cranfield University to study struvite nucleation and growth on both synthetic and real liquors (Figure 5.1). The process was composed of a 10 L reactor with two side sampling ports and a drain valve. A peristaltic pump injected simultaneously solutions of ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$ / Fisher Analytical Reagent Grade, UK) and magnesium chloride hexahydrate ($MgCl_2.6H_2O$ / Fisher analytical Reagent Grade, UK), prepared by dissolution of the corresponding solid compounds in deionised water.

Prior to mixing in the reactor, each solution was adjusted to the required pH value (usually 9, or 8.5 to 10.5 when the influence of pH on crystallisation was investigated) with sodium hydroxide (NaOH 2 N/ Fisher analytical reagent grade, UK) in stirred buckets. Both solutions were then transferred to the reactor. A pH probe was introduced in the reaction zone to control and maintain the pH constant during the crystallisation process. An upward air-flow and a liquid recirculation were used and adjusted (10 to 5 $L.min^{-1}$ for air, and 1.5 to 1.35 $L.min^{-1}$ for liquid) to ensure the mixing and growth of the particles formed so that they were always kept in suspension during the experiment.

The influence of water chemistry on struvite nucleation and growth was investigated by testing different magnesium concentrations ranging from 1.2 to 2.3 mM, in a molar ratio Mg:N:P 1:2:2 at pH 9. The impact of the pH of precipitation was investigated at the constant magnesium concentration 1.64 mM, and keeping the pH constant in the reactor. pHs tested were 8.5, 9, 9.5, 10 and 10.5.

Finally, for the experiments investigating the impact of foreign ions as calcium, various amount of calcium chloride dihydrate 0.4 M ($CaCl_2.2H_2O$ / Fisher Chemicals, UK) were injected in the bucket containing the $MgCl_2.6H_2O$ solution, whilst carbonates ions were added in the ammonium phosphate solution as sodium hydrogen carbonate 0.4 M ($NaHCO_3$ / AnalaR Fisher Chemicals, UK) to provide alkalinity so that the solutions were better analogues to real media (*i.e.* wastewater effluents/sludge liquors). The experiments were carried out at constant Mg concentration (*i.e.* 1.64mM) and constant pH (*i.e.* 9). The molar ratios Mg:Ca:CO_3 investigated were 2:1:1, 1:1:1 and 1:2:2.

All standard experiments were conducted at room temperature over 60 minutes, except for the experiments testing the influence of retention time on crystal growth for which experiments were carried out over 5 h and 24 h. Each set of experiment was repeated a three times.

During experiments, samples could be withdrawn for analysis from sampling ports situated on the side of the reactor at chosen height: top and bottom of the column shape part of the reactor and middle of the enlarged section. Struvite crystal recovery was achieved through a drain valve situated at the bottom of the reactor.

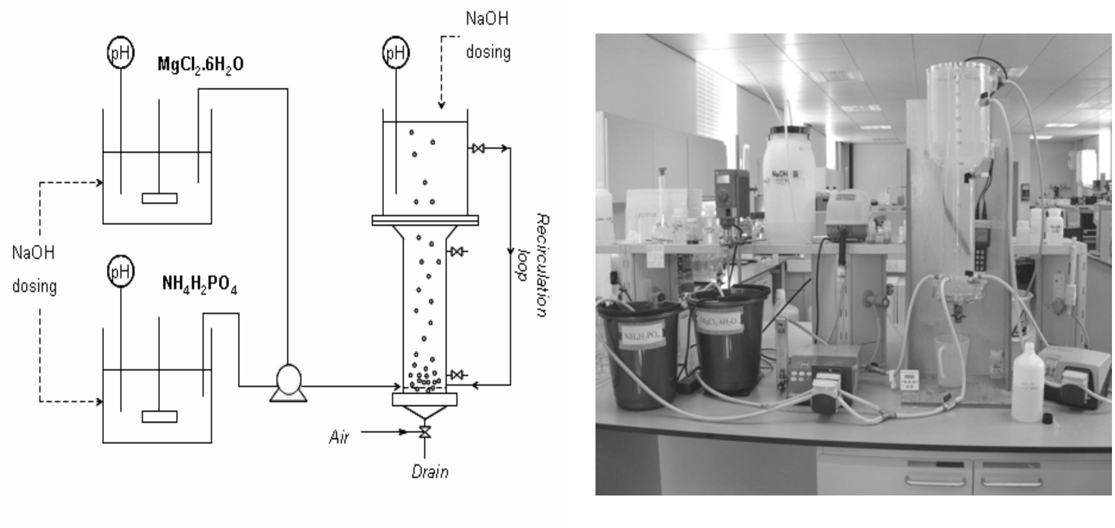


Figure 5.1. *Pilot scale unit*

5.2.2 Chemical analysis and crystal characterisation

5.2.2.1 Removal assessment

After filtration through 0.2 μm filters of 2 L samples taken at the end of each run, supernatants were also kept for ICP analysis (Inductively Coupled Plasma Emission Spectroscopy) to determine the remaining magnesium (Mg) and calcium (Ca) concentrations, while phosphate (PO_4-P) and ammonium (NH_4-N) levels were determined using Merck cell tests.

5.2.2.2. Particle size analysis

For each set of experiments, the average size ($d_{0.5}$) of particles was determined using laser diffraction (Mastersizer 2000, Malvern Instrument, UK). To assess the representative average size of particles in the overall reactor, 1 L samples were taken from each sampling port, and the drain valve. The average size of particles in the overall reactor was then calculated from the four $d_{0.5}$ determined at each outlet. Changes in particle size were followed for a range of initial Mg concentrations, and at constant Mg concentrations but under different constant pH of precipitation. To limit the effect of particle breakage, the peristaltic pump injecting the solution through the Mastersizer cell was set at 40 rpm.

5.2.2.3 Zeta-potential

The zeta-potential of suspended struvite particles was determined using a Zetasizer 2000 HSA (Malvern Instrument, UK).

5.2.2.4 Crystalline properties

Solid residues from 2 L filtrations were dried at room temperature and weighed to estimate the rate of struvite production in $mg.L^{-1}$. Dried samples were then characterised using a Scanning Electron Microscope coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS, Scanning Electron Microscope XL 30 SFEG, Philips, The Netherlands) and X-ray Diffraction (XRD, Powder X-ray Diffractometer D5005, Siemens, Germany) tools.

5.3 Results and discussion

5.3.1 Performance of the designed reactor in removing PO_4-P under various conditions

The first series of experiments aimed at assessing the influence Mg concentrations have on PO_4-P removal (Figure 5.2-a). At constant pH 9, and a Mg:N:P ratio of 1:2:2, it was found that varying the range of magnesium concentration tested, from 1.2 mM to 2.3 mM, the PO_4-P removals remained quasi constant with an average value of 77 ± 4 %. NH_4-N removals measured on the same samples were between 39 % and 56 %.

In presence of calcium ions (Figure 5.2-b), the remaining concentration of calcium in solution was also recorded to detect the potential removal of calcium as calcium phosphate. It was effectively demonstrated in our previous laboratory scale study (Le Corre *et al.*, 2005) that for Mg:Ca molar ratios 1:1 and above, struvite formation was inhibited due to the precipitation of an amorphous calcium phosphate. Here, for a molar ratio Mg:Ca 2:1, the PO_4-P removal was about the same as without calcium in solution, but a 44% calcium removal was achieved while less ammonium was removed, indicating that at this Mg:Ca molar ratio phosphate ions reacted not only with ammonium and magnesium to form struvite but also with calcium. For molar ratios Mg:Ca 1:1 and above, the PO_4-P removal increased up to 88 % while a calcium removal of 89 % was also measured but the ammonium removal dropped to below 20 %. These results suggest that under these specific conditions, calcium ions can limit struvite crystallisation

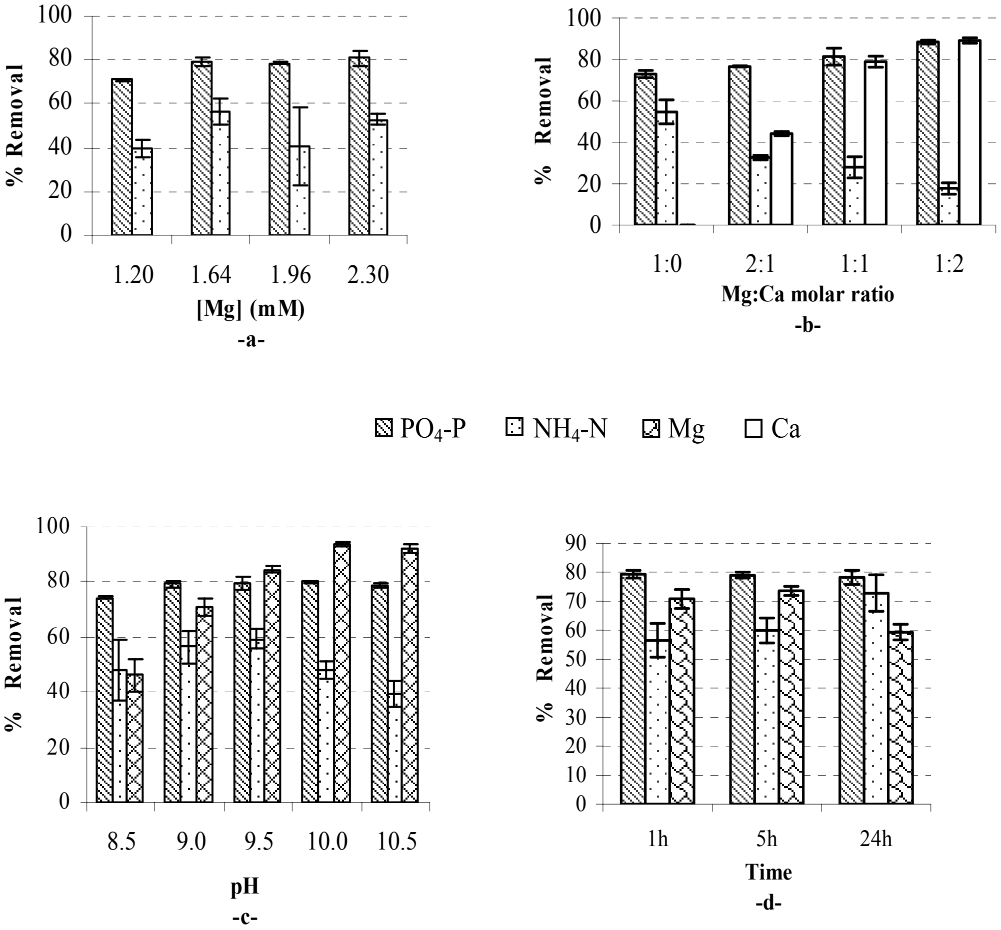


***Figure 5.2**. Effect of Mg concentration, calcium, pH and retention time on PO_4-P, NH_4-N and Mg removals.*

To assess the impact pH had on PO_4-P removal, experiments were performed at a selected constant pH ranging from 8.5 to 10.5. Results are presented on Figure 5.2-c.

Over the range of pHs tested, good PO_4-P removals were achieved with values comprised between 75 % at pH 8.5 and 80 % at pH 10. However, analysis of the residual NH_4-N and Mg indicated that if maximum ammonium removals were achieved for pH 9 and 9.5 with respective values of 56 % and 59 %, it was not the case for magnesium. Indeed, levels of magnesium measured in solution after 1 h experiment decreased over the range of pH tested with removals varying from 46 % at pH 8.5 up to 92 % at pH 10.5. pH 9, and 9.5 are the conditions identified here at which struvite crystallisation is optimised with regard to nutrients removal.

Finally the influence of retention time on nutrient removal was also evaluated. A series of runs were performed at pH 9, and magnesium concentration 1.64 mM but for the following contact times 1 h, 5 h and 24 h. The results revealed that retention did not affect significantly the amount of PO_4-P, NH_4-N and Mg removed (Figure 5.2-d) as good removals were achieved after only 1 h of experiment (79 %, 56 % and 70 % for respectively PO_4-P, NH_4-N and Mg).

5.3.2 Impact of operation conditions on struvite characteristics and production

The principal interest of recycling phosphorus from wastewater effluents as struvite is its potential reuse as a fertiliser. Therefore, the efficiency of any reactor does not only depend on phosphorus removal from effluents but also on the quality (*i.e.* size, morphology and purity) of the final product. It is thus necessary to understand how parameters such as water chemistry, pH, foreign ions, and retention time can affect struvite characteristics.

5.3.2.1 Impact on quality of the product formed

For the majority of experiments, conditions of operation have not affected the quality of struvite formed with regard to morphology and purity. Typical orthorhombic crystals were effectively observed (Figure 5.3-A), except for experiments undertaken in the presence of calcium or at pH 10.5.

In presence of calcium, SEM-EDS and XRD analysis of the recovered products showed no more struvite was observed for ratios 1:1 and above but an amorphous calcium phosphate confirming that high phosphorus removal previously showed (Figure 5.2-b) were due to the reaction of calcium ions with phosphates.

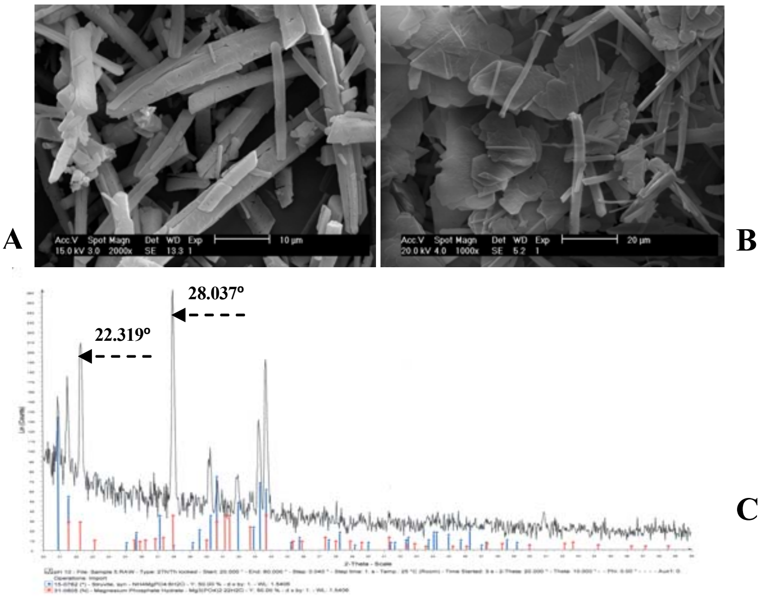
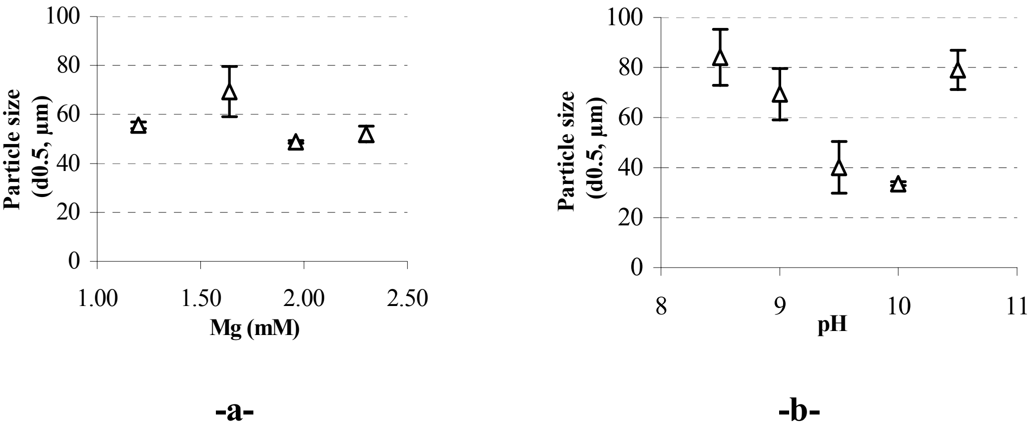


Figure 5.3. *SEM pictures of the of typical struvite crystals (A) and sample recovered at pH 10.5 (B); XRD analysis of the sample recovered at pH 10.5 (C).*

At pH 10.5, SEM pictures revealed that struvite crystals were still observable, but surrounded by a large amount of another compound of larger shape (Figure 5.3-B).

While XRD analysis undertaken on the recovered products validated that all other samples were pure struvite, the XRD diagram of the product generated at pH 10.5 (Figure 5.3-C) showed the presence of a second crystalline compound characterised by two high and thin peaks situated at 2-theta angles of 22.319° and 28.037°. By comparisons with models of the XRD database (PCPDWIN database), it was found that most of the peaks matched with the model for struvite while the two new peaks corresponded to a magnesium phosphate hydrate of chemical formula: $Mg_3(PO_4)_2.22H_2O$, which is known as a synthetic polytype of the cattiite (Britvin *et al.*, 2002). $Mg_3(PO_4)_2.22H_2O$ usually precipitates at pH 9 and above, and was mentioned previously by Tünay *et al.* (1997) as a compound susceptible to interfere in struvite precipitation depending on limiting conditions.

To describe the quality of the recovered product, the mean size ($d_{0.5}$) of particles formed was also assessed. No correlation was found to link the magnesium concentration or the retention time with the size of struvite crystals formed. For instance, values measured were 55.62 ± 1.37 µm, 69.36 ± 10.24 µm, 48.73 ± 0.58 µm and 51.99 ± 3.16 for respective magnesium concentrations of 1.2mM, 1.64 mM, 1.96mM and 2.3 mM. For a magnesium concentration of 1.64 mM, the average particle size was the highest determined with a mean value of 69.36 ± 10.24 µm but remained small (Figure 5.4-a). After 1 h, 5 h and 24 h, d0.5 were 69.4 ± 10.2 µm, 48.6 ± 7.7 µm and 54.3 ± 2.5 µm respectively, showing retention time had little effect here on struvite crystal size, though pH did have a significant impact on the size of the particle formed. An increase in pH from 8.5 to 10 linearly decreased the size of crystals formed from 84.0 ± 11.0 µm down to 33.5 ± 0.7 µm (Figure 5.4-b). However, this decrease in size was not observed at pH 10.5, for which the average particle size recorded was 79.0 ± 0.7 µm. But in that situation, the increase in size was not related to struvite but to the presence of $Mg_3(PO_4)_2.22H_2O$ as it was found to be the main compound formed at this pH. Those results were coherent with the one observed by Matynia *et al.* (2006) in their study on the influence of process parameters on struvite crystallisation kinetics where they reported that an increase of pH from 8 to 10 resulted in a significant decrease in struvite crystal size (*i.e.* a 5.5-fold decrease). However, for a pH of 11, Matynia *et al.* (2006) still observed a decrease in particle size, while in th present study, size of particles increased at a pH of 10.5.



-a- -b-

***Figure 5.4**. Average size of particles formed in the reactor at various [Mg^{2+}]and constant pH 9, and at various pH.*

Finally, no significant changes in size were observed between the samples taken from the different sampling port situated on the side of the reactor indicating a homogeneous mixing keeping the particles in suspension. But this also suggests that the growth was limited as particles taken from the drain valve should have been bigger due to settlement.

5.3.2.2 Impact on quantity of product formed

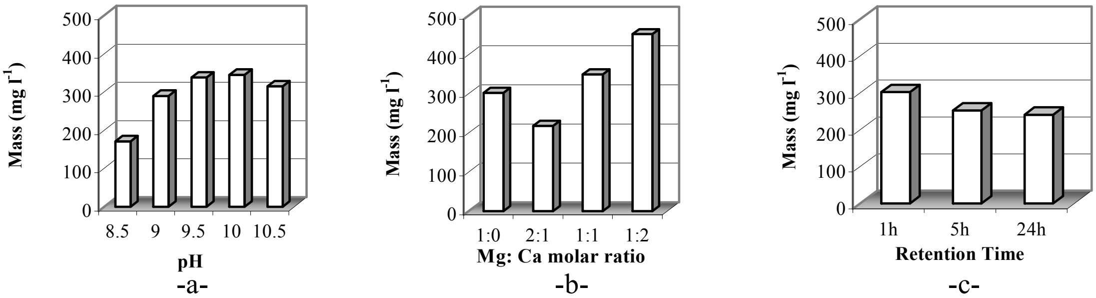
While size is important to facilitate struvite recovery, and purity is essential for reuse as a fertiliser, quantity is crucial to the economical viability of the process. The amount of struvite recovered has been quantified for each specific condition of precipitation previously tested (Figure 5.5).

For experiments undertaken with varying Mg concentrations the production logically increased as more Mg was available to form struvite. To illustrate, 75 mg.L^{-1} and 375 mg.L^{-1} of struvite were recovered when the Mg concentration was 1.2 mM and 2.3 mM respectively.

pH had a significant effect on quantity with the average mass of struvite in the reactor ranging from 290.1 to 345 mg.L^{-1} between pH 9 and 10, while at pH 8.5 the rate observed was low (171.3 mg.L^{-1}) when compared to the higher pHs (Figure 5.5-a).

Similar explanations are attributed to high rates of production observed in presence of high levels of calcium (Figure 5.5-b). By addition of calcium in a molar ratio Mg:Ca 2:1, less product was formed: 217.9 mg.L^{-1} instead of 302.2 mg.L^{-1} without any calcium. It shows at this particular Mg:Ca molar ratio that calcium partly inhibited struvite formation while calcium phosphate occurrence remained too low to affect the overall mass of product formed. For molar ratio 1:1 and above a significant increase of the mass of product recovered per litre was observed. Rates reached values of 400.0 mg.L^{-1} and more (Figure 5.5-b). As seen previously at this stage, this increase is not attributed to the formation of struvite but to an overproduction of calcium phosphate.

Finally, retention time had no major effects on production rate with an average value of 265.1 ± 32.7 mg.L^{-1} over the range of times trialled (Figure 5.5-c). Indeed, the decrease in mass of product generated observed between 1 h and 24 h was mainly due to particles overflowing from the reactor over longer period of time.



-a- -b- -c-

***Figure 5.5**. Effect of pH, calcium ions, and retention time on the mass of precipitate formed.*

In his economic evaluation of phosphorus recovery as struvite from digester supernatant, Shu *et al.* (2006) estimated that a WWTP treating 100 $m^3.d^{-1}$ of wastewater can reasonably recover 1 kg of struvite. In the current study, at constant pH 9, for a concentration of magnesium of 1.64 mM, and a molar ratio Mg:N:P 1:2:2, 290.1 $mg.L^{-1}$ of struvite were recovered. Theoretically, 100 m^3 of the identical synthetic liquors would then produce 29 kg of struvite. However the present tests were carried out in batch mode. Taking into account that 9 L of solution per hour were needed to produce 2.61 g of struvite, the present reactor could then only treat 0.216 m^3 per day. A scaling up of the reactor's volume, and adaptation of this latest to a continuous mode would be thus necessary to achieve a struvite production of 29 kg per 100 m^3 of identical wastewaters.

5.3.3 Limitation of the process

From those first series of experiments testing different conditions of precipitation at pilot scale in the designed reactor, limits of this latest have been showed. If most of the time good phosphorus removal were achieved and reasonable quantity of pure struvite were reached, growth was limited with final particle size ($d_{0.5}$) rarely exceeding 100 µm after 1 h of experiments. However, comparison with the literature showed that particle sizes observed here can be similar, and sometimes greater than struvite crystal sizes generally observed (Table 5.1).

For example, Kofina and Koutsoukos (2004) crystallised struvite from synthetic wastewaters at laboratory scale and did not formed crystals over 30 µm after 1 h of experiments. Conversely, in their study of struvite precipitation, Adnan *et al.* (2003), managed to form crystals of 2.5 mm average size but only after a minimum of 7 days in their pilot-scale fluidised bed reactor.

In systems precipitating struvite from real media (*i.e.* anaerobically digested sludge liquors, Table 5.1), struvite crystal sizes vary a lot from one type of reactor to another. This is mainly due to differences in operating conditions, especially crystal retention time, and probably to variations in quantities of impurities in liquors. To illustrate, Von Münch and Barr (2001) achieved mean crystal sizes of 110 µm after 24 h of operation in a pilot scale air agitated reactor, while Ueno and Fujii (2001) generated at full scale crystals comprised between 500 and 1000 µm after 10 days.

***Table 5.1**. Struvite crystal sizes reported in the literature*

Media	Type of reactor	Running Time	Particle size (µm)	References
Synthetic wastewaters	Stirred reactor V=0.6 L	15 min	5.6-45.6	Matynia et al. (2006)
	Stirred reactor V=0.25 L	25 to 90 min	10-30	Kofina and Koutsoukos (2004)
	Stirred reactors V=2 L	5 days	425-2360	Stratful et al. (2001 and 2004)
	Fluidised Bed V=24.4 L	7 to 17 days	2600-3700	Adnan et al. (2003)
Anaerobically digested sludge liquors	Air agitated reactor V=3.5 L	A few days	300	Jaffer an Pearce (2004)
	Air agitated column reactor V= 143 L	1 day	25-215	Von Münch and Barr (2001)
	Fluidised bed reactor V>25 m^3	10 days	500-1000	Ueno and Fujii (2001)

Nevertheless, comparisons of particle sizes can be delicate as sizes of struvite crystals strongly depend on morphology of the sample. For instance, Stratful *et al.* (2001) indicated that they formed crystals of 3 mm mean size, but in that case crystals were thin and elongated, while Adnan *et al.* (2003) formed comparable particles in size but in the latest case microscopic images revealed a strong agglomeration of single crystals. For an efficient recovery or ease of reuse, agglomerated particles are ideal. Indeed, thin crystals are fragile, and would increase settlement stages when compared to agglomerated crystals. However, reasons of struvite crystals agglomeration are unclear (Adnan *et al.*, 2003). A small variation in nature of feed, operating pH, and supersaturation, can have a major impact on growth, hence leading to big changes in struvite morphology.

Given that an excess formation of small crystals was observed in all set of experiments, the possible influence of zeta-potential on struvite growth through agglomeration was then investigated.

Zeta-potential measurements undertaken on struvite suspensions generated in the pilot reactor demonstrated that when the pH of precipitation increased from 8.5 to 10, average sizes of particles dropped from 80 down to 33 µm while associated zeta-potentials decreased from -17.5 ± 1.1 to -23.3 ± 0.6 mV (Table 5.2). At pH 10.5, the zeta-potential was the lowest value recorded but the associated size of particles increased significantly up to 70.9 µm. Nevertheless, this deviation could be due to the fact that at this pH a mix of struvite and $Mg_3(PO_4)_2.22H_2O$ was formed.

***Table 5.2**. Average struvite crystal sizes and respective zeta-potentials at different pH of crystallisation.*

	Present study		**Bouropoulos and Koutsoukos (2000)**
pH	**Zeta-potential (mV)**	**Size (µm)**	**Zeta-potential (mV) (estimated from graph)**
8.5	-17.5 ± 1.1	84.0 ± 11.2	-
9.0	-20.4 ± 2.4	69.4 ± 10.2	-
9.5	-23.1 ± 1.4	40.1 ± 10.3	~-21.5
10.0	-23.3 ± 0.6	33.5 ± 0.7	~-25.5
10.5	-27.6 ± 1.2	79.0 ± 7.8	-

Struvite zeta-potential was first reported by Bouropoulos and Koutsoukos (2000). They indicated that the influence struvite particle charge may have an influence on its agglomerative properties. As demonstrated here, they also found that the charge of struvite particles formed varied with the pH, and that struvite particles had higher zeta-potential at higher pH of crystallisation (Table 5.2). Although they did not link those values to particle size, they mentioned that such variations in zeta-potentials were susceptible to have an effect on crystals growth kinetics and lead to eventual destabilisation of particles by aggregation. Finally they remarked that an increase in pH above 10.5 caused visible flocculation of crystals, which could correlate with the precipitation of $Mg_3(PO_4)_2.22H_2O$ observed here at the same pH of crystallisation.

Experiments undertaken here proved that zeta-potential is another parameter that could influence struvite crystal characteristics. A small difference of pH can effectively cause a variation in zeta-potential, affecting thus struvite surface charge. According to zeta-potential values measured, struvite particles precipitated under the current operating conditions were then kept apart due to electrostatic repulsions (Duan and Gregory, 2003). This phenomenon limited then their tendency to attract each other and their subsequent growth through agglomeration. It would then explain why only single crystals of struvite have been observed here.

5.4 Conclusion

The operation of the present reactor under various conditions of precipitation including water chemistry, presence of foreign ions, pH of precipitation and reaction times showed its capacity to remove high amounts of phosphorus (~80% at constant pH 9) after rather short experimental time (1 hour). As illustrated on the following diagram (Figure 5.6), pH was found to be the most influent parameters as it can affect nutrient removal, quantity of product formed, and quality (*i.e.* size, morphology and purity) of the crystallised struvite, while foreign ions mainly affect quality of the product formed and PO_4-P removal. Magnesium concentrations and experimental times were of lowest influence with magnesium affecting only quantity of struvite formed and experimental time none of struvite characteristics or nutrient removal.

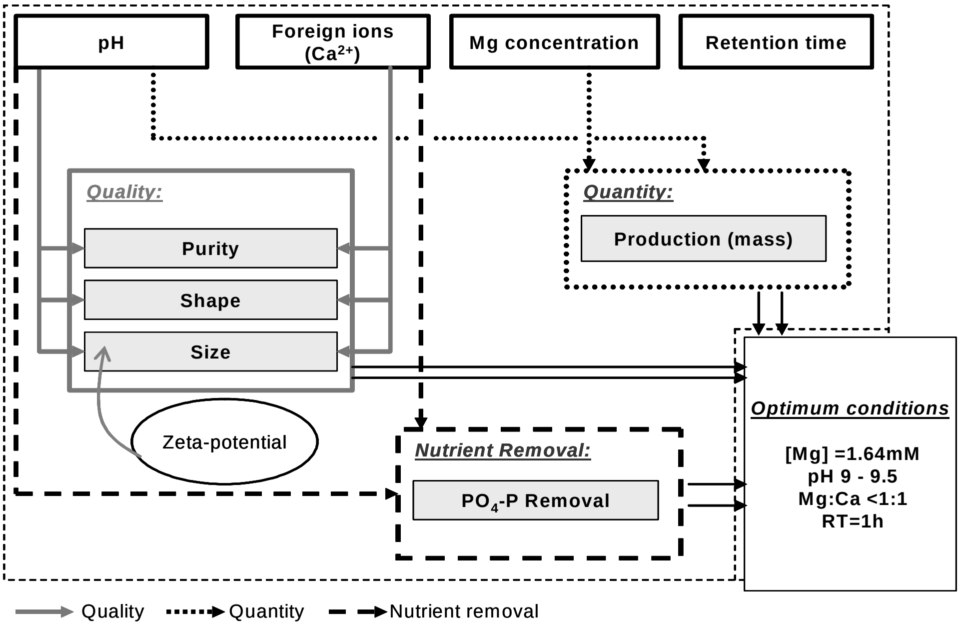


Figure 5.6. *Overview of operating parameters impact on struvite crystallisation*

However, the process showed limits with regards to the size of particles formed as an overproduction of small particles was observed. A possible explanation to this could come from the actual surface charge of struvite crystals. Negative zeta-potential of struvite particles demonstrated here indicated that agglomeration processes are not favoured. Possible solutions to remedy this problem of fine formation could then consist in:

- the coagulation of fine particles through coagulation by addition of positively charged compounds into struvite solution to initiate agglomeration.
- or the second option would be the utilisation of seed particles. The addition of materials such as sand, or preformed struvite crystal could effectively help to improve the growth step, as they would enable the agglomeration of struvite fine particles on those materials.

Both solutions were investigated and will be the object of future publications.

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CHAPTER 6

AGGLOMERATION OF STRUVITE CRYSTALS

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6. AGGLOMERATION OF STRUVITE CRYSTALS

Kristell S. Le Corre[1], Eugenia Valsami-Jones[2], Phil Hobbs[3], Bruce Jefferson[1], Simon A. Parsons[1*]

[1]School of Water Sciences, Cranfield University, Cranfield MK43 OAL, UK
[*]Tel: +44 (0)1234 754841, Fax: +44 (0)1234 751671
E-mail address: S.A.Parsons@Cranfield.ac.uk
[2] Department of Mineralogy, The Natural History Museum, Cromwell Road London, SW7 5BD, U.K
[3]Institute of Grassland and Environmental Research (IGER), North Wyke, Okehampton, Devon, EX20 2SB, UK

Abstract

Struvite crystallisation is widely studied as a way to remove phosphorus from wastewater effluents and simultaneously generates a valuable product for the fertiliser industry. However, to date, some crystallisation processes experimented at either pilot/or full scale face problems linked to the formation of fines. This paper presents results on the investigation of struvite agglomerative properties and the possible application of coagulants and/or flocculants to remove fines. Coagulants investigated were hydrolysing metals salts (Al^{3+} and Fe^{3+}), calcium compounds and a cationic polymer (polyDADMAC). The effects of a natural flocculant (alginate) have also been tested. Results demonstrated that destabilisation of struvite particles by chemical addition was feasible and identified polyDADMAC as a good option for the agglomeration of struvite particles. However, optimisation of its dosage under typical pH conditions for struvite formation showed floc formation to be very pH sensitive.

Keywords: struvite, particle size, polyDADMAC, coagulation, zeta-potential

6.1 Introduction

Struvite ($MgNH_4PO_4.6H_2O$) is a crystalline compound known to form a hard scale in specific areas of wastewater treatment plants such as in sludge liquors pipes, centrifuges, belt presses, and heat exchangers (Doyle and Parsons, 2002). Methods to control the formation of struvite have been studied including the dilution of struvite crystals with water effluents (Borgerding, 1972); preventive action by chemical dosing of iron salts (Mamais *et al.*, 1994) or addition of chemical inhibitors (Doyle and Parsons, 2004). However, the success of such schemes is not only determined by struvite removal, but also the costs associated with operational issues such as chemical addition, manpower, and maintenance (Neethling and Benisch*,* 2004). Since struvite was identified as a route to remove and recover phosphorus as a marketable fertiliser, the idea of its crystallisation in a specific reactor to prevent its spontaneous precipitation has been then widely investigated (Ohlinger *et al.*, 2000; Von Münch and Barr, 2001).
To date, struvite crystallisation reactors have been used at laboratory, pilot and full scale and have shown great potential in removing and recovering phosphorus as struvite crystals (Fujimoto *et al.*, 1991; Ueno and Fujii, 2001; Battistoni, 2004; Jaffer and Pearce, 2004). However, issues remain with regard to the degree of growth and the formation of fines. The production of fines in the reactor is indeed problematic as these small particles (*e.g.* ~ 100 µm mean size in the process used by Ishikawa *et al.*, 2004) can be flushed and recirculated back to the treatment as a result of high mixing speeds or flow rates required to maintain bigger particles in suspensions (Battistoni *et al.*, 2005). To control the fines, Shimamura *et al.* (2003) used a sub-reaction tank in which fines were grown up to 300 µm before being re-injected in the main reaction tank as a seed substrate. Other researchers used separating techniques to isolate fines and reuse them as seeds in their crystallisation process (Ueno and Fujii, 2001) or combined their plant with a filtration unit or external clarifier to limit loss of fines in effluents (Battistoni *et al.*, 2005; Adnan *et al.*, 2003). As an alternative, the present paper investigates the possibility of remediating struvite fines by coagulation.

The agglomeration of particles of various sizes and characteristics found in water and wastewater is typically achieved by addition of coagulant and/or flocculants such as metals salts and polymers (Delphos and Wesner*,* 2005; Crittenden *et al.*, 2005). Their role is to bring particles in suspension in contact by limiting forces which naturally keep them apart from one another. As particles in water invariably possess a negative surface charge (Duan and Gregory, 2003), their stability in water is principally the result of electrostatic repulsions (Letterman *et al.*, 1999). The role of coagulants and flocculants is then to affect the stability of particles and favour aggregation through physical collision and particle bridging (Gregory, 2006). Therefore, added chemicals are generally positively charged coagulants such as hydrolysing metal compounds (alum and iron salts) or natural or synthetic polymers. Here we have measured the surface charge properties of struvite crystals and investigated a range of coagulant and flocculants, including ferric and aluminium salts, calcium compounds, polyDADMAC and alginate as a flocculant aid, for their performance in destabilising and coagulating struvite particles. As a result of these preliminary tests, a series of experiment was carried out to optimise agglomerative properties of polyDADMAC over struvite under typical pHs of crystallisation.

6.2 Materials and methods

6.2.1 Struvite crystallisation

A pilot scale crystallisation reactor has been designed and developed at Cranfield University to study struvite nucleation and growth on both synthetic and real liquors (Figure 6.1).

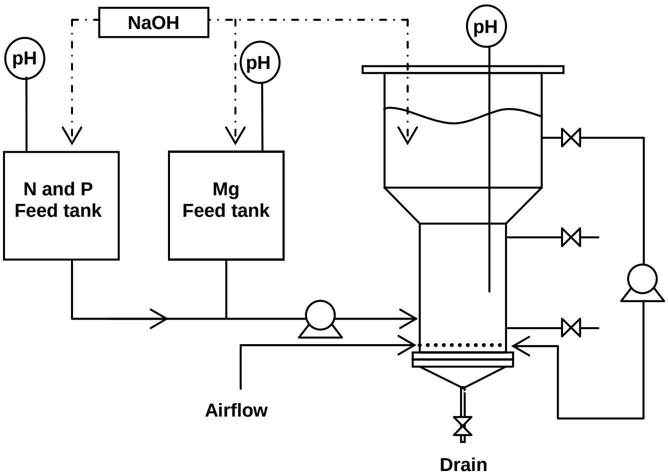


Figure 6.1. *Pilot scale crystallisation reactor.*

The process is composed of a 10 L reactor with two side sampling ports and a drain valve. A peristaltic pump injected simultaneously solutions of ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$ / Fisher Analytical Reagent Grade, UK) and magnesium chloride hexahydrate ($MgCl_2.6H_2O$ / Fisher analytical Reagent Grade, UK), prepared by dissolution of the corresponding solid compounds in deionised water.

Prior to mixing in the reactor, each solution was adjusted to the required pH value (8.5 to 10.5) with sodium hydroxide (NaOH 2N/ Fisher analytical reagent grade, UK) in stirred buckets. Both solutions were then transferred to the reactor. All experiments were conducted at the same initial Mg concentration of 1.64 mM and a final molar ratio Mg:N:P 1:2:2, at constant pH, over 60 minutes. A pH probe was introduced in the reaction zone to control and adjust the pH during the crystallisation process.

An upward air-flow and a liquid recirculation were used and adjusted (10 to 5 $L.min^{-1}$ for air, and 1.5 to 1.35 $L.min^{-1}$ for liquid) to ensure the mixing and growth of the particles formed so that they were kept in suspension during the experiment.

For each set of experiments, the final average size of particles was determined using laser diffraction (Mastersizer 2000, Malvern Instrument, UK), and associated to the zeta-potential measured at the corresponding pH. The zeta-potential of suspended struvite particles was determined using a Zetasizer 2000 HSA (Malvern Instrument, UK).

Struvite crystals harvesting was achieved through a drain valve situated at the bottom of the reactor. The major part of struvite particles recovered were maintained in suspension for coagulation / flocculation tests while 1 L was filtered through 0.2 µm filters (0.2 µm pore size Whatman membranes, Fisher scientific, UK). After filtration of the 1 L sample taken at the end of each pilot run, supernatants were kept for ICP-AES analysis (Inductively Coupled Plasma Atomic Emission Spectroscopy) to determine the remaining magnesium concentration, while phosphate (PO_4-P) and ammonium (NH_4-N) levels were determined using Merck cell tests. Struvite crystals were dried at room temperature for characterisation through SEM-EDS (Scanning Electron Microscope XL 30 SFEG, Philips, The Netherlands) and XRD (Powder X-ray Diffractometer D5005, Siemens, Germany).

6.2.2 Coagulation and flocculation tests

Coagulation tests were performed in 1 L jars using a jar test apparatus (PB 900 Phipps and Bird, Virginia, USA). 800 mL suspensions of struvite generated in the pilot reactor were rapid mixed at 100 rpm for 1 min, then coagulated during 15 min at 30 rpm and finally flocculated during 15 min at 20 rpm. Coagulants doses were always added during the rapid mix period, while flocculant doses, if used, were added after the 15 min of coagulation.

Coagulants evaluated were: ferric sulphate ($Fe_2(SO_4)_3$/ Ferripol xl, EA West), ferric chloride ($FeCl_3$/ BDH, AnalaR, UK), calcium chloride dihydrate ($CaCl_2.2H_2O$/ BDH, AnalaR, UK), calcium carbonate ($CaCO_3$/ Fisher, Reagent grade, UK), and aluminium sulphate ($Al_2(SO4)_3$/ BDH, GPR, UK) as well as a cationic polymer called polydiallyldimethylammoniumchloride (polyDADMAC) with a molecular weight between 100,000-200,000 (Sigma-Aldrich 20wt% aqueous solution, USA) diluted to 0.1%. In addition a natural flocculant agent has also been trialled. This flocculant agent was an algae based product: Alginate ($(C_6H_7NaO_6)_n$ / Fisher, UK). To screen the impact of the different coagulants on identical struvite suspensions, the doses added in jars were set at 1 $mg.L^{-1}$ as Fe, and for comparison at the same concentration as Al and Ca. The initial dose of polyDADMAC was also set at 1$mg.L^{-1}$.

The average particle size was recorded periodically as the experiment progressed using a Mastersizer 2000 (Malvern Instruments, UK). To limit the effect of particle or floc breakage, the peristaltic pump injecting the solution through the Mastersizer cell was set at 40 rpm.

6.2.3 Optimisation of struvite coagulation with polyDADMAC

Optimum agglomeration conditions with polyDADMAC were determined by adding increasing amount of this latest in 800 mL struvite suspensions of known solid concentration (250 $mg_{struvite}.L^{-1}$ at pH 8.5, 301 $mg_{struvite}.L^{-1}$ at pH 9.0, and 223.5 $mg_{struvite}.L^{-1}$ at pH 9.5) until the point of zero zeta-potential was reached. Doses previously found were then adjusted and applied to 1 L fresh suspensions of struvite particles. The same experimental procedure as for any other coagulation tests was followed that is to say that the optimum dose of polyDADMAC was added at the beginning of each jar tests during the 1 min rapid mix period, and left to coagulate and flocculate during 30 min. Floc size growth was measured using laser diffraction (Mastersizer 2000/ Malvern Instruments, UK). Pictures of the jars, at the three stages of the process (high mixing period, 30 rpm mixing period, and end of the 20 rpm mixing period) were taken to give a visual support of floc size formation.

All the experiments previously described were repeated three times to ensure reproducibility of the results.

6.3 Results and discussion

6.3.1 Struvite electrical properties

Preliminary struvite crystallisation trials undertaken without the addition of seed materials resulted in the production of struvite particles with $d_{0.5}$ ranging from 50 μm to 100 μm. This is small in comparison to sizes in the order of millimetres which have been observed in previous studies on struvite crystallisation from synthetic liquors (Table 6.1), indicating that growth was limited under the conditions tested in this study. Closer investigation of dried samples with SEM analysis revealed single distinct struvite crystals. Stratful, (2004) also formed single crystals but of 0.43 mm mean crystal size. However this size was reached after 5 days of continuous crystallisation whereas crystal formed here ranged from 0.05 to 0.1mm after 2 h. Conversely, Adnan *et al.*, (2003) observed large particles consisting of agglomeration of "*very fine and fused*" crystals, suggesting in the current work problems related to agglomeration rather than to direct growth.

Table 6.1. *Previously reported particle sizes for struvite formed without seed material.*

Particles size (mm)	Description	References
0.05-0.1	Orthorhombic single crystals	Present work
0.4-2.4	Single crystals	Stratful *et al.* (2004)
2.6-3.7	Tight aggregates of fine crystals	Adnan *et al.* (2003)
0.3	Star-like particles	Regy *et al.* (2002)

Individual struvite crystals exhibit a negative zeta-potential between -17.5 ± 1.1 and -27.6 ± 1.2 mV as the pH increased from 8.5 to 10.5 (Figure 6.2). Correlating the zeta-potential to $d_{0.5}$ showed that the crystal size increased from 33.5 ± 0.7 µm to 84.0 ± 11.2 µm as the zeta-potential decreased in magnitude from -23.3 ± 0.6 mV to -17.5 ± 1.1 (Figure 6.2). An exception to this was observed for struvite formed at pH 10.5 which generated a zeta-potential of -27.6 ± 1.2 mV corresponding to a median crystal size of 79.0 ± 7.8 µm. In that latest case, closer inspection of these crystals by SEM-EDS and XRD analysis demonstrated the sample was a blend of struvite and $Mg_3(PO_4)_2.22H_2O$ crystals, which would explain the difference in size and/or zeta-potential observed at this pH. The results suggest that crystal size may be restricted due to electrostatic repulsion limiting agglomeration of the individual crystals. Typical values of zeta-potential beyond which agglomeration is limited are below the values reported here: -10 mV for natural organic matter coagulation, -12 mV for algae and -20 mV for kaolin (Henderson *et al.*, 2006).

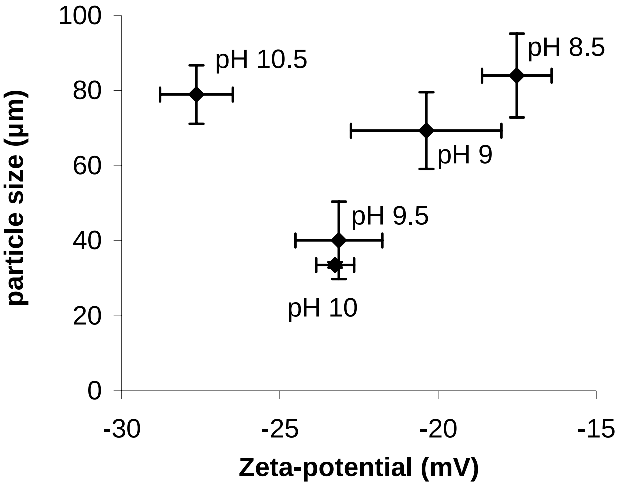
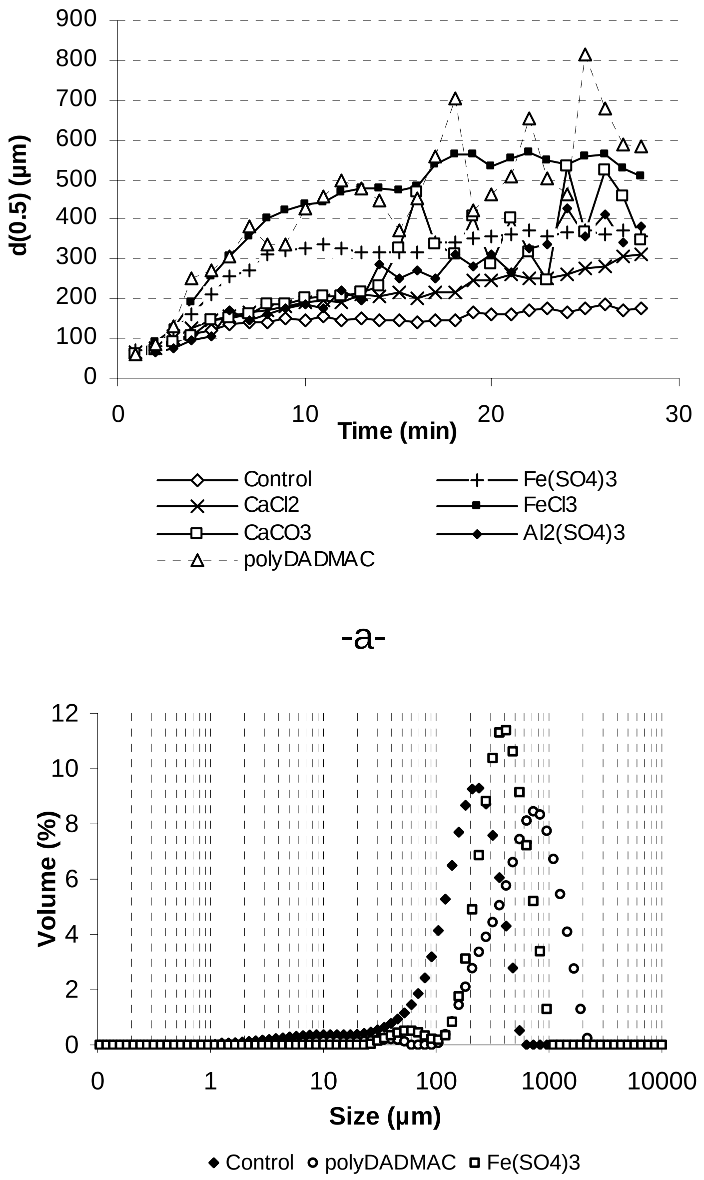


Figure 6.2. *Zeta-potential versus size at different pH.*

There has been only one study that has looked at the role of zeta-potential on struvite agglomeration. Bouropoulos and Koutsoukos (2000) reported similar zeta-potential values for struvite from -26 to -20 mV, over the pH range 9.2 to 10. Furthermore for a pH over 10.5, they reported that their suspensions started to flocculate due to an eventual destabilisation of the particles although they mentioned neither the zeta-potential nor the related size of struvite particles at this pH value. Such phenomena was not observed here at the same pH, however a net increase in struvite particle size was observed due to the precipitation of $Mg_3(PO_4)_2.22H_2O$ and could correlate with Bouropoulos and Koutsoukos (2000) observations at the same pH.

6.3.2 Effects of coagulants and flocculants on struvite particles stability

Chemically enhanced agglomeration increased the $d_{0.5}$ of the crystals for all the systems tested (Figure 6.3). The growth profiles followed a classical pattern whereby initial growth was relatively rapid followed by a period of slow growth (Jarvis *et al.*, 2006). The $d_{0.5}$ after 28 min was 581.2 µm, 506.8 µm, 355.5 µm, 346.63 µm, 310.9 µm and 383.9 µm for the polyDADMAC, $FeCl_3$, $Fe(SO_4)_3$, $CaCO_3$, $CaCl_2$ and alum systems respectively. Closer inspection of the particle size distributions revealed polyDADMAC was particularly efficient in agglomerating populations of particles below 100 µm (Figure 6.3), whereas for ferric and alum, distributions showed two peaks: a main one corresponding to the floc formed by coagulation and a low peak at 60 µm corresponding to fines. The observed results are in general agreement with other studies that have compared the relative growth of flocs with different coagulants. For instance, Gregory and Yukselen (2002) demonstrated that flocs formed by coagulation of inorganic clay particles with ferric had a greater flocculation index (F.I=1.1) than with alum (F.I=0.75). A similar pattern was also observed for coagulation of organic materials with reported differences in median floc sizes for the coagulation of natural organic matter (NOM) being 720 µm, 463 µm and 840 µm for ferric, alum and polyDADMAC respectively (Jarvis *et al.*, 2006). The exact reason for the differences in reported floc sizes are unclear in the literature but are believed to be due to differences in the hydrolysing species formed from the different coagulants.



-b-

Figure 6.3. *Effect of coagulant type (-a-); and focus on final particle size distribution obtained with polyDADMAC and Fe(SO$_4$)$_3$ (-b-).*

The impact of adding flocculant aid in combination with a coagulant was assessed by adding alginate to the jar test after 15 min of operation (Figure 6.4). An increase in floc sizes was only observed in the case of ferric based coagulants and at the end of the experiment the $d_{0.5}$ was 948.7 µm and 966.3 µm for $FeCl_3$ and $Fe(SO_4)_3$ respectively (Figure 6.4). Such observations are not surprising as alginates are known to be particularly suitable for use with ferric salts (Degremont, 1991). Anionic polymers provide effectively an inter-particle bridging between floc already formed by cationic coagulant, hence improving floc size and settlement (Shammas, 2005). Comparing the two studies indicates that the use of polymer components is beneficial in the agglomeration of struvite either as a direct coagulant (polyDADMAC) or as a flocculant aid (alginate).

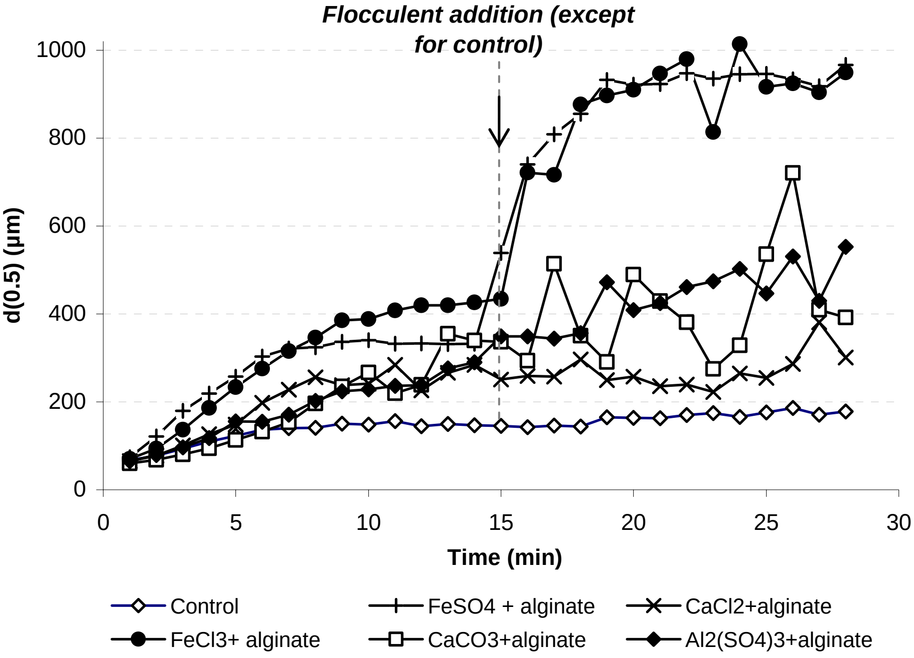


Figure 6.4. *Impact of a flocculant aid on flocs formation.*

Overall, the best options in terms of increased $d_{0.5}$ were polyDADMAC or the combination of ferric with alginate. In relation to struvite reuse as a fertiliser, polyDADMAC appears the suitable choice. In part this is because the presence of iron in the product can be a problem (He *et al.*, 2005) as well as the iron directly affecting crystal structure. For instance, microscope analyses revealed that flocs formed by polyDADMAC appeared to be a collection of individual struvite crystals, whereas with ferric it was less evident. A possible explanation is the solubilisation of struvite by iron salts and subsequent floc formation by reaction of Fe ions with other compounds such as phosphate. Mamais *et al.*, (1994) effectively reported that dosing of iron salts in digester effluents containing struvite crystals could cause the precipitate to dissolve and lead to the formation of vivianite ($Fe(PO_4)_2.8H_2O$).

6.3.3 Optimisation of struvite coagulation with polyDADMAC

Polymers are known to agglomerate particles through adsorption coupled with either charge neutralisation or inter-particle bridging (Ferreti *et al.*, 1997). In wastewater treatment, cationic polymers such as polyDADMAC are applied as a coagulant because they adsorb easily onto negatively charged particles leading to charge neutralisation, so to destabilisation and floc formation (Gregory, 2006). Assuming that with regards to struvite particles, charge neutralisation was the predominant mechanism for polyDADMAC, the dose corresponding to the point of zero zeta-potential should have also been associated with an optimum floc formation (Gill and Herrington, 1987; Sharp *et al.*, 2006). But this was not always the case for all sets of experiments (Figure 7.5).

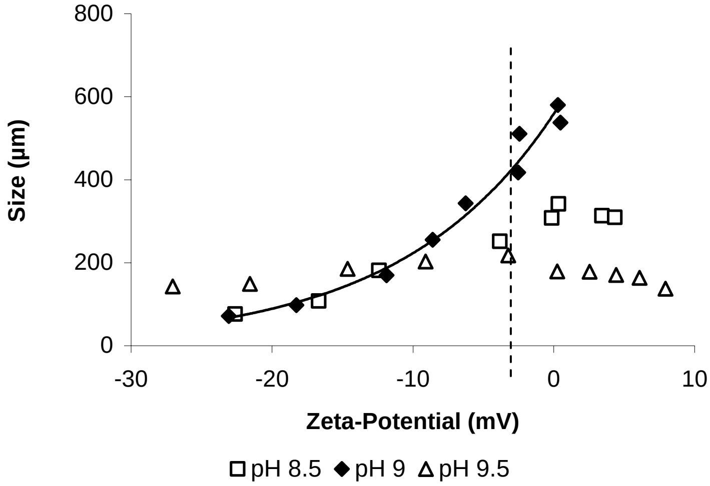


Figure 6.5. *Zeta-potential versus size for increasing polyDADMAC doses at pH 8.5, 9 and 9.5.*

Analysis of the relationship between $d_{0.5}$ and zeta-potential revealed a significant pH influence on agglomeration. This was manifested in that at either pH 8.5 and 9.5 less significant influence was observed compared to pH 9. For instance, the $d_{0.5}$ at a zero zeta-potential were 580 µm, 341 µm and 180 µm for respectively pH 9, 9.5 and 8.5 (Figure 6.5).

A series of jar tests were then performed on fresh struvite solutions at polyDADMAC doses found previously to give a zero zeta-potential that is to say 0.14, 0.17, and 0.15 mg.L^{-1} at pH 8.5, 9 and 9.5 in order to study floc formation in the zero zeta-potential zone.

Visual observations and floc size measurements showed as expected that at pH 9, agglomeration of particles was obvious and continuous over the 30 min of experiments. Initial and final particle size distributions generated at this pH showed an increase in mean size from 79.7 µm to 875.7 µm (Figure 6.6).

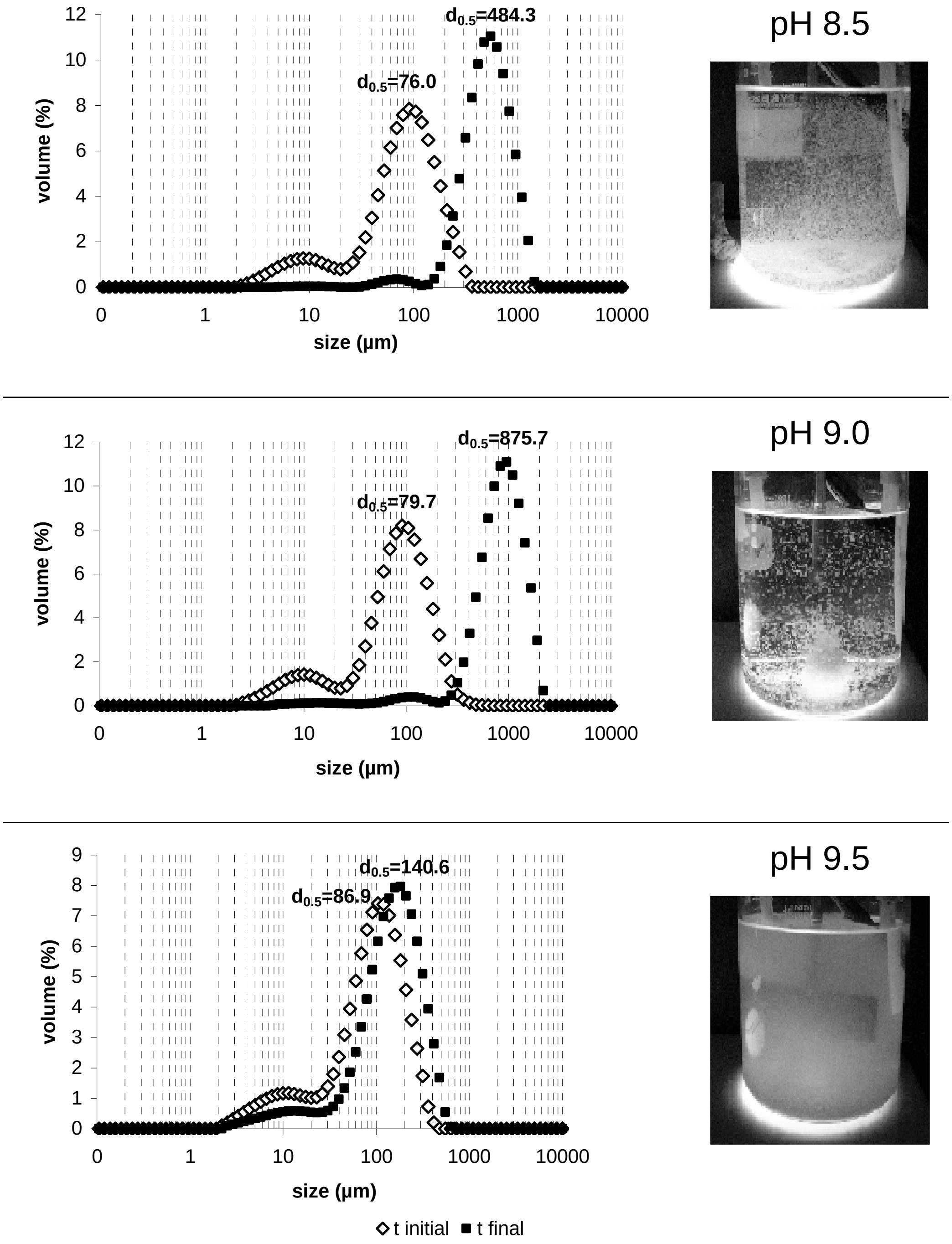


Figure 6.6. *Average growth of flocs observed by addition of polyDADMAC optimum doses at pH 8.5, 9.0 and 9.5.*

At pH 8.5, the mean size grew from 76.0 µm to 484.3 µm. In that case growth was very rapid as floc sizes reached a steady state after only 5 min. At pH 9.5, floc growth was insignificant with a final variation in size as $d_{0.5}$ of only 53.7 µm (Figure 6.6).

Gregory (2006) reported that polyDADMAC generally adsorbs onto negatively charged particles in a flat configuration. This means that segments of the chain constituting polyDADMAC are attracted by electrostatic forces to the surface of the negatively charge particle in *trains*. This phenomenon limits consequently its tendency to form bridges, and suggests that the main mechanism of particle destabilisation is charge neutralisation.

Previous results illustrated that neutralisation of struvite particles indeed occurred for all sets of experiments as the addition of polyDADMAC reduced the zeta-potential towards its zero value. However, polyDADMAC aptitude to form flocs only occurred at pH 9.0 and in a lower extent at pH 8.5 but not at pH 9.5 (Figure 6.6). This indicates that charge neutralisation was not always effective and probably not the only mechanism responsible of good agglomeration of struvite particle at pH 9.

A possible explanation could be the influence pH may have on the configuration of polyDADMAC chain, hence its adsorption mechanism onto particle surface. It is effectively known that ionic strength has an important effect on polyelectrolyte chain expansion in aqueous solution (Gregory, 2006). For instance, in their work on flocculation of kaolin suspensions by cationic polymers, Gill and Herrington (1987) confirmed through viscosity analysis of cationic polyacrylamides at different pH that the conformation of polymers changes with ionic strength and pH. For instance, they observed that polymer molecules adopted their flattest configuration at a pH around 5, while above and below pH 5 their coiling increased.

At pH 9.5, polyDADMAC may then have adopt a specific configuration and cover the totality of particles surface leading thus to charge neutralisation of the majority of particles in suspension through electrostatic attraction but consecutively causing restabilisation through steric repulsions (Letterman *et al.*, 1999).

With a different arrangement of its chain at pH 8.5 and 9.0, polyDADMAC may have followed the mechanism of electrostatic patch and not only charge neutralisation. Reports in the literature suggests that adsorption of cationic polymers by the charge patch mechanism can be very important (Gregory, 1973; Moody, 1995). According to Gill and Herrington (1987), neutralisation of particle charge by electrostatic patch occurs in order that a positive polymer patched on a negatively charged clay particle can interact with other clay particles negatively charged and / or with already patched particles through bridging. At pH 8.5 the configuration of the molecule may have allowed then this mechanism to occur, but with lower bridges formation than at pH 9.0 where another configuration helped the inter-particle bridging. This could then explain the good relationship observed between zeta-potential and size at pH 9 (Figure 6.5).

Investigation on struvite agglomerative properties proved here that the aggregation of struvite fines into bigger flocs by means of coagulant and/or flocculant addition was feasible. Under optimum conditions, flocs generated reached sizes similar to recovered struvite pellets (*i.e.* 0.5-1.0 mm) sold as fertiliser in Japan (Ueno and Fujii, 2001). In that sense, a coagulation step downstream crystallisation processes would allow rapid recovery of struvite fine particles flushed out in treated effluents, and recovered floc may be blended to the product generated by direct growth. However, as described previously, despite good agglomerative properties over struvite, the addition of metal salts coagulants may cause problems in the case of struvite reuse as a fertiliser. The application of a cationic polymer such as polyDADMAC may be consequently of interest although data on its biodegradability in soil and environmental impact does not seem readily available to date. Furthermore, particular attention has to be paid to pHs at which coagulants are applied. Indeed even for polyDADMAC which is not normally known to be pH sensitive (Nozaic *et al.,* 2001), small variation in pH caused a significant impact on floc size. In the perspective of an application at larger scale this would require an accurate pH control while adding the required polyDADMAC dose.

6.4 Conclusion

Undesired struvite fines particles are often generated in struvite crystallisation processes used for phosphorus recovery and reuse from wastewater effluents. Due to high mixing speeds or flow rate generated to maintain growing particles in suspension, these fines can be flushed out of the reactor leading to phosphates levels in treated effluents. A series of experiments was then carried out to assess the feasibility of recovering these fine particles by coagulation.

- Preliminary tests showed struvite have high negative zeta-potentials in the pH range 8.5-10.5 indicating a strong negative surface charge, therefore a natural stability through electrostatic repulsion.
- Destabilisation of struvite fines with hydrolysing metals salts (ferric and alum) or cationic polymer (polyDADMAC) proved here to be efficient in growing struvite flocs, but polyDADMAC showed greater potential than alum and ferric in removing struvite fines.
- Chemical addition (as polyDADMAC) to remove fines works, but the process appears very pH sensitive. The optimum floc formation occurred at pH 9 with particles size (as $d_{0.5}$) growing from 79.7 µm to 850.4 µm.

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CHAPTER 7

INFLUENCE OF SEED MATERIAL CHARCTERISTICS ON RAPID STRUVITE RECOVERY

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7. INFLUENCE OF SEED MATERIAL CHARACTERISTICS ON RAPID STRUVITE RECOVERY

K. S. Le Corre[1], E.Valsami-Jones[2], P. Hobbs[3], R. D. Boyd[1], B. Jefferson[1], S. A. Parsons[1]

[1]School of Water Sciences, Cranfield University, Cranfield MK43 OAL, UK
[2] Department of Mineralogy, The Natural History Museum, Cromwell Road London, SW7 5BD, U.K
[3]Institute of Grassland and Environmental Research (IGER), North Wyke, Okehampton, Devon, EX20 2SB, UK

Abstract

Four potential materials (sand, recycled concrete aggregates, struvite and a metallic mesh) for seeded crystallisation of struvite have been here selected to study their propensity to adhere struvite. Adhesion forces between struvite and those surfaces have been investigated using modified Atomic Force Microscopy (AFM) cantilevers. Results revealed that if the topography of the materials did not affect strongly struvite adhesion onto them, actual force measurements between a struvite modified tip and each surface illustrated variations in strength of adhesion. It was demonstrated that the metallic surface had greater potential to adhere struvite. Those measurements were then compared to analyses of the same type of seeds used for struvite crystallisation tests in a pilot scale reactor. AFM measurements were found to correlate well with pilot scale investigation in the sense that the metallic mesh proved to be the most efficient seed to adhere struvite under the conditions of precipitation tested here.

Keywords: phosphorus removal, struvite recovery, crystallisation, seed materials, Atomic Force Microscope

7.1 Introduction

Struvite ($MgNH_4PO_4.6H_2O$) was originally identified as a scale deposit occurring spontaneously in some wastewater processes by reaction of soluble magnesium, phosphorus and ammonium naturally available in wastewater effluents (Rawn *et al.*, 1937). Later on, its crystallisation was considered as an alternative way to traditional P-removal processes such as chemical precipitation or biological nutrient removal (*i.e.* BNR; EBPR) (Doyle and Parsons, 2004; Giesen, 1999). In wastewater treatment plants, the adhesion of struvite on pipelines, heat exchangers, and other pieces of equipment in contact with soluble P-rich wastewaters is source of severe maintenance problems. However, if spontaneous struvite nucleation and growth can be controlled in a specific reactor, it can reduce pollution linked to phosphorus (and ammonium) discharge in wastewater effluents and generate a valuable slow release fertiliser which sales could profit to wastewater companies (de-Bashan and Bashan, 2004).

As a consequence, struvite crystallisation principles have been widely investigated using laboratory, pilot, and sometimes full scale crystallisation reactors (Battistoni *et al.*, 2005, Suzuki *et al.*, 2005, Ueno and Fujii, 2001). The principal objective of those processes is to nucleate struvite embryos and enlarge them until they reach a reasonable size to facilitate recovery and reuse. Although some processes achieved formation of large struvite crystals up to 3 mm, crystal retention times needed to reach reasonable particle size are usually relatively long, frequently in the order of days (Adnan *et al.*, 2003). To optimise struvite growth and reduce operational time, one of the solutions often considered consists of introducing a seed material in the reacting zone of the crystallisation process so that struvite nuclei can agglomerate on its surface, producing thus larger struvite particles. This method has been successfully achieved by some authors with for instance precipitation of struvite onto sand or preformed struvite particles (Ohlinger *et al.*, 2000, Battistoni *et al.*, 2005, Shimamura *et al.*, 2003), but in some cases the coating is random and even not observable (Regy *et al.*, 2002). High mixing speeds or air agitation, and surface roughness of the material selected are the hypothesis to explain failure of struvite aggregation and attachment onto seed substrate. However, mechanisms of struvite adhesion onto such materials are unclear and the influence of seed material characteristics on strength of adhesion has never been investigated. Furthermore, the utilisation of seed materials to grow struvite does not seem to reduce significantly operational times when compared to non seeded crystallisation. Indeed, the success of struvite attachment onto seed material also requires long retention times. For instance, Shimamura *et al.* (2003) needed 12 days to achieve an average 195 µm growth in thickness onto struvite seeds of 0.79 mm in diameter.

Since its design and development in 1986 (Binnig *et al.*, 1986), the utilisation of the atomic force microscope (AFM) for probing surfaces and imaging their topography has been proven to be an efficient technique to study how surface characteristics can influence interactions with some specific substances (Assender *et al.*, 2002). For instance, the technique was used to understand the influence of biological surface topography on their capacity to grow cells (Curtis and Wilkinson, 1997), to assess the impact of surface roughness in the electro deposition of copper onto metals (Zhao *et al.*, 2006) or to investigate calcium carbonate scaling inhibition or crystal growth in aqueous solution (Yang *et al.*, 2001). Knowing surface characteristics of materials used for seeded crystallisation of struvite could then help to better understand variation in their aptitude to grow struvite. Furthermore, the AFM permits direct measurement of the force of adhesion between the tip and the surface under investigation. Modification of the tip with functionalised components enables direct measurements of adhesive properties of systems of interest (Ralston *et al.*, 2005). Previous examples include bacteria (Ong *et al.*, 1999), gold or paraffin films (Eastman and Zhu, 1996) and yeast cells (Bowen *et al.*, 2001).

The aim of this study was to understand the impact of different seed material characteristics on struvite nucleation and growth and to identify if attachment of struvite onto seed could occur in shorter contact times than the one typically reported in the literature. Le Corre *et al.* (2006) effectively showed that in their crystallisation reactor running in batch mode, phosphorus removals achieved after 1 h were similar to the one observed after 24 h. This suggested that without affecting the efficiency of the process in removing phosphorus, operational times could be reduced significantly if struvite could be recovered more rapidly. In the present work, four types of materials, which have been tested by some authors as seeds for phosphorus recovery by crystallisation, have been selected. Those included sand (Ohlinger *et al.*, 2000; Battistoni, 2004), struvite (Shimamura, 2003), recycled concrete aggregates (Berg *et al.*, 2005) and stainless steel (Suzuki *et al.*, 2005). The surface topographies of each material and their propensities to adhere struvite have been investigated with an AFM. Results have then been related to the performance of each type of material in growing struvite in a purposely built reactor.

7.2 Material and methods

7.2.1 Seed material characterisation

Four materials including sand, recycled concrete aggregates (RCA), struvite and a metallic wire mesh were selected as potential sources for seeded crystallisation of struvite and to study struvite adhesion properties onto them (Table 7.1).

Table 7.1. *Characteristics of seed substrate investigated*

Material	Supplier	Use/ properties	Size
Sand Fontainebleau	VWR international (UK)	Colourless silica sand.	150-300 µm
RCA	Tarmac Industries (UK)	Waste material from the construction industry. Media tested for P removal	0-2 mm
Struvite	Treviso wastewater treatment plant (Italy)	Agricultural fertiliser ($MgNH_4PO_4.6H_2O$) $d=1.71 g.cm^3$	170-800 µm
Metallic wire mesh	H&B Wire Fabrications Ltd (UK)	Used for screening and filtration purposes	1 mm hole 0.35 mm wire

In the present work, seed materials were characterised using a Scanning Electron Microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDS, Scanning Electron Microscope XL 30 SFEG, Philips, The Netherlands) and XRD (Powder X-ray Diffractometer D5005, Siemens, Germany) tools.

7.2.1.1. Surface analysis

Imaging of each specific surface and surface roughness determination were performed using a Topometrix Explorer^{TM} AFM mounted with a POINTPROBE-PLUS® Silicon-SPM-Sensor, silicon cantilever (Nanosensor, Windsor Scientific, UK). For each material, surface imaging was performed over 30 different areas (10x10 µm or 5x5 µm) in both 'topography forward' and 'reverse' modes using a scan rate of 20 $\mu m.s^{-1}$. The surface roughness (Ra) of each area was then determined using images generated.

7.2.2 AFM force measurements

Two types of force measurements were performed: one using a struvite modified POINTPROBE® tipless silicon cantilever (Nanosensor, Windsor Scientific, UK) and the other one using an unmodified cantilever (POINTPROBE-PLUS®, silicon cantilever / Nanosensor, Windsor Scientific, UK).

7.2.2.1 Modification of Atomic Force Microscopy cantilevers

To study adhesion properties of struvite onto sand, RCA, struvite and the metallic mesh, two tipless cantilevers were modified by sticking a struvite crystal at their extremity.

To attach each struvite crystal to the cantilever, a microscope coupled with a micromanipulator (MMO-202NP, Saitama Japan) was used. A thin and sharp ended glass probe was mounted on the micromanipulator and carefully dip into an adhesive (Araldite ®, UK) until a small amount was attached to it and then pulled back.

The unmodified cantilever was then placed under the microscope and the glass probe was carefully lowered until the adhesive came in contact with the tip so that a tiny amount of adhesive was put down. The glass probe was then removed and replaced by a new one. This new glass probe was used to collect a single crystal of struvite and deposit it on the amount of glue left on the cantilever. The struvite modified cantilever (Figure 7.1) was then left to dry out over 24 h before utilisation.

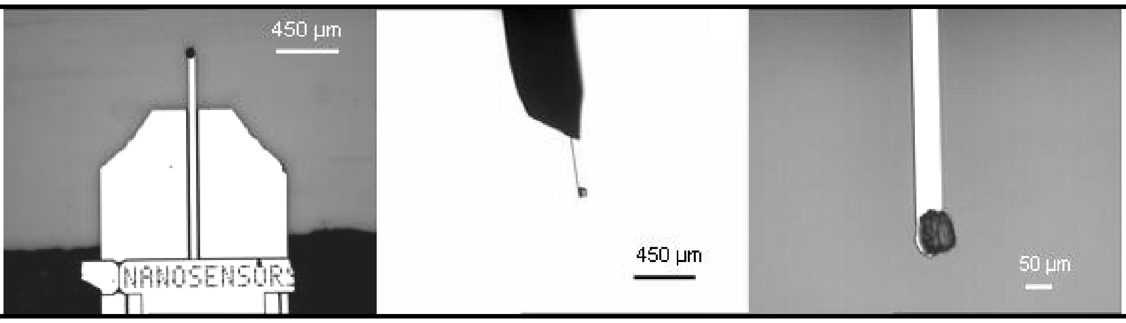


Figure 7.1. *Struvite modified POINTPROBE® tipless silicon cantilever (Nanosensor, Windsor Scientific, UK)*

7.2.2.2. Force measurements

All force measurements were performed in deionised water at room temperature. The z value of the force scan generally ranged from 0 to 3000 nm. For each series of experiments, 100 force measurements were performed over randomly selected area of the surface under investigation. Then force curves generated were plot as average deflection (nA) versus distance (nm) covered by the tip movement.

The force corresponding to the recorded deflection (D, nA) was then converted into force as deflection (F, nN) using the spring constant (N/m) and the sensor response (nA/nm) obtained by sensor calibration with the thermal noise method (Hutter and Bechhoefer, 1993).

7.2.3 Struvite crystallisation tests

Struvite generally occurs when magnesium, phosphate and ammonium ions reach a molar ratio 1:1:1 at pH 9 (equation 7.*i*).

$$Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + nH^+ \qquad (7.i)$$

Seeded crystallisation of struvite from synthetic liquors was tested at pilot scale in a 10 L reactor designed at Cranfield University (Le Corre *et al.*, 2006). The reactor was fed with solutions of ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$ / Fisher Analytical Reagent Grade, UK) and magnesium chloride hexahydrate ($MgCl_2.6H_2O$ / Fisher analytical Reagent Grade, UK), prepared by dissolution of the corresponding solid compounds in deionised water. Prior to mixing in the reactor, each solution was adjusted to pH 9 with sodium hydroxide (NaOH 2 N/ Fisher analytical reagent grade, UK). Both solutions were then transferred to the reactor in presence of seed materials. The HRT was 2 h as it was previously demonstrated that longer times did not improve P removal and recovery (Le Corre *et al.*, 2006). An upward air-flow and a liquid recirculation were used and adjusted to ensure the mixing of the sand, RCA and struvite seeds. In those tests, the air flow was set a 10 L.min^{-1} which corresponded to the maximum air flow possible to fluidise the particles and avoid flush out of the solution from the top of the reactor. For the experiment testing the mesh as a seeding material a system composed of two concentric circular meshes was dip into the reactor. The airflow rate was set at 3 L.min^{-1} so that struvite crystals formed during the test were always kept in suspension. For all experiments the recirculation was set at 250 rpm.

At the end of each run, seeds were sampled and characterised by SEM-EDS to detect signs of agglomeration.

7.2.4 Particle size analysis

For each set of experiments, the average size ($d_{0.5}$) of particles remaining in solutions after 2 h was determined using laser diffraction (Mastersizer 2000, Malvern Instrument, UK). To limit the effect of particle breakage, the peristaltic pump injecting the solution through the Mastersizer cell was set at 40 rpm.

7.3 Results

7.3.1 Seed material characterisation

The SEM pictures revealed that, apart from the metallic mesh, surfaces topography could vary a lot from one area to another (Figure 7.2). This was particularly evident for sand and RCA where smooth and rough grains were observed. For struvite, the analyses of the pictures showed grains were principally an agglomeration of particles of lower sizes. Analysis of the seed materials by X-ray diffraction and EDS revealed that the Fontainebleau sand consisted of pure silica in the form of quartz. Similarly, the recycled concrete aggregates were found to mainly consist of quartz mixed with calcium deposits. Finally, the struvite pellets were revealed to be a mix of struvite and newberyite ($MgHPO_4.3H_2O$).

Quantification of the topographies by AFM confirmed the visual observations. To illustrate Ra measurements were 269.8, 171.5, 154.1 and 94.4 nm for the sand grains, struvite, RCA and the metallic mesh respectively (Figure 7.3A). The topography of a material depends on several factors such as erosion, mechanical roughening, nature of the material or ways how the materials are processed (Assender *et al.*, 2002). Materials of the same nature can then present significant variation of surface roughness. To illustrate, previous studies on stainless steel surfaces showed that their roughness (as Ra) could be in the range 20 to 100 nm for “mirror like” stainless steel (Keysar *et al.*, 1994), 166 to 247 nm for slide of 2 B grade stainless steel (Bachmann and Edyvean, 2006) and up to 1510 nm for stainless steel 1/23 coupons (Dunn *et al.*, 2004). Comparison with surface roughness of the stainless steel mesh investigated here showed that it could be classified in the same category as the stainless steel surface probed by Keysar *et al.* (1994), that is to say an extremely smooth surface.

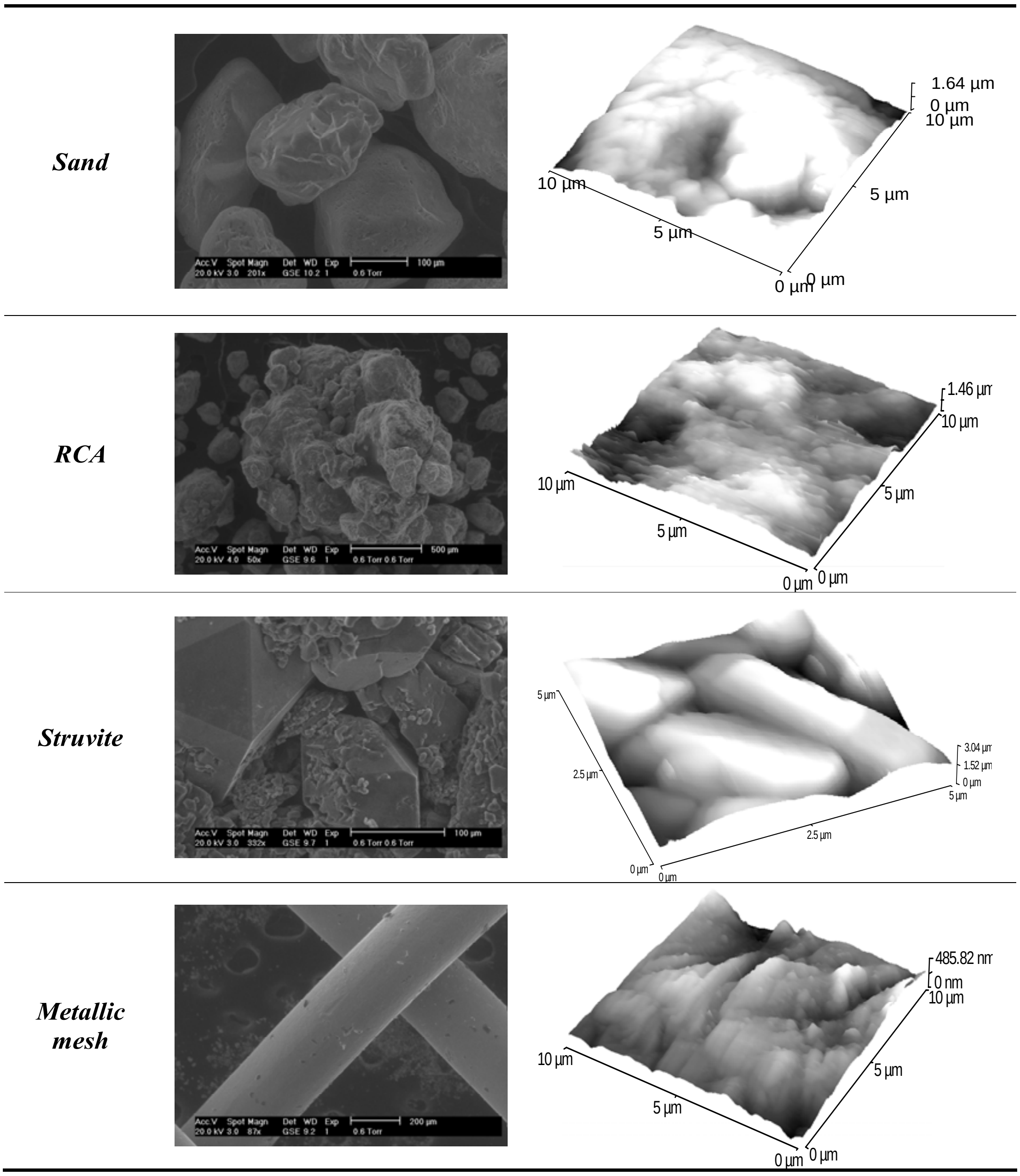
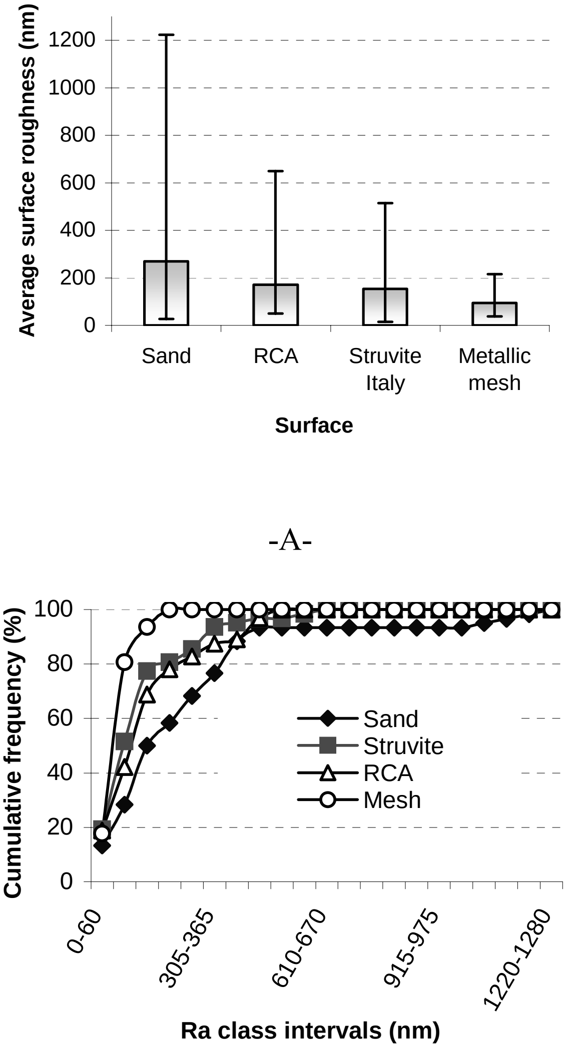


Figure 7.2. *SEM pictures of Sand, RCA, Struvite and the metallic mesh and respective topographical analysis.*

Analysis of the distribution of roughness values revealed that the mesh was not only the smoothest on average but it also had the least variation in topography (Figure 7.3B). To illustrate, the steep slope observed for the metallic mesh distribution indicated that the majority of the Ra values measured were concentrated in one zone with 93.5 % of the measures situated below 182 nm. Conversely, the slope observed for the Ra sand distribution showed a more disperse distribution of the values and even a discontinuity in the distribution (*i.e.* flat part synonym of a multimodal distribution), although 88.3 % of the surface roughnesses were situated below 426 nm. Finally distributions generated for the struvite and the RCA, demonstrated that those two surfaces had similar topographies with respectively 61.3 % and 59.4 % situated in the interval 61-243 nm.



-B-

Figure 7.3. *Surface roughness cumulative distributions per surface probed and their respective average surface roughness.*

7.3.2 AFM force measurements

Force measurements obtained by interaction of an unmodified cantilever with sand, RCA, struvite and the metallic mesh revealed that the strengths of adhesion measured with an unmodified cantilever were 29.19 ± 19.1 nN, 8.01 ± 7.1 nN, 24.83 ± 12.0 nN, 36.81 ± 16.6 nN for respectively sand, the mesh, RCA and struvite (Figure 7.4A). When compared to force measurements obtained with unmodified tips on various surfaces reported in the literature, the adhesive forces measured here seem strong. To illustrate, Dunn *et al.* (2004) obtained average interactions of 1.48 ± 0.49 nN between an unmodified tip and a stainless steel surface; Boyd *et al.* (2006) measured forces between an unmodified tip and calcite crystals ranging from 0.354 ± 0.373 nN to 3.151 ± 2.015 nN depending on the crystal face investigated and Jones *et al.* (2002) observed forces ranging from 15 to 60 nN for a bare tip interacting with and hydrophilic glass surface.

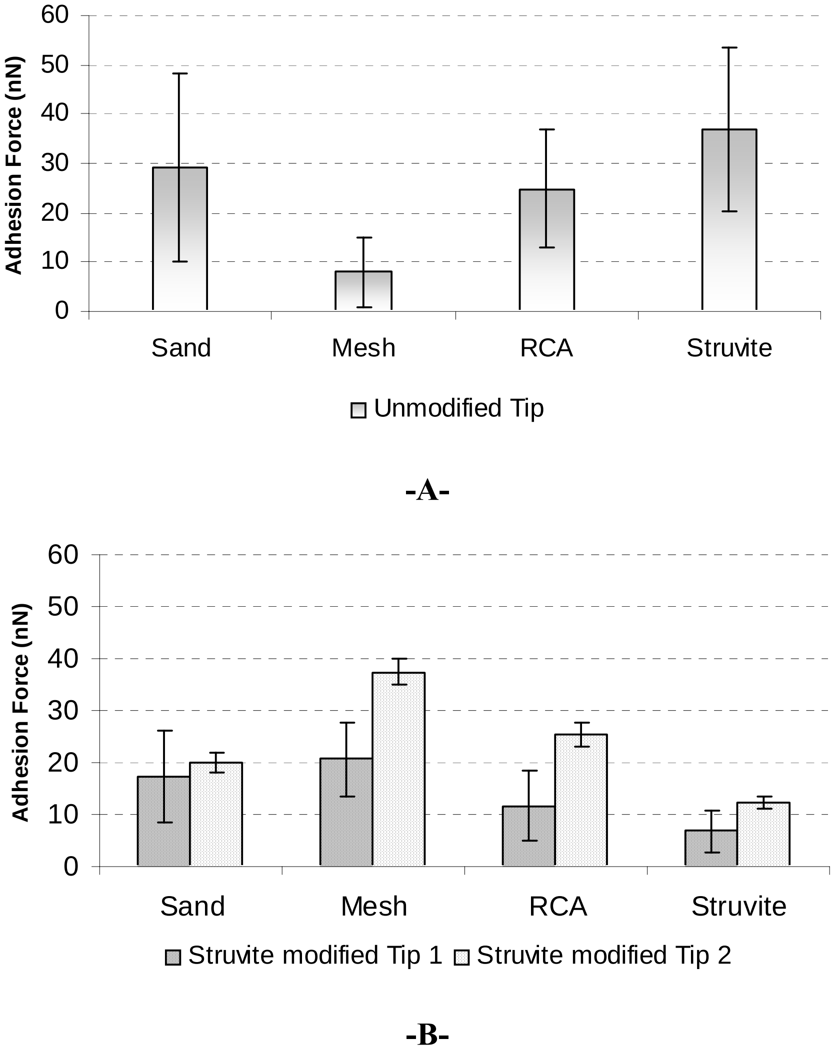


***Figure 7.4**. Adhesion forces (in de-ionised water) between an unmodified tip and sand, mesh, RCA and struvite (A) and between struvite and the same materials (B).*

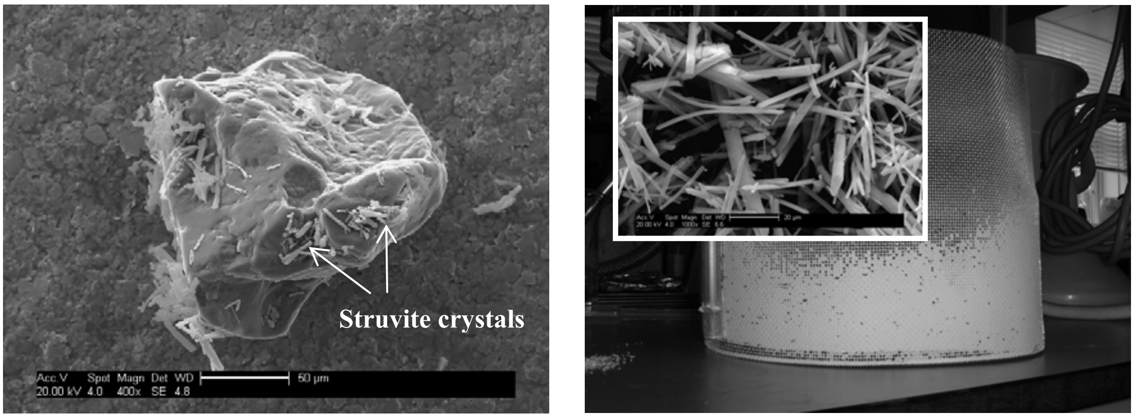
Comparison between the different average forces measured with struvite modified tips (Figure 7.1) showed significant variations from one type of surface to another one. The strengths of adhesion between struvite and the mesh were the highest observed with an average value of 28.97 ± 4.85 nN (Figure 7.4B). Adhesive forces between struvite and sand and struvite and RCA were of 17.4 ± 8.9 nN and 11.6 ± 6.7 nN respectively with the first modified tip and 20.19 ± 1.92 nN and 25.19 ± 2.34 nN respectively with the second modified tip (Figure 7.4B). Finally, interactions struvite-struvite were found to be the lowest one in each series of tests with adhesion forces of 6.7 ± 4.1 nN and 12.3 ± 1.1 nN for modified tip 1 and 2 respectively.

Comparison with other studies revealed that the adhesion onto the seeds chosen in this investigation is greater than on polymer materials. To illustrate, Dunn *et al.* (2004) measured adhesion forces of 8.7 ± 2.2 and 12.0 ± 2.6 nN between a struvite modified tip and respectively a polymethylacrylate (Ra= 59.2 nm) and polytetrafluoroethylene (Ra= 2270 nm) coupons. Further comparison is limited by differences in tip geometries but the general trend is as expected. Interestingly, comparison between modified and unmodified tips revealed a switch in the order of adhesion forces demonstrating that cantilever modification is important when investigating the affinity of a material for adhesion. Overall, the surface analysis demonstrated the metallic mesh had the smoothest surface with the strongest adhesion to struvite

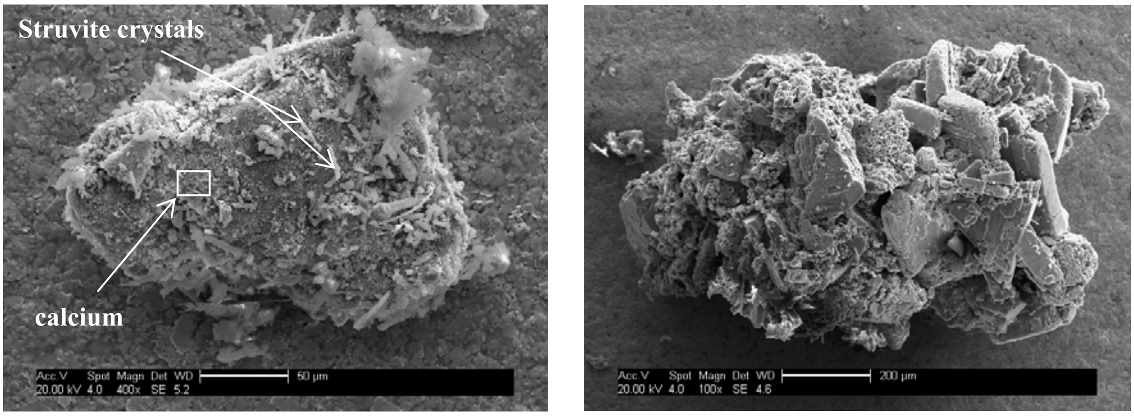
7.3.3 Seeded crystallisation of struvite

SEM-EDS investigations on seed materials recovered after 2 h of crystallisation showed that synthetic struvite crystals were present at the surface of sand while none were seen on struvite seeds surface (Figure 7.5). However the amount of synthetic struvite agglomerated at the surface of seed grains was limited and dispersed. For instance, small struvite crystals could be seen in dips of the sand surface but not on the struvite grains. Conversely, little bits of struvite and an amorphous substance appeared all over the RCA surface. EDS analyses undertaken on RCA samples demonstrated the amorphous substance to be mainly composed of calcium and phosphorus.

Growth rates on sand, RCA and struvite were insignificant under the reactor operation conditions tested here whereas agglomeration of synthetic struvite crystals on the mesh was significant and visible by eye after only few minutes of reactor operation. After 2 h, agglomeration of struvite on the mesh was obvious (Figure 7.5B) and the crystal growth rate calculated was of 7.6 $g.m^{-2}.h^{-1}$.



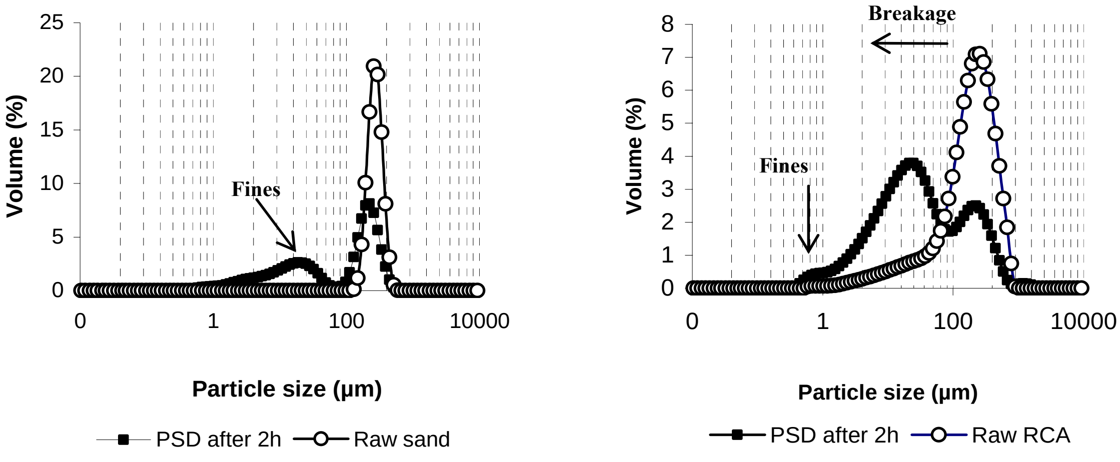
-A- Sand grain -B- Metallic mesh



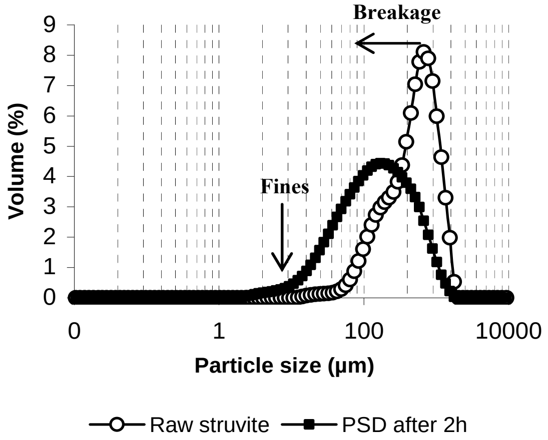
-C- RCA grain -D- Struvite grain

***Figure 7.5**. SEM pictures of sand, RCA, and struvite grains as well as struvite crystals recovered on the metallic mesh after pilot scale crystallisation investigations.*

The particle size distributions of solutions withdrawn from the enlarged section of the reactor after 2 h of operation confirmed the previous observations in that no significant growth occurred on seed surfaces (Figure 7.6). To illustrate, initial particle size for sand showed a monomodal distribution with a peak at 257.5 µm while after 2 h the distribution showed two populations of particles of respectively 21.4 µm and 224.4 µm in size. Similar trends were observed with RCA which had an initial $d_{0.5}$ of 257.65 µm whereas after 2 h experiment particle size analyses revealed a bimodal distribution with a peak at 24.6 µm and 257.6 µm. With regards to struvite seeded tests, monomodal distributions were observed before and after the tests, however the $d_{0.5}$ decreased significantly from 778 µm to 195 µm. As solutions after 2 h of precipitation in presence of the metallic mesh were clear (*i.e.* absorbance of 0.012), particle size measurements were not performed.



Sand **RCA**



Struvite

Figure 7.6. *Particle size distributions in the enlarged section of the reactor after 2 h of crystallisation with sand, RCA and struvite seeds*

The previous observations revealed that when sand was applied as a seed material, the pattern of the particle size distribution was due to the formation of significant amounts of fines, whereas for RCA and struvite phenomena of seed material breakage were dominant. Overall, SEM and particle size analysis demonstrated that when crystallisation was performed during 2 h in presence of sand, RCA and struvite, struvite had either not time to precipitate onto seed materials (*i.e.* struvite as seed), or was probably sheared off due to the intensity of air flowrates needed to ensure particles were kept in suspension (*i.e.* sand and RCA). High flowrates were also responsible of seed particle breakage, hence decreasing the chance for struvite to attach onto them. Lower flowrates needed for struvite crystallisation on the metallic mesh would then explain its success in recovering struvite.

7.4 Discussion

AFM force measurements taken using the two different modified probes showed a large difference in forces measured, although for both modified tips the trend was the same with the stainless steel mesh having the highest adhesive force followed by RCA, sand and struvite being the least. The difference answers from each modified cantilever are expected as different crystals will have different contact mechanics and, therefore, adhesion forces (Capella *et al.*, 1999). The fact that the trend is reproducible and opposite of that seen with the unmodified tips indicates that the effect is due to changes in the struvite adhesive properties.

The strength of adhesion is known to be affected by both the surface topography and composition (Assender *et al.*, 2002). Conversely, there appears here to be no definite relationship between surface roughness and struvite adhesion, with the smoothest surface, the metallic mesh, having the strongest force, which is actually the opposite of the expected trend (Keysar *et al.*, 1994). Furthermore, the study of struvite surface topography (Figure 7.2) demonstrated that it consists of very smooth crystal planes 1.28 to 1.73 microns apart, whereas all of the other surfaces are more amorphous with for example features 245 to 635 nm apart. The latter surfaces could then present a larger area for adhesion of nanometre sized elements than struvite crystals explaining the variations in strength of adhesion observed with modified cantilevers. Both sand and RCA primarily consist of silica type materials with similar topographies (at least on the nanometre scale), and unsurprisingly their adhesive properties were similar.

Visual and microscopic observations presented on Figure 7.5 seem to correlate well with adhesion force measurements. They confirmed the weak adhesive properties of struvite for struvite, and strong agglomerative properties of struvite onto the metallic mesh observed by AFM force measurements. By comparison of surface force measurements measured here with results of seeded crystallisation of struvite on various substrates reported in the literature, the link between force and characteristic of the seed is less evident than the one demonstrated in the present study.

Struvite scaling deposits have been widely observed on walls of stainless steel pipes of WWTP indicating an affinity of metallic support for struvite deposition (Mohajit *et al.* 1989, Doyle *et al.,* 2002). However, seeded crystallisation of struvite has mainly been trialled on granular materials such as sand and preformed struvite with more or less success (Table 7.2). For instance, Regy *et al.* (2002) tried seeded crystallisation in a stirred reactor on sand Fontainebleau and struvite pellets at high concentrations to force struvite deposition onto seeds but with no success after either 3 h or 69 h of operation. Conversely, Battistoni *et al.* (2001), managed to agglomerate struvite on silica sand of mean size 265 µm, with an average increase in thickness of 40.3 µm after 16 to 44 h. Struvite crystallisation on struvite particles have also been trialled at full scale in Japan (Shimamura *et al.*, 2003; Ueno and Fujii, 2001). They reported particles growing up to 195 µm in thickness. However, all successful crystallisation tests on granular seeds also implied operating time relatively long in the order of days (Table 7.2). Success of struvite deposition on granular material seems then to be dependant on retention time although longer retention does not always guarantee success of struvite crystallisation (Regy *et al*., 2002, Table 7.2).

Table 7.2. *Results of seeded crystallisation of struvite trials in the literature*

Reference	Process	Type of seed	RT	Results/observations
Regy *et al.* (2002)	Pilot stirred reactor	Sand Fontainebleau	3h	No agglomeration of struvite on sand. 2 separate phases (sand and struvite).
		Struvite pellets	69h	No deposition or growth.
Battistoni *et al.* (2001)	Fluidised bed reactor	Silica sand ($d_{0.5}$=0.27mm)	16-44h	Maximum growth of 40.3 µm in thickness but mainly due to calcite formation
Battistoni *et al.* (2005)	Full scale FBR	Silica sand		0.5 to 1.4 mm in the packed zone of the FBR
Shimamura *et al.* (2003)	2 tank type reactor	Struvite fines ($d_{0.5}$=0.79mm)	12 days	Up to 195 µm in thickness after 12 days.
Suzuki *et al.* (2005)	Aerated reactor	Stainless steel mesh device	30 days	1.037 kg of struvite on mesh after 30 days.

In the present work, the different attempts to crystallise struvite onto seed material using short residence times confirmed this hypothesis with regards to granular type materials.

In 2 h residence time, struvite deposition onto sand, RCA and struvite was effectively not feasible. During these tests, only fines formation or seed breakage happened probably due to higher shear environments around seed particles. Indeed, high mixing energy or aeration were necessary to ensure seeds fluidisation. This suggests that for high mixing energies, particles need longer time to get acclimatised before substantial crystallisation occurs at the seed surface. Overall, the growth of struvite onto those surfaces is balance of adhesion force onto the material and the shear forces pulling the crystals off.

The application of a metallic mesh acting as a growth support proved to be a more reliable solution to recover struvite when short residence times are used. When using such a system, mixing conditions can effectively be reduced significantly. This supposes that crystallisation on a metallic mesh works not only because it presents a stronger affinity for struvite than other materials but also because more gentle conditions are permissible, shifting the force balance towards more favourable conditions.

Furthermore, from comparisons with the literature, growth of struvite on seed substrates also seems to be influenced by the nature of media from which struvite is precipitated, influencing then forces of adhesion. Indeed, for Regy *et al.* (2002) struvite was precipitated from synthetic liquors as during the present pilot scale investigations. In that case, our force measurements correlated well with their observation in that Fontainebleau sand and struvite had weak, or even none aptitude to agglomerate struvite. Conversely, results observed by Battistoni *et al.* (2005) and Ueno and Fujii (2001) proved that struvite crystallisation onto sand grain and struvite fines was feasible and successful, but in those cases, struvite precipitation was always carried out in real liquors (anaerobically treated sludge liquors) and over long period of time.

However, force measurements could explain differences in rates of agglomeration observed in the literature. Rates of agglomeration on sand or struvite seem effectively to be lower than the one observed on metallic supports (Table 7.2). For example, the only study of intentional crystallisation on a metallic support was carried out by Suzuki *et al.* (2005). They reported efficient accumulations of struvite on stainless steel rods with rates of agglomerations up to 16.7 $g.m^{-2}.h^{-1}$. Shimamura *et al.* (2003) who precipitated struvite onto fine particles in real liquors, had rate of agglomeration (calculated from the increase in mean particle size they reported) of 1.82 $g.m^{-2}.h^{-1}$ after 12 days.

7.5 Conclusion

Different materials, including sand, RCA, struvite and a metallic mesh, have been selected as possible seeds for struvite crystallisation. Topographical investigations using AFM and SEM revealed here that no correlation existed between surface characteristics and the capacity of materials to adhere struvite. However, assessment of the actual adhesion forces between struvite and the different surfaces using a struvite modified cantilever demonstrated that the mesh had greater potential to adhere struvite than the three other substrates. This was confirmed by the analyses of seeds recovered after 2 h of crystallisation in the pilot scale reactor. Furthermore it was proved that the type of seed material was determinant in the success of struvite recovery when using short contact times. Fluidisation requirements when using granular type materials resulted in limited growth as fines were produced or breakage occurred, compromising then rapid attachment of struvite onto them. Conversely, the utilisation of a metallic support submerged in the reactor required lower mixing energy; hence favoured struvite adhesion and recovery. The current work has showed that material characterisation and force measurements between struvite and a potential seed material using AFM can give helpful information to identify the capacity of a material to grow struvite.

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CHAPTER 8

STRUVITE CRYSTALLISATION AND RECOVERY USING A STAINLESS STEEL STRUCTURE AS A SEED MATERIAL

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8. STRUVITE CRYSTALLISATION AND RECOVERY USING A STAINLESS STEEL STRUCTURE AS A SEED MATERIAL

K. S. Le Corre[1], E.Valsami-Jones[2], P. Hobbs[3], R. D. Boyd[1], B. Jefferson[1], S. A. Parsons[1]

[1]School of Water Sciences, Cranfield University, Cranfield MK43 OAL, UK
[2] Department of Mineralogy, The Natural History Museum, Cromwell Road London, SW7 5BD, U.K
[3]Institute of Grassland and Environmental Research (IGER), North Wyke, Okehampton, Devon, EX20 2SB, UK

Abstract

Crystallisation on seed materials is a common technique used in industrial processes to improve the size of the final product to be recovered. With regards to struvite crystallisation from wastewater effluents, materials which have been tested in that sense are mainly sand and preformed struvite crystals. Following a recent study that has compared the propensity of a range of material to adhere struvite and showed metallic surfaces to have greater potential to grow struvite than compared to sand and struvite, a metallic system acting as a seed substrate for struvite crystallisation has been designed and developed. The objective was to assess the efficiency of such a device in removing and recovering phosphorus as struvite. The immersion of the system, consisting of two concentric stainless steel meshes, into a pilot struvite crystallisation reactor showed promising results. Under the specific operating conditions tested here PO_4-P removals achieved in presence of the system were up to 81 % and the meshes were capable of accumulating struvite at a rate of 7.6 $g.m^{-2}.h^{-1}$ after only 2 h operation. The simplicity of the system and its success in removing and recovering struvite make it a promising solution for phosphorus recovery that will need further investigation at larger scale.

Keywords: Seeded crystallisation, struvite, metallic accumulation system, P removal and recovery

8.1 Introduction

Blockage of pipes, breakdowns of centrifuges, pumps, heat exchangers and other pieces of equipments in contact with anaerobically digested effluents are typical consequences of the deposition in wastewater treatment plants of a white hard scale called struvite (Doyle and Parsons, 2002; Van Rensburg *et al.*, 2003). Primarily considered as a problem to eliminate or inhibit (Borgerding, 1972; Doyle *et al.*, 2003), struvite ($MgNH_4PO_4.6H_2O$) potential as a fertiliser has led wastewater companies to study its recovery (de-Bashan and Bashan, 2004).

The principles of struvite nucleation and growth as well as the efficiency of a variety of crystallisation reactors have been widely investigated and are well documented in the literature (Bouropoulos and Koutsoukos, 2000, Doyle and Parsons 2004; Le Corre *et al.*, 2005; Von Münch and Barr, 2001; Stratful *et al.*, 2004; Battistoni *et al.*, 2005). However, the application of struvite crystallisation processes at full scale remains limited, with for instance Japan being the only country where a complete phosphorus removal and recovery from anaerobically digested sludge liquors as struvite has been implemented and the resulting production sold to fertiliser companies (Gaterell *et al.*, 2000; Ueno and Fujii, 2001). The reason why struvite crystallisation is not more widely applied is a combination of the unknown economical value of the process and the product, the need of pH control, and the formation of crystal fines (Adnan *et al.*, 2003).

To optimise the size of the recovered struvite crystals, researchers have often tested crystallisation onto seed materials such as sand (Battistoni *et al.,* 2002) or preformed struvite crystals (Shimamura *et al.*, 2003). The impact of seeding can be seen on the final particle size distribution. To illustrate, Shimamura *et al.* (2003), who used struvite fines as a seed in their demonstrative reactor, observed a growth of particles from 0.79 mm to 1.18 mm in 12 days. However, if the use of a seed material to grow struvite has proved to be efficient, the operation of such processes requires strong mixing energy to insure the bed of seeds is continuously fluidised. As a result, when compared to a non-seeded crystallisation reactor, Battistoni *et al.* (2005) demonstrated that seeded crystallisation operative costs are increased due to extra pumping and air mixing energy. As a substitute to conventional particle seed materials, Suzuki *et al.* (2005) recently reported the use of a metallic support to recover struvite from swine wastewater and showed the system could accumulate up to 1 kg of struvite after 30 days of submersion in their reactor. Studies on the scaling properties of struvite previously showed metallic materials to favour struvite deposition (Doyle *et al.*, 2002). Furthermore, a recent study on the ability of a range of materials, including sand, struvite and a stainless steel mesh, demonstrated adhesion forces between struvite and a metallic surface to be the strongest (Le Corre *et al.*, 2006b). The development of a simple, robust and innovative metallic system that could be integrated to any crystallisation reactor to therefore improve struvite recovery and offer an alternative to existing seeded fluidised bed reactors. Such systems could reduce energy consumptions when compare to typical fluidised bed reactor filled with sand or struvite. A device has been designed at Cranfield University, and this paper presents results on its performances in recovering struvite formed from synthetic liquors.

8.2 Material and methods

8.2.1 Reactor design and operating conditions

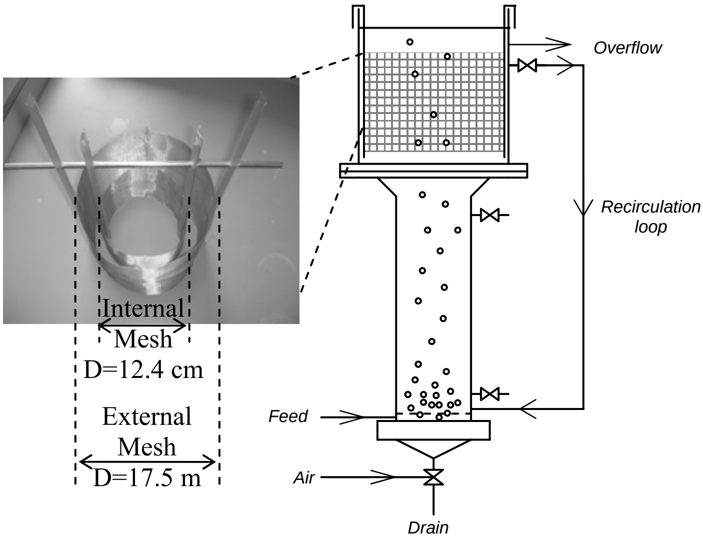
A pilot scale crystallisation reactor was designed and developed at Cranfield University to study struvite nucleation and growth (Le Corre *et al.*, 2006a). It was tested here for seeded crystallisation of struvite from synthetic liquors (Figure 8.1). The process was composed of a 10 L reactor with two side sampling ports and a drain valve. A peristaltic pump injected simultaneously solutions of ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$ / Fisher Analytical Reagent Grade, UK) and magnesium chloride hexahydrate ($MgCl_2.6H_2O$ / Fisher analytical Reagent Grade, UK), prepared by dissolution of the corresponding solid compounds in deionised water.

Prior to mixing in the reactor, each solution was adjusted to pH 9 with sodium hydroxide (NaOH 2 N/ Fisher analytical reagent grade, UK) in stirred buckets. Both solutions were then transferred to the reactor. A pH probe was introduced in the reaction zone to control and maintain the pH constant during the crystallisation process. An upward air-flow and a liquid recirculation were adjusted (3-4 $L.min^{-1}$ for air, and 1.5 to 1.35 $L.min^{-1}$ for liquid) to ensure the mixing and growth of the particles formed so that they were always kept in suspension during the experiment.

The experiments presented here were carried out at two different Mg concentrations 1.64 mM and 2.3 mM, ratios Mg:N:P 1:2:2 and constant pH, with and without the accumulation system. All experiments were conducted at room temperature over 120 minutes. During experiments, samples could be withdrawn for analysis from sampling ports situated on the side of the reactor at chosen height: top and bottom of the column shape part of the reactor and middle of the enlarged section.

8.2.2 Accumulation system design and configuration

A system composed of 2 concentric meshes was designed for use as a seed material to grow struvite. Both meshes were made of woven wire stainless steel 1 mm hole, 0.35 mm wire (T316-H&B Wire Fabrications Ltd, UK) and dimensioned to fit in the enlarged section of the reactor (Figure 8.1). The external mesh was 55 x 14 cm and the internal mesh was 39 x 9 cm.



[Mg]	1.64 mM	2.3m M
	pH 9 Air flow =3 L.min^{-1} Recirculation= 1.35 L.min^{-1}	
External Mesh	☑	☒
Internal mesh	☑	☒
Combined system	☑	☑

***Figure 8.1.** Process design and configurations tested*

The meshes were independently removable to study the efficiency of the system under the various configurations summarised in Figure 8.1.

8.2.3 Sampling and analyses

The evolution of struvite crystallisation in the reactor was followed by absorbance measurements. Samples were taken every 2 minutes during 30 minutes of crystallisation, then every 5 minutes until the 60th minute and finally every 15 minutes during the last 60 minutes. Each sample was analysed for absorbance (6505 UV/Vis Spectrophotometer, Jenway, UK) at the specific wavelength for struvite of 385 nm.

At the end of each test 2 L of solution were withdrawn from the reactor and filtered through 0.2 µm filters. Supernatants recovered were tested for phosphate (PO_4-P) and ammonium (NH_4-N) using Merck cell tests, while the recovered struvite particles were dried at room temperature and weighted to assess the remaining quantity of struvite in suspension.

The submerged system was removed and left to dry. Pictures of the meshes were taken to give a visual support of struvite accumulation onto the system. The meshes were also weighted to determine the mass of struvite accumulated. Struvite crystals were then recovered by light brushing for characterisation by SEM-EDS (Scanning Electron Microscope XL 30 SFEG, Philips, The Netherlands) and XRD (Powder X-ray Diffractometer D5005, Siemens, Germany).

8.3 Results

PO_4-P and NH_4-N removals obtained under various operating conditions are presented on Figure 8.2. Comparisons of the experiments over the range of mesh configurations tested and without the mesh gave similar PO_4-P removals. To illustrate, at [Mg] = 1.64 mM PO_4-P removals were 80 %, 79 % and 79 % with the combined meshes, the internal mesh and the external mesh respectively where at a similar concentration the PO_4-P removal without mesh was 79 %. At a higher magnesium dose (2.3 mM), the capacity of the reactor in removing phosphorus was also excellent, and was not affected by the immersion of the mesh as PO_4-P removals were 81 % and 86 % without mesh and with both meshes respectively.

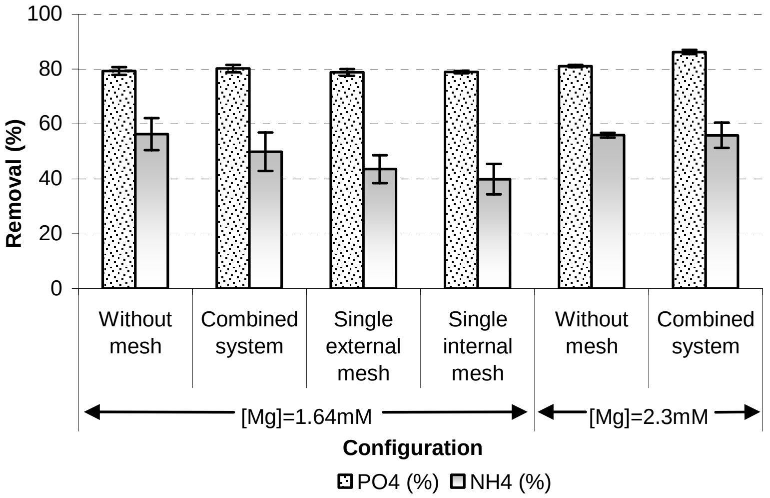


Figure 8.2. *Effect of process running configurations on PO_4-P and NH_4-N removals.*

With regards to levels of ammonium remaining in solution after 2 h of experiments, results showed that for similar conditions of precipitations (1.64 mM or 2.3 mM) the application of the metallic meshes in a combined configuration made no great difference when compared to crystallisation tests without it. For instance, at a magnesium concentration of 1.64 mM, NH_4-N removals were 56 % and 50 % either without the system or with the combined one, while at a magnesium concentration of 2.3 mM NH_4-N removals were identical without the system and with the combined meshes with values of 56 %. A slight increase of levels of ammonium remaining in solution only occurred when the meshes were submerged in an individual configuration as NH_4-N removals were 43 % and 39 % with respectively the external mesh and the internal mesh.

Changes in absorbance during the crystallisation can be used to follow nucleation and crystal growth processes (Barrett and Parsons, 1998). The absorbance of a precipitating solution typically increases during nucleation due to crystal birth, while decreases as particles grow due to their settlement (Higashitani *et al.*, 1993). According to Higashitani *et al.* (1993), who used the same methods to characterise $CaCO_3$ formation, when absorbance measurements reach a maximum value, this value is representative of the amount of particle formed. In the present study, the absorbance measurements were then undertaken to follow struvite crystallisation progress and determine the impact of the meshes on recovery. Results were compared to crystallisation tests carried out under similar conditions without accumulation system (Figure 8.3).

For crystallisation tests at an initial Mg concentration of 1.64 mM without the mesh, the absorbance profile showed that struvite nucleation occurred rapidly with absorbance increasing from 0.043 to 0.255 in less than 15 min, and reaching a steady state for the remaining experimental time with an absorbance value of 0.230 after 2 h. This indicated that once the totality of the ions available to form struvite had reacted, the crystal growth step was insignificant as no drop of absorbance was observed.

With the internal mesh, absorbance was increased to a maximum value of 0.204 after 16 min, and then decreased slowly down to 0.155 after 2 h suggesting capture of some of the crystals onto the mesh. Visual observations of the mesh after 2 h reinforced this hypothesis as a white deposit was visible on its surface. Using only the external mesh, the absorbance profile reached a maximum value of 0.176 after 12 min. The absorbance decreased continuously and reached a final value of 0.065 after 2 h indicating significantly less struvite crystals were suspended in solution.

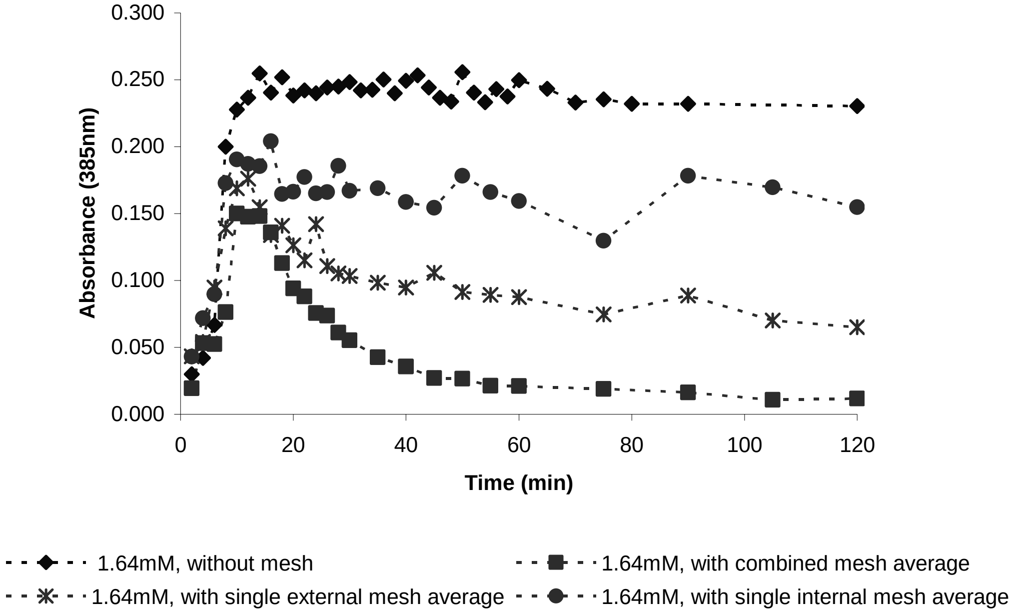


Figure 8.3. *Absorbance versus time for different configuration of system*

When struvite was crystallised in presence of the combined meshes, the absorbance profile was similar to the one observed with the external mesh, but again even more struvite was captured as an absorbance peak at 0.150 was observed after only 10 min, and then measures dropped down to 0.021 in less than 50 min to finally stabilise around only 0.012.

Visual observations of the mesh (Figure 8.4) showed that in a combined configuration the system accumulated a great amount of struvite particles, explaining the dramatic decrease in absorbance in the overall reactor. Interestingly, struvite adhered primarily on the external mesh of the system filling progressively holes situated in the bottom half of the mesh (Figure 8.4A), while accumulation of struvite particles on the internal mesh was lower as a light white deposit was only visible on the wire surface of the mesh (Figure 8.4B). As the internal mesh was positioned in the middle of the enlarged section right above the air diffuser, higher turbulence in this zone due to air may have then led to displacement of attached crystals.

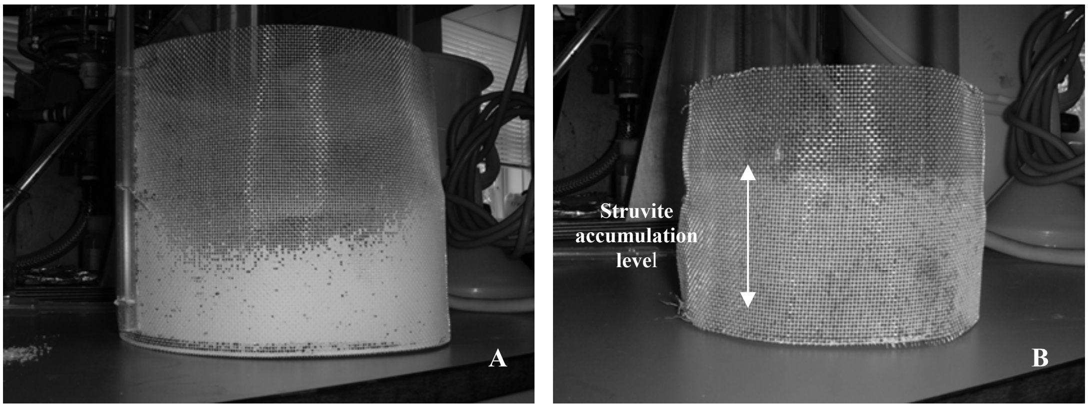


Figure 8.4. *Pictures of the external (A) and internal (B) meshes used combined after 2 h of crystallisation at [Mg] =1.64 mM*

The amount of struvite particles remaining in solution after 2 h was also measured for the different operating conditions (Figure 8.5). At an Mg concentration of 1.64 mM, the amount of particles in suspension after 2 hours fell from 302.2 mg.L^{-1} with no mesh to 138.3, 69.9 and 12.2 mg.L^{-1} with the single internal mesh, the single external mesh and the combined system respectively. This corresponded to reductions of 96 %, 77 % and 54 % of suspended particles with respectively the combined system, the single external mesh and the single internal mesh when compared to test without mesh.

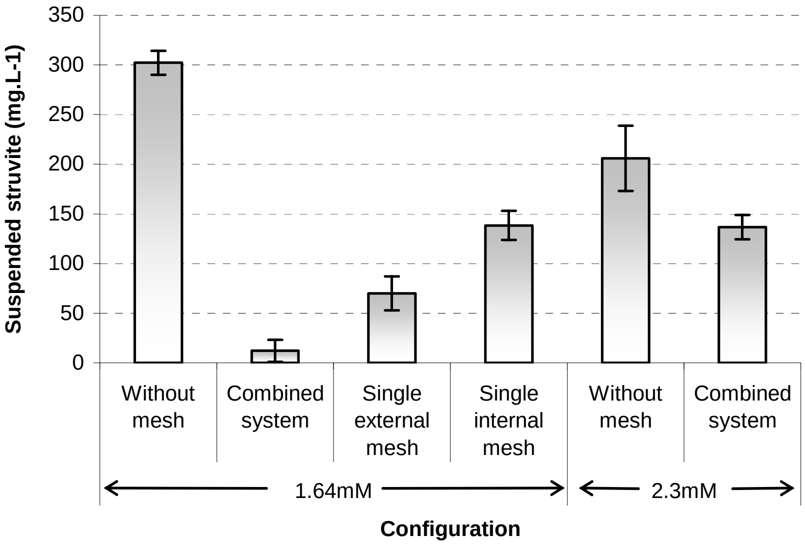


***Figure 8.5.** Suspended struvite particles in solution after 2 h.*

The efficiency of the system in removing suspended solid seemed to not only depend on the configuration tested but also on the magnesium stoichiometric dose. To illustrate, at high concentrations (2.3 mM as Mg) in a combined configuration, there was still 136.6 mg.L^{-1} of suspended struvite after 2 h of experiments corresponding to a 34 % of suspended solids removal. As a comparison, at 1.64 mM in the same configuration the quasi totally of suspended solid was capture by the system (Figure 8.5). However, at 2.3 mM the levels of suspended struvite particles in the control test without mesh were already lower than in the same conditions at a concentration of 1.64 mM. A settlement of particles at high concentrations may be at the origin of this difference and may explain lower removals of suspended struvite crystals.

The amount of struvite recovered from the mesh has been quantified for each specific condition of precipitation previously tested and converted into rates of production per hour (Figure 8.6).

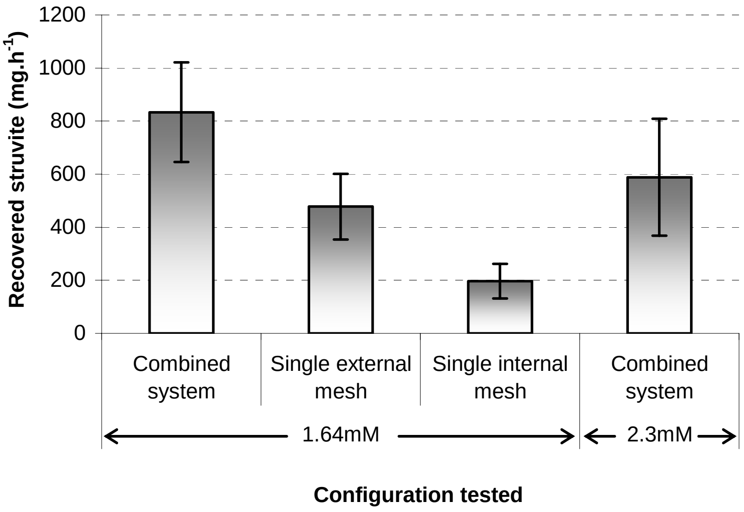


Figure 8.6. *Effect of process running configurations on struvite recovery.*

When submerged in the reactor for 2 h, the metallic mesh could accumulate up to 1020 mg.h^{-1} of struvite when the combined system was used at an Mg concentration of 1.64 mM, making this configuration the optimum one in recovering struvite. Indeed, under the other configurations tested the average quantities of struvite accumulated at the same concentration were reduced to 477 mg.h^{-1} for the external mesh and 196 mg.h^{-1} for the internal mesh. When linked to the actual surface of metal available for struvite to adhere on, the average accumulation rate of struvite under the optimum conditions (*i.e.* dual mesh system / [Mg] = 1.64 mM) was of 7.6 g.m^{-2}.h^{-1}. At [Mg] = 2.3 mM, the potential to form greater quantities of struvite are higher due to higher concentrations of compounds available to form struvite. However, results revealed in that case that the mesh was not able to attach more particles as the accumulation rate was only 588 mg.h^{-1} corresponding to an average rate of accumulation of 5.3 g.m^{-2}.h^{-1}.

After drying of the meshes, the struvite was easily recoverable by gentle scraping. SEM-EDS analyses of the dried samples revealed particles present on each mesh surfaces were actually an agglomeration of single orthorhombic crystals (Figure 8.7). As expected, the XRD and EDS analyses also confirmed that the recovered product was pure struvite with EDS highest peaks obtained for Mg, P and O indicating the metallic mesh characteristics had no influence on purity of the crystal formed (Figure 8.7).

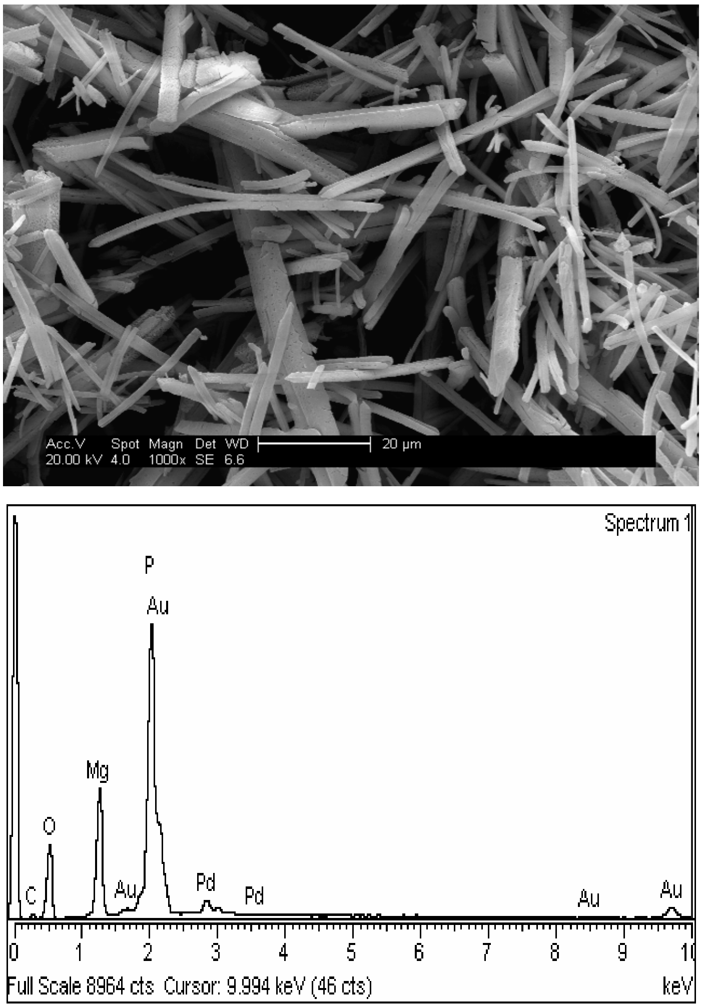


Figure 8.7. *SEM image and EDS spectrum of the recovered struvite.*

8.4 Discussion

In their study on the adhesion properties of potential seed materials for struvite crystallisation Le Corre *et al.* (2006b), demonstrated that a metallic surface should adhere struvite. They measured the strength of adhesion between struvite and a range of surfaces and demonstrated the adhesion forces between struvite and a metallic surface were higher than between struvite and the other surfaces investigated (*i.e.* sand, recycled concrete aggregates and preformed struvite crystals). Those results were in accordance with previous works (Doyle *et al.*, 2002) that have studied the scaling properties of struvite in pipes and other pieces of equipment in contact with wastewater effluents and demonstrated a strong affinity of metallic support for struvite deposition (Mohajit *et al.,* 1989). Booram *et al.* (1975) in one of the first studies of struvite deposition in a wastewater treatment plant deduced that metallic interfaces acted preferentially as active growth site for struvite deposition. Later on, Doyle *et al.* (2002) confirmed that stainless steel coupons placed for 8 h in centrate liquors adhered struvite significantly with scaling rates ranging 0.4 $g.m^{-2}.h^{-1}$ to 5.4 $g.m^{-2}.h^{-1}$ depending on the operating conditions. According to these observations a well designed system composed of stainless steel and submerged in a struvite crystallisation reactor should be able to act as a seed material to grow struvite.

The metallic system consisting of two circular meshes tested in the present study confirmed our expectations in that it was able to accumulate large amounts of struvite at its surface in rather short time (*i.e.* in 2 h). For instance, a struvite scaling rate of 7.6 $g.m^{-2}.h^{-1}$ was achieved under optimum conditions of operation that is to say here using the combined system submerged in the upper section of the reactor fed with synthetic liquors of Mg concentration of 1.64 mM. In fact, it was found that the position of the mesh in the reactor was influencing its capacity in recovering struvite. For instance, the external mesh which was placed above the air diffuser was not able to accumulate high amounts of struvite when compared to the external mesh. Overall, absorbance and suspended solids measurements suggested that rather than growing struvite at its surface, the mesh was trapping crystals that formed in the reactor. Indeed, in the early stages of crystallisation (within 20 minutes), absorbance measurements followed a similar pattern with or without mesh indicating similar rates of nucleation. After this period, the absorbance remained constant over the remaining experimental time without the mesh whereas after 2 h the absorbance had decrease down to 0.012 under optimal conditions of operation. These absorbance values correlated well with the 12 $mg.L^{-1}$ of suspended solids remaining in solution after 2 h when the system was submerged in the reactor instead of the 302.2 $mg.L^{-1}$ obtained without mesh. Finally, results showed the excellent performance of the meshes in removing phosphorus, as PO_4-P removals achieved were ranging from 79 to 81 % under the various configurations tested.

In the literature, only one study has explored and made use of the adhesive properties of metallic surfaces for intentional crystallisation of struvite. Suzuki *et al.* (2005) designed a rectangular stainless steel device for struvite crystallisation from swine wastewaters. Their system which was immersed in the aeration column of a demonstrative reactor operating in a continuous mode recovered up to 1,037 g of struvite on its accumulation face after 30 days of operation. By comparison, considering the optimum struvite accumulation rate of 7.6 $g.m^{-2}.h^{-1}$ calculated here to be constant, if the meshes had been submerged over 30 days in the pilot reactor running in a continuous mode, up to 602 g of struvite could have been theoretically recovered from the mesh. This is more than 1.5-fold lower than what Suzuki *et al.* (2005) observed but still promising when considering that this was achieved in synthetic liquors. Furthermore, rates of agglomeration on sand or struvite as seed material seem much lower than the rate observed on metallic supports. For instance, Shimamura *et al.* (2003) who precipitated struvite onto fine particles in real liquors, had rate of agglomeration (estimated from the increase in mean particle size they reported) of only 1.82 $g.m^{-2}.h^{-1}$ after 12 days.

The advantages of struvite crystallisation on a static support are numerous. Indeed, as stated by Stratful *et al.*, 2004, one of the reason why wastewater companies have not adopted the struvite crystallisation technique, especially fluidised bed reactors (FBR), to remove and recover phosphorus is related to their complex design and the need of qualified operators to constantly control and maximise their efficiency. Accumulation devices like the one used here could limit these problems as they are relatively simple to design and require very low maintenance. Moreover, recovery of struvite can simply be achieved by light scraping of the mesh. Suzuki *et al.* (2005) concluded that the ease of use and robustness of similar recovery systems would be particularly attractive for swine farmers. The utilisation of this type of processes would also decrease the risk of operational failures or reduction of the process efficiency that can be observed when crystallising struvite on granular materials. Ohlinger *et al.* (2000) have for example underlined that when using granular material as seed for struvite crystallisation in an FBR, mass of particles increased due to growth and could provoke bulking of the media. To avoid this phenomenon, a part of the media needed to be refreshed periodically and this regeneration could affect the efficiency of the FBR in removing phosphorus. Shimamura *et al.* (2003) also indicated that with traditional FBRs, the growth of struvite crystals reduces their fluidisation, and limits the surface area available for its precipitation reducing then struvite recovery. Furthermore, in some cases the recovery of struvite on a regular basis can also require a temporary shutdown of the crystallisation process during the settlement of the product (Adnan *et al.*, 2003), whereas the operation of the present reactor in a continuous mode would only require spare accumulation systems so that the fully loaded mesh could be replaced by a fresh one without having to stop all feeding and/or air pumps.

Battistoni *et al.* (2005) explained that operational costs of their fluidised bed reactor were increased because of the energy consumption linked to pumping equipments and costs of the raw seed material (*i.e.* sand). To illustrate, they indicated that struvite production using seed materials as sand would cost about 0.28 €.m^{-3} including pumping energy and regeneration of seeds whereas without seed material the costs of production could be reduced down to 0.19 €.m^{-3}. It can be then assume that the utilisation of the metallic mesh system which require lower feeding and air flow rates than the one necessary to fluidise a bed of growing granular seed materials would also save energy significantly.

8.5 Conclusion

In the current work the performance of a stainless style mesh system acting as a seed substrate for struvite crystallisation in synthetic liquors has been investigated. Various tests in different configurations demonstrated that the system combining two concentric meshes placed in the enlarged section of the pilot scale crystallisation reactor was able to accumulate struvite at a rate of 7.6 $g.m^{-2}.h^{-1}$ under optimum conditions of precipitation and to achieve excellent PO_4-P removals up to 81%. The mesh was particularly efficient when placed on the edge of the enlarged section of the reactor, as it was showed that mixing energy could be responsible of crystals detachment from the mesh. Finally, rather than growing struvite directly on its surface, the mesh system is thought to capture struvite crystal already formed in solution. Further investigations in real liquors are currently being undertaken at Cranfield University. However, the conclusions resulting from this work and the comparisons with other seeded processes showed that a struvite crystallisation reactor combined with the current metallic system is a promising solution for maximising phosphorus recycling in wastewater treatment plants.

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CHAPTER 9

PRACTICAL IMPLICATIONS FOR WATER UTILITIES

9. PRACTICAL IMPLICATIONS FOR WATER UTILITIES

A review of the literature (chapter 2) has highlighted the growing interest of water utilities in preferential struvite crystallisation as a way to control the problems of spontaneous deposition of struvite in post digestion treatment lines and limiting phosphorus recycling in their wastes. However, the application of full scale struvite crystallisation processes in WWTP is limited due to problems associated to quality and quantity control of the product generated. The results of this investigation has broadened the understanding of struvite crystallisation principles and offered alternative solutions to problems of limited growth which can be easily encountered in struvite crystallisation processes. Overall, the findings of this study have permitted the development of a series of flow sheet diagrams which could be used by water utilities that would like to consider and implement struvite crystallisation processes as a way to remove and recover phosphorus (Figure 9.1 and 9.2).

One of the first points that water utilities should take into account when considering struvite crystallisation concerns the selection of the most appropriate waste stream to precipitate and recover struvite. Anaerobically digested sludge liquors where concentrations in phosphorus and ammonium are relatively high seem the most suitable for this as in that type of liquors Mg and pH should remain the only factors to adjust in order to initiate struvite crystallisation, while other streams may require additional ammonium adjustment, hence increasing costs of production link to chemical additions (Chapter 2-section 4).

The second step is then to precisely determine the chemical and physical characteristics of the liquors to be used for the crystallisation process (Figure 9.1). Indeed results of the present work demonstrated that key parameters such as solution supersaturation, presence of foreign ions, pH and mixing energy could be responsible of dramatic changes in struvite crystal characteristics in terms of size, shape and purity as well as on quantity of product generated. To illustrate the purity of the crystals formed was found to be affected by the pH at which precipitation occurs (Chapter 5- Section 5.3.2.1) and by the presence of calcium ions. The optimum pH of precipitation was identified to be pH 9 whereas Ca ions needed to stay in a Mg:Ca ratios below 1:1 to avoid competition between struvite and calcium phosphate precipitation (Chapter 4). This implies that application of struvite crystallisation processes at full scale would require a regular and accurate monitoring of liquors chemical characteristics to regulate pH and chemically counterbalance Mg:N:P and Mg:Ca ratios when needed. Magnesium ions are commonly known to be the limiting ions that prevent struvite precipitation from real liquors, moreover they were found here to be of great influence on struvite precipitation kinetics as increasing doses of magnesium could reduce significantly struvite induction times and increase rates of crystallisation. However, the magnesium dosing should not be too excessive, as this would result in excessive supersaturation ratios which would cause rapid nucleation, hence overproduction of fines (chapter 2 and chapter 3). In the crystallisation tests carried out here in synthetic liquors, a magnesium dose of 39.8 $mg.L^{-1}$ for a $Mg:NH_4:PO_4$ molar ratio 1:2:2 was found as a good compromise between the induction period and quality of the resulting product. Water utilities would then have to determine the appropriate dose of magnesium (as $MgCl_2$, or $Mg(OH)_2$) and the NaOH (for pH control) necessary to form struvite in order to ensure the selectivity of the process toward struvite and to control the quality of the product formed (Figure 9.1).

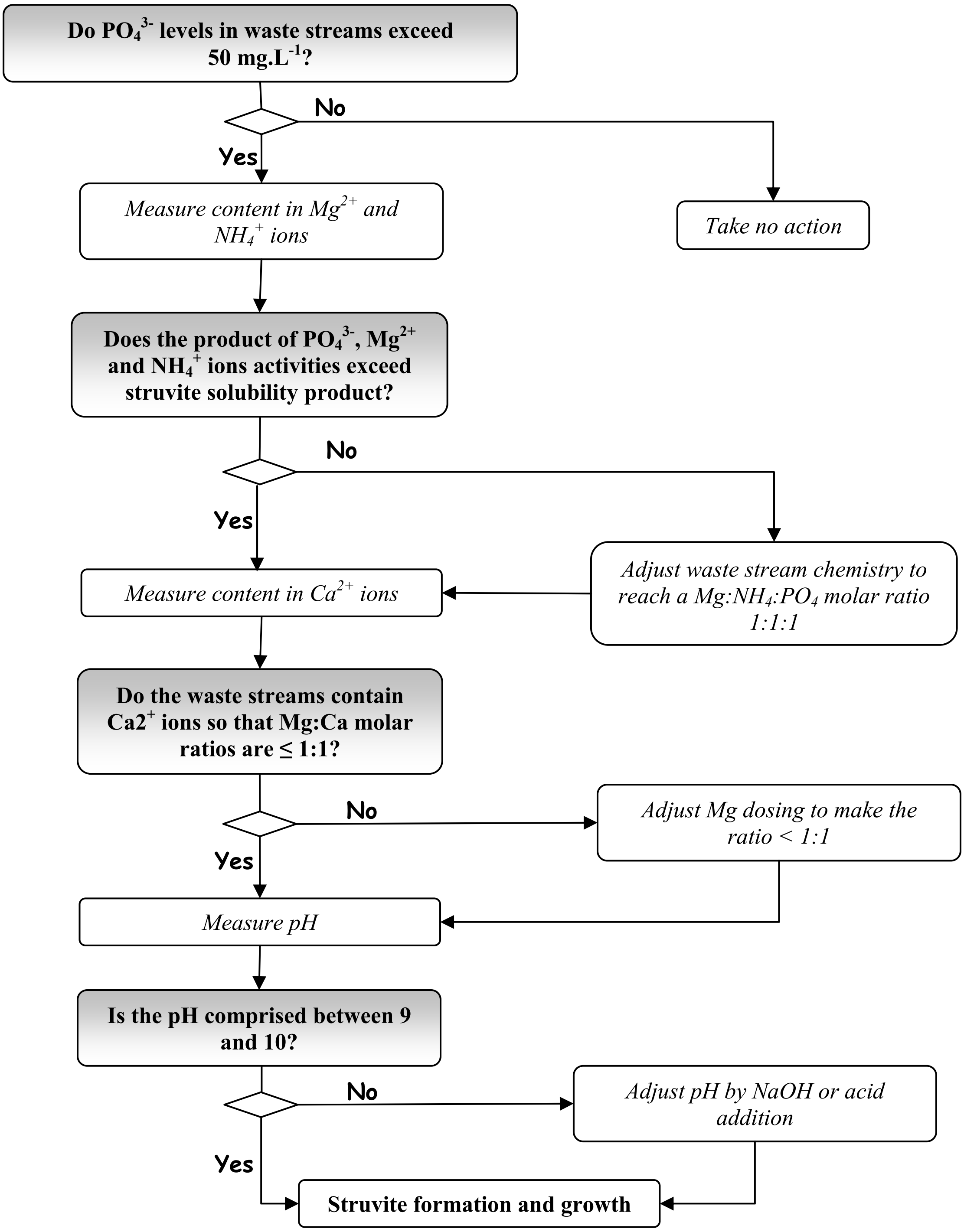

Figure 9.1. *Operational check list for the implementation of a struvite crystallisation process*

When water utilities have established that they meet the requirements for the application of struvite crystallisation processes, they will have to take in consideration the efficiency of the process in recovering phosphorus as a premium fertiliser in order to generate benefits from the sale of the product formed. In fact the size and purity of struvite crystals is important in terms of recovery as a fertiliser: the size and strength of the granule must be sufficient for a practical recovery from the reactor and application, while the purity is essential for environmental reasons. To illustrate, in Japan struvite precipitated from anaerobically digested supernatants has already been sold to fertilisers companies and the average size of the pellets formed was comprised between 0.5 and 1 mm (Chapter 2-Tables 2.10a). In Treviso (Italy) wastewater treatment plant where a full scale fluidised bed reactor for struvite formation and recovery has been implemented, the size of the recovered product typically reaches 1.4 mm (Chapter 2- 2.10b). The size of struvite particles issued from any crystallisation reactor should then be ideally in that range (*i.e.* 0.5-1.4 mm) to ensure a practical recovery and reuse of the product as a fertiliser.

However, the better understanding of struvite crystallisation principles provided here by the analyses of the effect of water chemistry, presence of foreign ions, pH and reactor operation on struvite characteristics showed that the control of struvite size was probably the most complex characteristic water utilities should have to deal with as it can be influenced by pH, mixing energy, presence of foreign ions, impurities and seed materials. Indeed, when precipitating struvite from synthetic liquors, it was found that the occurrence of crystals was generally rapid but their growth was extremely slow, resulting in the overproduction of fines. The overproduction of fines can be a major problem when running crystallisation processes as this phenomenon can affect recovery efficiencies due to higher settling times, and can result in loss of fines in treated effluents (Battistoni *et al.*, 2005). When facing problems of fines formation or limited growth, researchers have isolated fines and reused them as seeds in their crystallisation process (Ueno and Fujii, 2001) or have combined their plant with filtration units to limit loss of fines in effluents (Battistoni *et al.*, 2005; Adnan *et al.*, 2003).

As an alternative, the findings of this investigation have allowed to develop two new methods to prevent fine formation and better manage struvite crystal growth (Figure 9.2). The first one consisted in the possibilities of recovering struvite fines by coagulation (chapter 6). The second one investigated optimisation of struvite crystal growth by precipitation onto seed materials (chapter 7 and 8).

The coagulation method was developed as struvite was found to present high negative zeta-potentials responsible of crystals stability in suspension which limited their natural agglomerative properties. The addition of positively charged coagulants such as hydrolysing metal compounds (alum and iron salts) or natural or synthetic polymers was then investigated as a way to enhance aggregation of crystals through physical collision and particle bridging (Chapter 6-section 6.2.3). This solution proved to be really efficient when facing excess formation of struvite fines. Under optimum conditions of coagulation, size of flocs could reach more than 10 times the initial size of struvite crystals which was comparable in size to struvite pellets recovered and sold in Japan (Ueno and Fujii, 2001). Besides, results suggested that the coagulation option also has considerably reduced reaction times. Coagulation could then be applied as soon as equilibrium is reached without affecting removal and recovery efficiencies. When implementing struvite crystallisation processes, water utilities could then choose to combine a coagulation step to their reactor to rapidly recover fines flushed out in treated effluents and/or complement struvite recovery by direct growth (Figure 9.2). However, as discussed in chapter 6, the success of coagulation of struvite particles proved not only to be dependant on nature of the coagulant used but also on pH (section 6.3.2). This means that at large scale the recovery of fines by coagulation would require precise pH control and adjustment during coagulant dosing.

The second option water utilities could take into account to improve struvite crystal growth and to recover struvite fines consist in the utilisation of seed material, and more precisely the utilisation of a metallic mesh system to capture struvite forming in the main reaction tank (Figure 9.2). Indeed the findings of the previous investigations demonstrated that a metallic support submerged in the crystallisation reactor could rapidly accumulate high amounts of struvite while achieving excellent PO_4-P removals up to 81% (chapter 8). Practically, it was demonstrated that for such systems to work, it has to be placed in a section of the reactor where turbulence are minimised to favour attachment of crystals and avoid detachment of accumulated crystals from the mesh (chapter 7 section 7.3.3). However, this is an option that could be easily applied at larger scale as such systems are rather simple to design and do not require a specific adaptation of the main reactor. Furthermore, it was demonstrated that this solution could help reducing struvite costs of production by limiting the mixing energy and air fluidisation which are usually high when precipitating struvite on traditional seed material such as sand (Chapter 7- section 7.4). The only disadvantage known to date that may prevent water utilities from applying this solution regards the manipulation of the mesh. The accumulation of high amounts of struvite to a scaled-up mesh system would cause a significant increase of its total mass. A specific lift system to regularly recover struvite would then be required. Further investigations in order to find alternative ways of recovering the struvite from the mesh without maybe removing the accumulation system from the reactor could then definitively validate this option.

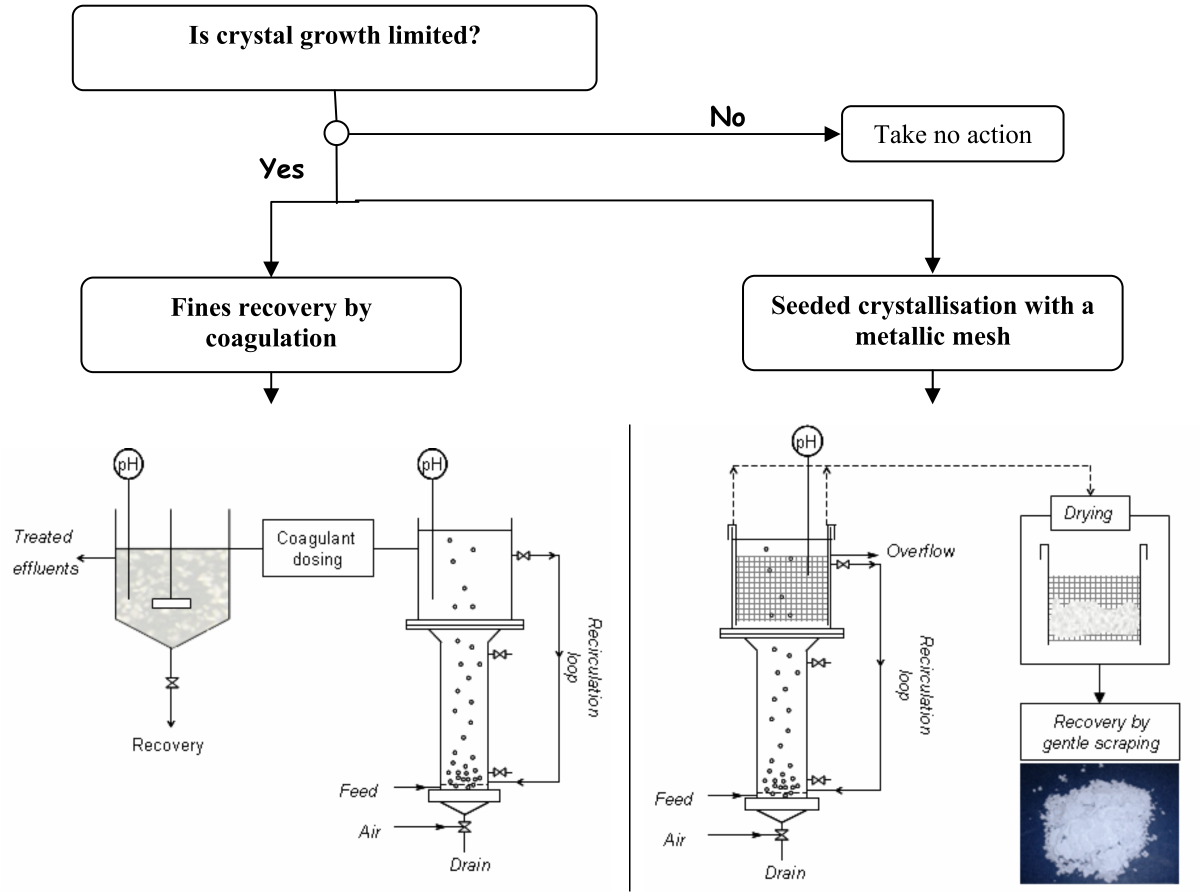

Figure 9.2. *Process adaptation to manage crystal growth problems*

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CHAPTER 10

CONCLUSIONS AND FURTHER WORK

10 CONCLUSIONS AND FURTHER WORK

10.1 Conclusions

This project has extended the understanding of struvite crystallisation principles by providing information on how specific chemical and physical parameters could influence struvite crystal quality. Furthermore pilot scale investigations have demonstrated the importance of crystal growth in the optimisation of crystallisation processes. The conclusions arising from this work are the following:

- Magnesium ions play an important role in struvite precipitation kinetics. An increase in magnesium dose in solution causes a rise in rate of struvite precipitation. However, variations of magnesium levels in precipitating solution do not affect struvite crystal characteristics. A relationship was found between pH and the concentration of magnesium ions that react to form struvite. This allowed to identify that struvite nucleation followed a first-order kinetic model.
- The presence of foreign ions as calcium is responsible of major changes in purity of the product formed. For Mg:Ca ratios 1:1 the formation of struvite crystals is still observable, but compete with the formation of calcium phosphate. Above this ratio, only amorphous calcium phosphate is visible.
- The development of a pilot scale fluidised bed reactor revealed the importance of operating conditions on success of P removal and recovery as struvite. Among the parameters investigated, pH was found to be the most influent on struvite crystallisation as it affected nutrient removals, struvite crystals quality and quantities of product formed. To illustrate pH increases from 8.5 to 10 resulted in a decrease in size of crystals formed from 84 to 33 microns, and an increase in Mg removal from 46% up to 92 % whereas PO_4-P removals remained relatively constant (~ 80%). For a pH of 10.5, purity of the product formed was affected by the precipitation of cattiite ($Mg_3(PO_4)_2.22H_2O$).
- The operation of the pilot scale under various conditions of precipitation revealed its limit in growing struvite. Although good phosphorus removal and recovery could be achieved, crystals formed remained under 100 µm in size. Zeta-potential measurement carried out on crystals formed during those tests revealed that struvite crystals invariably possessed a negative surface charge

over the range of pH 8.5-10.5. This limited then their agglomerative properties in solution due to electrostatic repulsion, and lead to overproductions of fines.

- Given its electrical properties, the agglomeration of struvite crystals with cationic coagulants have been investigated. Ferric and aluminium salts, calcium compounds, and polyDADMAC were able to all increase particle size distribution by formation of struvite flocs. polyDADMAC was found as the best option for struvite coagulation with formation of flocs 10 times bigger than initial struvite crystals although its success in forming flocs was very pH sensitive. Its application at large scale would then improve significantly operational times and rates of recovery but would require an accurate pH control.
- The impact of seed materials on struvite growth was investigated at microscopic scale by Atomic Force Microscopy before further investigations at pilot scale. The forces of adhesion measured between struvite and a range of seeds including sand, struvite, recycled concrete aggregates and a metallic mesh were found to be the strongest with the metallic surface. Applications of the different seed materials at pilot scale revealed that granular type materials were not able to accumulate struvite in short contact times conversely to the metallic system. The success of struvite deposition on seeds occurred as a combination of adhesion forces and mixing conditions under which crystallisation is performed. Indeed, the application of granular seeds requires a strong aeration to maintain particles in suspension which does not favour struvite adhesion especially for short contact times.
- As the application of a metallic mesh system allows lower agitation than the other types of seeds, this system was able to capture large quantities of struvite in short operational times. To illustrate, within 2 h of operation under optimal conditions of precipitation around 81% of phosphorus as phosphate was removed at a struvite accumulation rate of 7.6 $g.m^{-2}.h^{-1}$. Its application at larger scale would then help to reduce significantly operational times, improve recovery of struvite and further reduce costs linked to mixing energy when compared to the traditional seeded crystallisation on sand or struvite.

10.2 Further work

The results of the present study highlighted the importance of controlling struvite crystals size, shape and purity to improve process operation and struvite recovery. However, all the findings resulted from both laboratory and pilot scale investigations carried out in synthetic liquors. Further research will then have to focus on transfer of these laboratory findings to real sludge liquors, and should concentrate on:

- The evaluation of the impact of real liquors on struvite crystals characteristics. This work highlighted the influence of calcium on purity of struvite crystals, and the impact of Mg ions on struvite crystallisation kinetics. Therefore, it is suggested to screen a range of sludge liquors for their chemical characteristics in order to identify the sources that would be the best suitable to ensure crystal purity.
- The presented pilot scale reactor has been principally used in batch mode in Cranfield laboratories. It would be then essential to scale it up and evaluate the performance of this process at longer term by for example integrating it to a real wastewater treatment line.
- The development of a kinetic model on real liquors to predict the time necessary to form struvite in a specific reactor would also be an asset to optimise struvite crystallisation and recovery processes.
- In the present work, coagulation has been identified as a possible solution to control problems linked to the formation of fine crystals. This study has identified polyDADMAC as the best option to enhance struvite agglomeration and recovery through floc formation. However, the success of this cationic polymer in coagulating struvite was found to be very pH sensitive, which could limit its application at larger scale. It would be then interesting to investigate the performance of other cationic polymer for struvite removal and recovery and identify if pH is also a limiting parameter in their success to form struvite flocs.
- From the investigations on the characteristics of seed materials and their impact on struvite crystal growth, the application of a metallic mesh system occurred as a promising solution for rapid phosphorus removal and recovery as struvite. More research in terms of the effect of the type of material used, its design and the configuration under which it is applied (flow rates intensity, impact of real

liquors) is then needed to optimise its performances and to validate its application to future full scale application.

- Furthermore, more research has to be carried out on alternative strategies to mesh removal and recovery if applied at larger scale. The development of a rotating mesh which would not have to be removed from the reactor to recover the accumulated struvite could be a solution to investigate.