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Phosphate Recovery where do we stand today ?

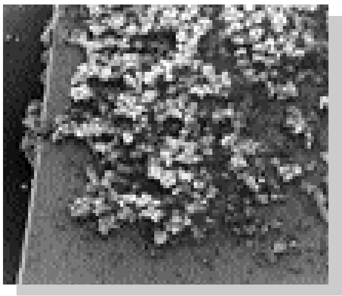
In preparation to the 2nd International Conference on Phosphorus Recovery for Recycling from sew-age and animal wastes, Noordwijkerhout (near Amsterdam) Holland, 12-14th March 2001.

information : phosphates@lgce.nl

This SCOPE Newsletter is intended to provide an update of current developments into phosphorus recovery for recycling, in particular as a basis for discussion and progress for the 2nd International Conference on this subject **in Holland, 12-14th March 2001.**

This Special Edition thus adds to existing information published regularly in the SCOPE Newsletter and in vol.20 n°7 of "Environmental Technology" July 1999 (presenting the main papers from the First International P-Recovery Conference, Warwick University UK, May 1998).

Researchers and operators working on phosphorus recycling are invited to send us a summary to be included in a future SCOPE Newsletter and/or to be presented as a paper or poster at this Conference.



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http://www.nhm.ac.uk./mineralogy/phos/index.htm

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Articles and information concerning P-recovery available on request from CEEP.

Please use materials request form on the rear cover of this Newsletter or order material via the P-recovery web site :

http://www.nhm.ac.uk/mineralogy/phos/index.htm

THE PHOSPHATE INDUSTRY'S EDITORIAL :

Where to and why ?

The CEFIC Sector Group CEEP (the joint research association of the West European detergent and technical phosphate industry) has been actively supporting and promoting phosphorus recycling for a number of years now. This engagement includes direct funding of research activities, co-ordination of a European R&D project, and dissemination of information via the SCOPE Newsletter and through organisation of the First International Conference on Phosphorus Recycling (Warwick University UK, 1998) and now the Second Conference in Holland, 12-14th March 2001 (information : phosphates@lgce.nl).

The West European phosphate industry has fixed **an objective of using 25% recovered phosphates within a decade**. CEEP is convinced that phosphorus can, and indeed must, be a central part of a sustainable future, because it is irreplaceable for life: essential for bones, teeth, DNA, nerve and muscle function. **Phosphates are probably also the only reyclable detergent ingredient.**

The most ecological pathway for recycling phosphorus is the agricultural application of biosolids (sewage sludges, manures), because this also ensures recycling of organic and other nutrient values, but this is increasingly limited or impossible in many circumstances, for reasons of social acceptance, soil nutrient saturation or pollutant contamination/health issues. For this reason, industrial recovery and recycling of phosphorus is essential for the sustainable future of society.

And where from ?

Over the last few years, there has been a significant development in interest in phosphorus recycling, particularly within the water industry concerning sewage, but also concerning agricultural and industrial wastes. In Europe and Japan, **several water companies have built or tested phosphorus recovery systems over the last few years, and others are currently doing so.** New knowledge and technologies have appeared from researchers across the world, increasingly with direct water industry support.

At the same time, regulatory and socio-environmental pressures are making phosphorus recovery significantly more attractive, both through the implementation of phosphorus removal from sewage and through increasing costs of sewage sludge and agricultural manure disposal. Sweden, for example, increasingly requires phosphorus recovery in sludge incineration permits whilst also moving towards an end to sludge recycling in agriculture.

Despite the interest, **many challenges have to be addressed** before phosphorus recycling can develop on a significant scale. These concern technological aspects (biological and chemical processes, reactor design, etc…), interactions with sewage works operation (including implications for the overall biosolids management cycle), and economic, logistic and regulatory questions concerning the re-use of recovered phosphate products.

Where phosphorus cannot be recycled by agricultural spreading of biosolids, **a number of pathways are possible for industrial recovery for recycling :** precipitation of phosphates in a re-useable form, production of high-phosphate composts or other manageable products, extraction of phosphorus from sewage sludges or sludge incineration ashes, and other innovative technologies currently at the design level.

Industrial recycling

The most developed pathways at present are **phosphate precipitation as either calcium phosphates or struvite (magnesium ammonium phosphate) pellets.** The chemistry of these two compounds is somewhat different, but the integration of their precipitation into sewage treatment and sludge handling is very similar. Calcium phosphates can be recycled into industrial processes (and recovered calcium phosphates from one sewage works are already re-used by Thermphos in Holland), or processed simply to locally manufacture fertilisers. Struvite can probably be used directly as a fertiliser (although further research is needed to better evaluate its agronomic value) or it can be incorporated into fertiliser manufacture (as is the case already at several sites in Japan).

For these reasons, CEEP has commissioned, as key sections of this Newsletter, articles presenting the current state of knowledge into calcium phosphate and struvite precipitation. In addition, information concerning economic and logistic feasibility and involving other possible phosphorus recycling pathways are presented.

We hope that you will find this information useful and look forward to working on it with you at the Second International Conference on Phosphorus Recovery for Recycling, Noordwijkerhout (near Amsterdam airport) Holland, 12-14th March 2001.

David Fielding, President of CEEP.

Integrating P-recovery into waste water treatment.

When assessing the feasibility and economics of phosphate recovery from municipal waste waters, a number of different questions have to be addressed. These include :

- the quantity and quality of phosphates which can be potentially recovered (including total phosphate mass balance)
- suitability for P-recovery reactor operation (chemical conditions, including phosphate concentration)
- effects on treatment works operation (P-removal, economics …)
- implications for biosolids management.

The answers to these questions will depend considerably on whereabouts in the treatment plant the recovery operation is undertaken (possibly including mixing different streams or pretreating them to optimise conditions) and the answers may vary widely from one treatment plant type or one local situation (waste water characteristics, biosolids disposal routes ….) to another.
Below are presented two approaches to these questions, as taken by Berliner Wasser Betriebe, Germany, and Thames Water, UK. Both look at municipal waste water treatment works using biological nutrient removal which offer streams which could be particularly attractive for phosphate precipitation.

For both water companies, struvite deposits have posed major operating problems and one of the objectives of phosphate recovery would be to pre-empt problem struvite deposits, thus improving both operating reliability and process economics. .

Biological P-removal in municipal waste water treatment plants :

possibilities for integrating P-recovery.

Bernd Heinzmann, Berliner Wasser Betriebe, Germany.
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1. Introduction

Berliner Wasserbetriebe are one of the foremost German sewage treatment companies which remove phosphate from the wastewater by the Bio-P process. In the two largest wastewater treatment plants of BWB, which have a treatment capacity of about 370.000 m³/d, effluent values less than 0.5 mg/l P_{total} are achieved with this process.

In the Bio-P process, phosphate is stored by bacteria in the form of polyphosphates and then deposited in the activated sludge. Thus, removing excess sludge also means removing substantial quantities of phosphorus from the system. In anaerobic sludge treatment, the biologically bound phosphorus is transformed into chemical P compounds, which are mainly made up of calcium phosphates and struvites (MAP: magnesium ammonia phosphates). These hardly soluble compounds precipitate and mostly intercalate in the digested sludge.

However, there are several locations in the excess sludge treatment process, where P-rich liquor could be separated from the sludge and a P-recovery would be possible. The advantage of the Bio-P process is that a precipitation with iron and aluminum salts is avoided.

2. P-rich liquor in wastewater treatment plants and methods for P-recovery

The wastewater treatment plants (wwtp) Waßmannsdorf and Ruhleben remove, as already mentioned above, the phosphorus by the Bio-P process. However, the excess sludge is treated differently:

- the wwtp Waßmannsdorf has an anaerobic sludge digestion
- and the wwtp Ruhleben uses a sludge incineration.

In the wwtp Waßmannsdorf, the sludge water from the anaerobic sludge treatment has a high P-level, which is caused by biological P-release during the anaerobic sludge treatment process. The consequence is a higher P-loading in the activated sludge process. A phosphorus recovery during the sludge treatment process would reduce the P-loading and stabilize the activated sludge process. This would have a positive effect on the effluent quality.

In wastewater treatment plants P-rich liquors mainly occur during sludge treatment. In the following chapters the locations in the treatment process and the possible methods for P-recovery are described.

2.1 Centrate of the digested sludge

Location of the P-recovery

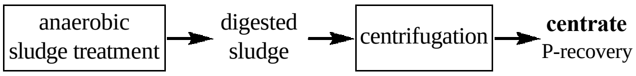

Figure 1: Sludge digestion and dewatering in the wwtp Waßmannsdorf

- Quantity of the centrate: 1000 m^3/d per 100,000 m^3/d wastewater (1 % of the inflow)
- Quality of the centrate: 1 g/l dried solid matter
- Phosphorus concentration: 200 g/m^3 P
- Ammonia concentration: 700-1000 g/m^3 NH_4-N

A P-recovery at this location would cover 15 % of the influent P-load. In addition to the P-recovery, a precipitation of ammonia would also be possible.

Methods of P-recovery (ammonia recovery)

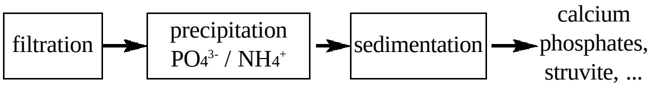

Figure 2: Phosphorus removal at the sludge digestion site in the sludge treatment plant Waßmannsdorf

2.2 Centrate of the biological excess sludge

Location of the P-recovery

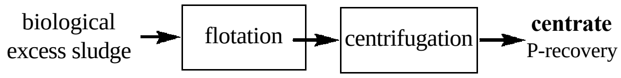

Figure 3: Sludge dewatering in the wwtp Waßmannsdorf

- Quantity of the centrate: 660 m^3/d per 100,000 m^3/d wastewater (maximum 1 % of inflow)
- Phosphorus concentration: 500 g/m^3

A P-recovery at this location would cover 25-30 % of the total P-load in the influent of the wwtp.

Methods for P-recovery

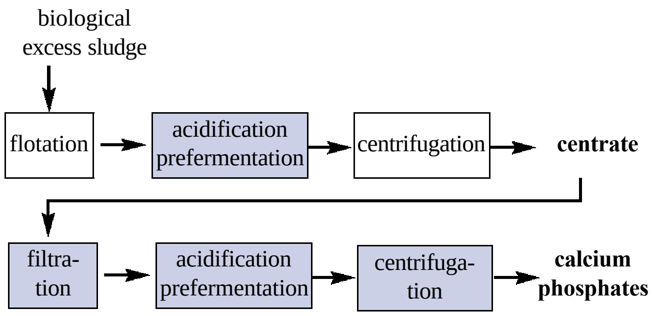

Figure 4: Phosphorus removal at the sludge dewatering site in the sludge treatment plant Waßmannsdorf by lime precipitation

2.3 Centrate of the combined sludge (primary and biological excess sludge)

Methods for P-recovery

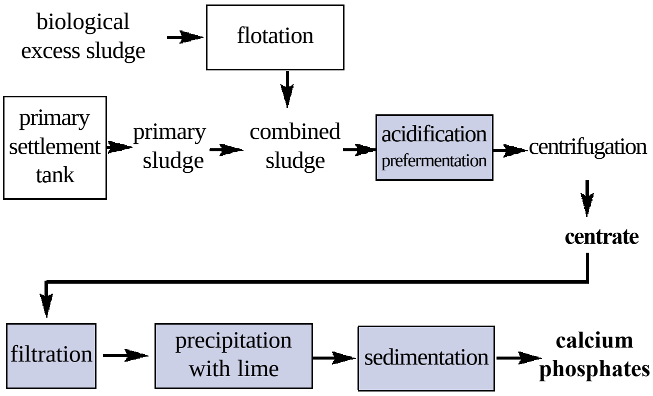

Figure 5: phosphorus recovery in the sludge dewatering in the wwtp Waßmannsdorf

- Quantity of the centrate: 660 m^3/d (maximum 1 % of inflow)
- Phosphorus concentration: 500 g/ m^3

P-recovery at this location would cover 25-30 % of the total influent P-load.

3. Problems with incrustation

In 1994, for the first time massive incrustations in the centrifuges treating the digested sludge were detected in some sewage treatment plants of the Berliner Wasserbetriebe, which were, as was found out later, mainly due to the precipitation of various phosphates. These incrustations caused a lot of problems. In the wwtp Waßmannsdorf, for example, a precipitation of nearly insoluble phosphorus compounds in the centrate of the digested sludge treatment cycle occurred, which was so massive that during two weeks a newly commissioned centrate pumping station together with the connecting pipelines was completely clogged. Therefore, these hard crystalline incrustations had to be removed by means of mechanical cleaning techniques. This operational trouble occurred nearly every two weeks, and this was the reason to look for a way to avoid such incrustations, which is described below.

4. Studies and measures

Caused by this operational trouble, several studies have been performed to describe the phosphorus dynamics in the sludge treatment. The chemical analysis of the crystalline matter indicated first of all the formation of struvite and of calcium phosphate compounds.
On the basis of these findings, several studies have been brought on the way:

●1. **Technical laboratory tests** were performed to study the phosphorus dynamics in the anaerobic sludge treatment (chemistry and kinetics of the P precipitation during digestion).

●2. The results were used to prepare a catalogue of **measures to be taken in order to avoid incrustations**. The majority of these measures aimed at inducing a precipitation of struvite and calcium phosphates to counteract the undesired precipitation in the pipelines and centrifuges (incrustation).

●3. The studies showed that the incrustation problem may only be solved by applying a combination of several measures. The considerations concentrate on a **combination of chemical and plant engineering measures**.

●4. Laboratory studies were performed dealing with the **induced precipitation of struvite and calcium phosphates** by changes of the pH value either by degassing the digested sludge or by lime addition.

●5. Moreover, BWB have prepared a study dealing with **degassing of digested sludge** by applying engineering measures.

Finally, the studies resulted in a concept to avoid incrustations in the wwtp Waßmannsdorf.
The following measures were undertaken in the meantime:

●1. All pipes from the digestion tank are **kept under pressure** to avoid a degassing, which would immediately cause a precipitation together with incrustations.

●2. **Dosage of $MgCl_2$** into the sludge pipe from the digestion tank to the interim sludge storage tank.

●3. This interim sludge storage tank runs also as a degassing reactor. Air is fed and subsequently CO_2 is degassing. The result is an increasing of the pH. A trigger **struvite and calcium phosphate precipitation** occurs . This precipitate is at the moment deposited together with the sludge. It seems of interest on the other hand to reuse the phosphate by separating this precipitation product from the sludge. But, for this more basic research work is necessary

●4. Furthermore small amounts of special chemicals (**complexing agents**) are dosed on some specific places, e.g. the pipe of the centrate to avoid incrustations.

5 Conclusions

In order to fulfill the main goal - i.e. to avoid the formation of incrustations - the general idea is to enhance the chemical engineering techniques by a distinct and efficient phosphorus recovery. By this, also the quality of the secondary effluent of the wwtp Waßmannsdorf is improved and the sludge treatment process will be optimized.

Slough sewage treatment works,

UK potential for struvite recovery

Summary of an MSc project by Jasmin Jaffer, now at Thames Water.

Slough sewage treatment works (STW) UK, treats around 250,000 pe of which 114,000 pe is from industrial effluent. There are two treatment streams, one of which is conventional activated sludge and the other a Bardenpho biological nutrient removal (BNR) plant. The works has a history of significant struvite (magnesium ammonium phosphate) deposit problems and the aim of the reported work was to establish the struvite precipitation potential at different places in the works and to assess the feasibility of using controlled struvite precipitation to resolve operational problems. Recovered struvite could then be marketed.

Eight months after commissioning the BNR extension at Slough STW, the pipes from the sludge digesters to the digested sludge holding tank became blocked with an accumulation of small struvite crystals held in a sludge matrix. Four months later, the diameter of the pipeline between the holding tank and the centrifuge had become so restricted that sludge transfer was no longer possible (reduced from 100 to 50 mm).

Mass balance

The precipitation of struvite is related to concentrations of its three molecular components (magnesium, ammonium and phosphate). **A mass balance of total nitrogen, total phosphorus and magnesium was established** showing the daily flows of each element into the STW and at various sites in the treatment and sludge streams.
The mass balance showed that **26% of the works influent phosphorus originated from return liquors phosphates released during sludge processing**. This is consistent with figures given elsewhere by other authors (20% Pitman et al

1991, 20-50% Von Münch and Barr unpublished, 40% Jardin and Popel 1994). Magnesium in the return liquors made up20% of the works influent The struvite precipitation potential (SPP) was calculated for each of the measured sites in the works process, using the South African Water Research Commission model "Struvite v3.1" (Lowenthal et al., 1994). The SPP was calculated on the basis of ionic concentrations, pH and the solubility product of struvite.

Struvite precipitation potential

Three streams at Slough STW appeared as having a positive SPP ; the digested sludge (198 mg/l), the centrifuge liquor (140 mg/l) and the centrifuge cake (420 mg/l). Each of these had a high concentration of phosphate.

The thickened secondary activated sludge had the highest magnesium concentration of any stream at the works, but with a pH below 7 a negative SPP. However the SPP would become positive (51mg/l) if the pH increased to 7.5.

The struvite model indicated that the pH of the digested sludge would have to be reduced from 7.3 to 6.2 to avoid having a positive SPP.

Bench recovery experiments

Controlled precipitation of struvite from the works centrifuge liquor was considered as a possible means of avoiding struvite deposit problems and reducing the concentration of phosphorus returned to the works influent.

Struvite precipitation from this liquor was tested using a bench scale pilot plant. The pilot plant consisted of a 3.5 litre vessel lined with a porous pot. The reactor contents were mixed using aeration, at a rate of 220ml/min. The pH of the centrifuge liquors was raised from 7.6 to 9.0, using sodium hydroxide, prior to being pumped into the reactor. The concentration of magnesium in the centrate liquors was insufficient to remove the majority of the phosphorus present, as struvite. The reactor was therefore dosed with magnesium, in the form of magnesium chloride, to maximise the production of struvite. The flow of magnesium chloride was 63% of the total flow to the reactor. Crystals were produced within 24 hours and X-ray diffraction confirmed they were struvite.

A molar ratio of 1.05:1 magnesium:phosphorus enabled 95% of the total phosphorus to be removed from the centrifuge liquor as struvite. Fujimoto et al (1991) also found a ratio of 1.05:1 whereas Siegrist et al (1992) found 1.3:1.
It should be noted that in the experiments, the pH was raised to 9.0 in the storage containers before entering the reactor vessel where magnesium was dosed. This caused the calcium:magnesium ratio to fall from 1.2:1 to 0.04:1. Thus the reactor contained a low soluble calcium concentration and a consequent lack of competing reactions, resulting in a relatively low magnesium requirement for struvite precipitation.. At full-scale a ratio of 1.3:1 magnesium : phosphorus would be more suitable.The storage reactor and the batch operation also enabled suspended solids to be settled out before the liquid entered the reactor, which again may have facilitated reactor operation.

Economics

The chemical consumption costs for operating a pilot plant with sufficient capacity to treat an average centrifuge liquor flow of 393 m^3/day were estimated. Magnesium chloride was costed at UK£90/tonne and NaOH at UK£59/tonne. The total annual chemical costs were between UK£ 51,500 - 52,000, depending on the magnesium dose.

97% of the chemical operating costs came from the use of NaOH to adjust the pH from 7.5 to 9.0. This is because the waste water has a considerable buffering capacity which needs to be overcome to achieve the higher pH.
On the basis of the bench test results, an estimated 42-99 tonnes/year of struvite could be recovered, estimated to have a market value of around UK£8,500-20,000/year (assuming a retail value of UK£200/tonne).

The authors conclude that if a side-stream treatment was operated in the above manner, the potential revenue from struvite sales would cover only one third of the chemical operating costs. However this is not the only factor to be taken into account. Operational costs such as increased pumping costs, pipe replacements, downtime, etc., related to struvite deposit problems have to be offset against production costs. Also by adapting the above methodology, chemical costs could be significantly reduced.

These results also underline the importance of the operating pH; **if struvite recovery can be achieved without chemical pH adjustment or at lower pH, then the process would become economic** (other work, such as Battistoni et al see SCOPE Newsletter 39, 35 and Matsumiya et al see SCOPE Newsletter 39, suggests that it is possible to achieve this by aeration).

Summary of an MSc project "Assessing the Potential of Full-scale Phosphorus Recovery by Struvite Precipitation", Yasmin Jaffer, Cranfield University, UK, 1999

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Phosphate precipitation from waste waters : recent scientific and technical developments

In many circumstances, including in a number of municipal waste water streams but also from manures, one of the most attractive pathways for recovering phosphates in an industrial recyclable form is the precipitation of phosphates from liquids containing dissolved phosphates. It can be hoped in this way, by developing appropriate operating conditions, to obtain relatively pure phosphates in a physical form adapted to transport, processing and recycling (dry pellets) either back into industry or as a fertiliser. A number of waste treatment processes, in particular biological nutrient removal and sludge digestion offer supernatant streams with relatively high concentrations of dissolved phosphates which particularly lend themselves to such precipitation processes.

Precipitation of phosphates as calcium phosphates or as struvites (magnesium ammonium phosphates) currently appears as the most likely route to both achieving effective precipitation in accessible operating conditions in waste water streams whilst also producing a product with an industrial recycling value. Appropriately controlled precipitation of phosphates from liquid streams, even in waste waters, is likely to be able to produce materials of relatively high purity and consistent physical characteristics, appropriate for transport and industrial recycling.

Calcium phosphate is essentially the same material as the mined phosphate rock used as feedstock by the phosphate and fertiliser industries worldwide, so it can readily be accepted into industrial processes for recycling, subject to obtaining an appropriate material quality (reasonably high phosphate content, limited levels of certain heavy metal contaminants, low water and organics content, physical and handling properties). Struvite, on the other hand, cannot be accepted by either existing or realistically modified phosphate industry processes, but is claimed by many authors to be a marketable fertiliser. There is, to date, insufficient published data concerning the agronomic value of struvite, but it is apparent that in the few cases where it is or has been produced on an industrial scale nearby fertiliser factories have purchased it (currently for around 1,000 Euros/tonne in Japan, for example).

Recent scientific and technical developments :

Calcium phosphate precipitation

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1. Introduction

The past decade has seen a number of engineering solutions aiming to address phosphorus recovery from wastewaters by precipitation of calcium phosphates in a recyclable form. Despite a considerable volume of work, including laboratory, pilot and full-scale trials, phosphorus recycling from wastewaters has not, yet, been widely adopted. This is mainly due to a number of scientific and technical problems still requiring resolution, before such an option becomes commercially viable. Some key scientific problems remaining include difficulties in controlling precipitation, due to poor understanding of the role of interfering ions (such as carbonate and organic ligands) and pH, extensive formation of fines and problems with the quality/use of the recovered phosphate. Technical areas that require further improvement include reactor design, particularly in terms of efficiency and practicality, reactor optimum positioning in wastewater works and a need to assess how phosphorus recycling will fit within normal wastewater works operations.
The present article introduces the chemical principles of calcium phosphate precipitation, reviews recent work carried out on scientific and technical developments and considers the research challenges still remaining. The article does not cover recent work on the precipitation of struvite, which is discussed in an article by Parsons (this issue).

2. Chemical principles of calcium phosphate precipitation

2.1. Calcium phosphate solubility

Solubility represents a measure of the concentration in solution necessary for a phase to precipitate. Phosphate precipitation occurs when saturation of its component ions is reached. However, **in environments such as wastewater, where ion association is significant (due to high ionic strength), the free ion concentrations** contributing to saturation will be lower than the total ion concentration, and thus significant supersaturation is necessary for precipitation to occur. The degree of supersaturation required can be predicted theoretically, or assessed experimentally.

In solutions containing calcium and phosphate, a number of calcium phosphate phases may form (Table 1), depending on the pH and solution composition. As a result calcium phosphate saturation will depend on the phase closest to saturation at the prevailing solution conditions. However, the precipitated phase will most likely eventually transform into the thermodynamically more stable hydroxylapatite (HAP) (e.g. Kibalczyc, 1989). For that reason, the majority of published experimental solubility studies regarding calcium phosphates focus on HAP, although basic equilibrium solubility data are available in the literature for most calcium phosphates (see Table 1).

The mechanism of HAP dissolution is still under consideration, but it is most likely a mineral surface controlled property (Christoffersen et al., 1978; Valsami-Jones et al., 1998). Little is currently known about the levels of supersaturation necessary to overcome the effect of organic and inorganic inhibitors.

2.2. Kinetics of calcium phosphate precipitation

Precipitation kinetics provide a measure of the rate of formation of new phases, and thus can assist reac-tor design by defining optimum residence time and precipitation conditions. Two steps control formation by precipitation from solution: nucleation and growth.

Nucleation : in a supersaturated solution, for nucleation to occur, the newly formed nuclei have to exceed a critical size. Precipitation can take place in several different ways: **spontaneous growth of individual crystallites in solution, a process known as homogeneous nucleation, or aggregation of crystallites on existing surfaces (e.g. seed crystals), known as heterogeneous nucleation**. Heterogeneous nucleation is less energetically demanding, and a better analogue for wastewater environments where a multitude of surfaces exist (suspended particles, pipe surfaces). Epitaxial growth, where the newly-formed crystals nucleate on a seed phase of different structure requires a suitable crystal lattice match between the two phases (Nan-collas, 1984), particularly if the degree of supersaturation is low.

Crystal growth : again takes place in a number of steps. **Transport from the bulk solution to the nuclei surface, followed by adsorption to the surface** and a number of steps through which the location of the newly adsorbed species changes on the surface to gain an energetically favourable position.

It is well established that kinetic factors may be more important in determining the nature, and hence the characteristics, of the solid deposits formed during the precipitation process than equilibrium considerations. In other words, what is thermodynamically the most stable phase, may not precipitate, because its precipitation kinetics are slow; an alternative less stable phase, able to nucleate faster, may precipitate instead, or precipitation may not happen at all, or not until an appropriate "trigger" (e.g. seeding) becomes available. Complications may also arise from the formation of mixed solid phases resulting from the overgrowth of one crystalline phase onto another.

Current understanding of calcium phosphate kinetics suggests that a precursor phase will precipitate from supersaturated solutions, but this will eventually recrystallise to form HAP. The precursor phase may be

Brushite or dicalcium phosphate dihydrate (DCPD)	$CaHPO_4*2H_2O$	MR = 1.0	SP =2.49 x 10^{-7}
Monetite (DCPA)	$CaHPO_4$ (Anhydrous DCPD)	MR = 1.0	SP = 1.26 x 10^{-7}
Octacalcium phosphate (OCP)	$Ca_4H(PO_4)_3*2.5H_2O$	MR = 1.33	SP = 1.25 x 10^{-47}
Amorphous calcium phosphate (ACP)	$Ca_3(PO_4)_2$	MR = 1.5	SP = 1.20 x 10^{-29}
Hydroxylapatite (HAP)	$Ca_5(PO_4)_3O$	MR= 1.67	SP = 4.7 x 10^{-59}
Tricalcium Phosphate (TCP)	$Ca_3(PO_4)_2$	MR= undefined	SP = variable, more soluble than crystalline phosphates

Table 1: Calcium phosphates, their molar ratios and solubilities

MR= molar ratio of calcium : phosphate.
SP = Thermodynamic solubility product (as listed in Nancollas, 1984); units are omitted for simplicity.

dicalcium phosphate dihydrate (DCPD), octacalcium phosphate (OCP), tricalcium phosphate (TCP) or an amorphous calcium phosphate (ACP) depending on the conditions (Kibalczyc, 1989; Meyer, 1983; Nancollas, 1984).

A number of kinetic studies have attempted to establish the specific conditions and order of formation of the precursor phases. Some of these studies showed that optimum experimental environment is achieved using a constant composition method (e.g. Heughebaert et al., 1990). Heterogeneous and epitaxial growth of phosphates have been studied, but the results from different studies are variable. For example, by using the constant composition method Zawacki et al. (1990) observed a nucleation of calcium deficient HAP on HAP seeds, while Barone et al. (1976), using a pH-stating method, ob-served a precipitation of DCPD onto the HAP seeding crystals. Frèche & Heughebaert. (1989) and Heughebaert et al. (1986) observed the precipitation of OCP and DCPD onto seed crystals of OCP and DCPD, but not hydroxylapatite.

It is often suggested that at pH>7 and high supersaturation, the precursor phase is an amorphous calcium phosphate (ACP). The ACP may dissolve again and forms HAP nuclei (Boskey & Posner, 1973). A three stage formation of hydroxylapatite starting with the formation of ACP, followed by OCP has also been suggested (Meyer, 1983). Kibalczyc (1989), using a pH drift-method, observed a transformation of one type of ACP into another ACP, which then transformed into HAP, at a pH-range of 7.0-9.0. He concluded that under such experimental conditions OCP was not a possible precursor phase to HAP. Precipitation of non-stoichiometric apatites has also been observed (Heugebaert et al., 1990, Zawacki et al. 1990).

Ion inhibition : **a number of ions have been shown to act as inhibitors to precipitating phases, by forming a surface complex on the newly forming surfaces, and blocking further precipitation.** The influence of inhibitor ions, such as carbonate and magnesium, to calcium phosphate precipitation has been discussed by many authors (e.g. Abbona & Franchini-Angela, 1990). Co-precipitation of magnesium with the calcium phosphates for example may induce firstly the formation of ACP, which will transform into the more stable HAP. It is possible for HAP to incorporate a small percentage of magnesium into its structure, but this causes structural changes and has an inhibitory effect to further HAP formation (Kibalczyc et al., 1990). Salimi et al. (1985) studied the crystal growth of DCPD and OCP in the presence of magnesium and carbonate using constant composition and pH stating methods.

They found that the crystal growth of DCPD was not affected while the OCP crystal growth rate decreased con-siderably. The presence of CO_2 may also affect precipitation of HAP, either by blocking phosphate nucleation sites, or by inducing calcium carbonate precipitation instead (e.g. House, 1999). Other dissolved cations in solution may also block calcium phosphate formation, or even cause HAP dissolution. Examples include the dissolution of HAP to form the less soluble fluorapatite in the presence of fluoride ions (Brown, 1981) or to form metal phosphates in the presence of lead or cadmium (Val-sami-Jones et al., 1998). The influence of temperature and pH on HAP precipitation was investigated by Zoltek (1974), who demonstrated that supersaturation may be achieved by a simple increase in pH.

Organic ligands : the effect of organic ligands has been the subject of a few recent studies (Frèche et al. 1992; Grossl & Innskeep, 1992). Seed crystals were used in experiments, which showed a decrease in calcium phosphate growth due to adsorption of the acids onto the calcium phosphate seed crystals. **Natural amino acids with hydrophobic non-polar groups were found to inhibit HAP growth**; this was interpreted as being the result of the amino acids blocking active growth sites and relates to the adsorption affinity of each amino acid to the crystal surface (Koutsopoulos & Dalas, 2000).

On the other hand, enhanced nucleation of calcium phosphate crystals was observed on polyelectrolyte multi-layers compared to silica; the type of precipitated phosphate also varied, HAP and OCP being the phases precipitating on the polyelectrolyte and DCPD on silica (Ngankam et al., 2000).
This discussion suggests that a substantial body of work exists on calcium phosphate precipitation kinetics. However this work cannot be directly applied to wastewater systems. This is because the majority of the above studies were carried out in low ionic strength solutions, and have not been tested in wastewater analogues, where the presence of organic and other species may inhibit or alter the stability of calcium phosphates. If we were to apply the above studies to wastewater conditions, we would, almost certainly, overestimate the calcium phosphate potential to precipitate. Furthermore, a large number of early studies relied on chemical composition to identify the forming calcium phosphate phase. It is now known that HAP often precipitates in a non-stoichiometric form (e.g. Heugebaert et al., 1990, Zawacki et al. 1990), and therefore some previous work requires further validation.

2.3. Reactor design

Water companies and researchers in a number of countries have shown interest in phosphorus recovery from wastewater for nearly thirty years (Grace/Dearborn, 1969; Salutsky et al., 1992). Phosphorus recovery for *recycling* however has not so far developed beyond sporadic isolated pilot experiments. Examples include waste water treatment plants in Australia (Angel, 1999), South Africa (Momberg & Oellermann, 1992), Germany (Schultze-Rettmer, 1991), Japan (Joko, 1984; Yamane et al., 1998); animal manure treatment in Australia (Webb et al., 1995), Holland (Schuiling & Andrade, 1999), and industrial waste streams in Germany (Donnert & Salecker, 1999), Korea (Shin & Lee, 1997) and Turkey (Tünay et al.,1997), Italy (Pavan et al., 2000). In most of these cases struvite is the precipitating phosphate. Other research carried out into struvite precipitation, with the objective of removing ammonia, has taken place (Liberti et al., 1986) and there is an operating fluidised bed struvite pellet reactor at Shimane Prefecture, Japan (Katsuura & Ueno, 1998). Phosphates recovered from some full-scale plants are currently recycled (see also below and article by Schipper, page 25).

Most current working systems are variations of the fluidised bed principle and use seeding material, most often sand grains. The influent enters the reactor from below keeping the bed of sand grains fluidised. Current working experience shows that for crystallisation to take place a high state of supersaturation is necessary and this has to be achieved by an extreme increase in pH (via CO_2 stripping, addition of an alkaline solution or, usually, both) and the addition of other ions (calcium or magnesium). Different precipitates may form, depending on the initial solution composition or the selection of additives. There is only one study investigating the efficiency of alternative seeding materials; this study found that bone char and phosphorus rock gave the best results (Kobori & Kyosai, unpublished report); the authors propose that this is due to the high surface area.

Common operational problems : the majority of tested processes for calcium phosphate precipitation require chemically induced high pH, and CO_2 stripping prior to entering the precipitation reactor. Problems with fines and non-recyclable quality precipitates have been reported. Only sand seeds have been tested in full-scale operations to date and the process needs further development if a recyclable product is to be produced. The process has been tested in a limited number of works, mostly at pilot scale. Further testing of alternative reactor configurations and in new wastewater works would be the way forward.

3. Scientific developments in progress

Germany

Forschungszentrum Karlsruhe (Germany) : A project recently completed by Donnert and Chabanis investigated the effect of calcite seeds on phosphate precipitation and kinetics. The study compared calcite seeds with apatite and sand. It was shown that the surface area of the seeds, rather than their composition was the main controlling factor in phosphorus removal from solution. There was no evidence for calcite inducing a better removal of phosphate, despite such indications from previous work. The presence of dissolved carbonate in solution decreased the efficiency of phosphorus removal with or without seeding. Precipitation kinetics were faster at higher supersaturation in the range 10-80 mg/L P. When calcium phosphate was used as a seed for the first time there was a demand for additional calcium during precipitation; this effect disappeared in subsequent uses of the same material. This may indicate precipitation of a precursor phase, with higher calcium content; this phase perhaps "conditions" the surface and facilitates subsequent re-use. Identification of this phase in future work would be very important.

Institut für Siedlungswasserwirtschaft Universität Fridericiana, Karlsruhe (Germany) : Song, Hahn and Hoffmann have investigated the effect of Ca/P ratio and carbonate concentration on the precipitation of calcium phosphates. The work to date suggests that the precipitation rate and efficiency of calcium phosphate is enhanced by either an increase in pH or Ca/P ratio (above stoichiometric) and reduced by the presence of carbonate. Ageing of the precipitate for up to 120 hours or precipitation at high pH does not improve crystallinity.

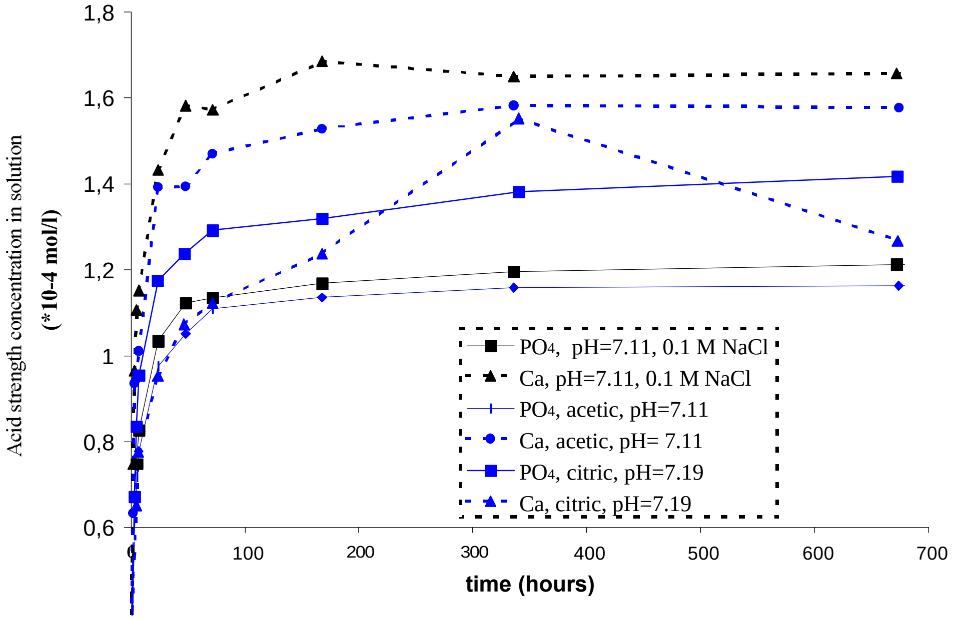

Figure 1: Comparative release of calcium and phosphate in the presence of 10-4M organic acids

United Kingdom

Centre of Ecology and Hydrology (Dorset, UK), Alan House and Lorraine Plant, are working on precipitation reactions involving calcite and calcium phosphate. The aim of their project is to develop a better understanding of the kinetics of precipitation of calcium phosphate salts in conditions found in treated sewage effluent. Their study initially examined the co-precipitation of phosphate with calcium carbonate (in the form of calcite) at relatively low concentrations of soluble reactive phosphorus (0 to 0.6 mg l^{-1}). Their results to date indicate that dissolved inorganic phosphate co-precipitates at a rate consistent with the adsorption of hydrogen phosphate and phosphate ions to calcite and loss of calcium from solution as calcite growth occurred. The faster that calcite grew the greater the loss of phosphate from solution, in agreement with a previously developed co-precipitation model (House, 1999).

The research was then extended to examine the effects of higher concentrations of phosphate in solutions otherwise similar to those described above. Phosphate concentrations of 3, 7.5 and 15 mg l^{-1} were used with calcite seed addition to induce crystal growth. These results indicated the slow growth of a calcium phosphate phase prior to seed addition, and the absence of calcite growth during the reaction. Further work is now in progress to ascertain whether calcium phosphate phases will nucleate on calcite seed material. The initial results indicate the possibility of homogeneous (unseeded) nucleation of a calcium phosphate phase in the presence of calcite and further work is now in progress to determine the conditions for growth of calcium phosphate.

The precipitated calcium phosphates will be identified in future larger scale preparations using pH stat/chemstat reactors with reaction pathways estimated through chemical speciation programs. The precipitation conditions will be as found in the "free-drift" laboratory experiments described above. The phases will be identified by X-ray diffraction and analysis of the solids by digestion. Particles will be thoroughly characterised, e.g. particle size distribution and wet analysis. The final stage of the project will test the results using sewage effluents in the reaction conditions determined from the laboratory experiments and chemical speciation program.

Natural History Museum (London, UK) : Éva Valsami-Jones and Jacqueline van der Houwen are working on the effects of organic acids on dissolution and precipitation of calcium phosphates. More specifically, they are investigating the effect of the number of acid functional groups and of acid concentration on the release of calcium and phosphate from the hydroxylapatite.

Acetic, oxalic and citric acids, with one, two and three functional groups respectively are studied. To investigate the influence of the concentration of organic acids, the experiments were carried out in the concentration range of 10^{-4} to 10^{-2} M, and at an initial pH of 6.7. As expected dissolution was found to increase as a function of organic acid concentration and this was shown to be independent of pH. When considering the variation between organic acids, the results indicate that there was a diverse effect on the release of calcium compared to phosphate during hydroxylapatite dissolution. It was found that the equilibrium release of calcium decreases as the number of functional groups in the organic acid increases, whereas the release of phosphorus increases (see Figure 1, page 11).

The effect is most apparent when considering the calcium : phosphate ratio in solution, which varies from 0.71 (3 functional groups) to 1.43 (no organic acid in solution); the ratio in the synthetic hydroxylapatite used in the experiments is 1.55. The result is interpreted as the effect of the organic acid functional groups inhibiting the release of calcium from apatite surfaces. The work suggests that a higher than stoichiometric phosphate : calcium ratio is likely to be needed for apatite to precipitate in organic-rich systems such as wastewaters. Future work will apply these findings to precipitation (homogeneous and heterogeneous) experiments.

Greece

FORTH-ICETH (Patras, Greece) : Professor Koutsoukos and his co-workers investigate the heterogeneous formation of calcium phosphates from aqueous supersaturated solutions. The studies include investigations on HAP seed crystals and on polymeric or ceramic substrates. The key finding in the case of polymer substrates is that the presence of carboxyl or phosphonic groups promotes the nucleation of HAP. The initiation of the formation of mineral phase on the polymer is ascribed to the formation of surface ion-pairs between the dissociated groups and the calcium ions.

Increase of the phosphorus containing dissociable groups increased the calcium phosphate promoting capability (Dalas et al., 1991). The effect of presence of carbonate ions on the formation of calcium phosphates has recently been investigated (Kapolos & Koutsoukos, 1999). The results showed a differentiation depending on the solution supersaturation and the levels of carbonate concentrations. At relatively high supersaturations carbonate ions have an accelerating effect, while at lower supersaturations carbonate ions inhibit the seeded crystal growth of HAP.

In the latter case, carbonate ions are incorporated into the apatite lattice to extents up to ca. 5% replacing phosphate groups. Small molecules like the aminoacids bearing both amino and other ionizable groups retard the formation of HAP in supersaturated solutions by adsorption dominated by electrostatic interactions. Analysis of the adsorption isotherms of Phospho-L-Serine onto HAP showed that they are located at the Inner Helm-holtz plane while the adsorption, caused the shift of the HAP potential to more negative values. (Spanos and Koutsoukos, 2000).

Most important from the phosphorus recovery point of view is the finding that sand grains promote the formation of calcium phosphates (Paraskeva et al., 2000). Depending

on the solution supersaturation it is possible to form DCPD, OCP or HAP on the sand grains. HAP formation in the sand bed used is achieved through in-situ precipitation of calcium phosphate within the granular stratum (see Figure 2, below), achieved by alternating injection, mixing and reaction between two aqueous solutions of calcium chloride and potassium phosphate. Calcium phosphate precipitates and grows on the grain surfaces.

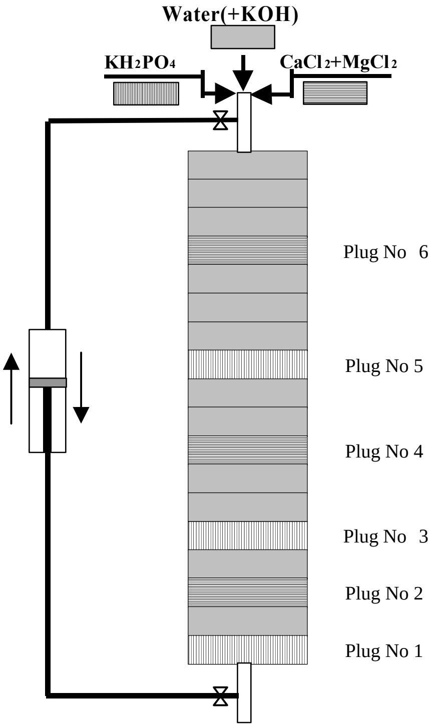

Figure 2: Placement of the chemical solutions and in-situ mixing in experimental sand bed.

4. Technical developments in progress

Holland

Work by Seckler and co-workers (Seckler, 1994; Seckler et al., 1990, 1996) at *Delft University of Technology* introduced fluidised bed technology for the precipitation of calcium phosphates from wastewaters. The laboratory work indicated that the technology of retaining seeds for crystallisation in suspension was particularly versatile, although problems with fines were recognised. Removal efficiency of 80% at P-concentrations of 1.6×10^{-3} kmol/m^3 was achieved by optimising the fluidization conditions.

In parallel *DHV developed the Crystalactor® technology*, also following the fluidised bed reactor principle. The first DHV reactor was built in Westerbork, the Netherlands, in 1988. Further Crystallactors® operated at Chelmsford, UK (Essex and Suffolk Water [Compagnie Générale des Eaux]/DHV, 1997-1998, pilot scale), and at Heemstede and the AVEBE factory, in the Netherlands. However, direct phosphate removal from wastewater using this technology is no longer economic in the Netherlands (Giesen, 1999), and there is currently only one operational Crystalactor® at Geestmerambacht sewage works. The effluent to this reactor comes from a side stream of biological phosphorus removal. The recovery of phosphate takes place as calcium phosphate, on silica sand seeds. The product from Geestmerambacht is currently recycled by THERMPHOS (see article by Schipper page 25).

The Crystalactor â technology achieved significant progress towards phosphorus recycling, by solving problems such as recovery and product quality. However, the need for carbon dioxide stripping and the high operational pH to achieve precipitation meant that there are some technological disadvantages that still need to be overcome.

Japan

At *Kyushu Kyoritsu University*, K. Moriyama has tested the precipitation of calcium phosphate on a synthetic calcium silicate hydrate (tobermorite) seed in experiments using secondary effluents and side streams of different sewage works. A pilot reactor was tested both with a fixed bed and a 25% expanded bed, using an upstream circulator, at a flow rate of 50 ml/hour (equivalent to a residence time of approximately one hour). Calcium was introduced via the addition of calcium chlorite or sea-water (seawater contains around 400 mg/l calcium). Runs of up to 400 days were carried out. The efficiency of phosphate removal varied from 80% (pH 9) to 70% (pH 8.5).

Further trials, using sludge treatment side stream containing 10-50 mg/l phosphate at a flow rate of 250 ml/hour were conducted for up to four months. Addition of calcium chloride was not found to improve performance. Phosphate removal rates of 80% at pH of 8 were achieved. The precipitation product, poorly crystallised calcium phosphate, was found to be appropriate for fertiliser use, and to contain low amounts of inorganic contaminants. The precipitate was layered, consisting of a calcium phosphate of unknown structure on the surface of the seed, followed by poorly crystallised hydroxylapatite and then a microcrystalline hydroxylapatite. Finally, this research showed that the crystal form of the seed did not influence calcium phosphate precipitation efficiency.

A new pilot plant in Tokyo is starting operations in October 2000, investigating crystallisation of calcium phosphate from side stream. In the preliminary experiment that used a reactor of 250ml volume, SV1/hr, pH 8.0, 80-90% of PO_4-P 30mg/l in influent was recovered. The reactor volume of the pilot plant will be 10 litre. Other usage of the artificial calcium silicate seed material is being considered. More specifically, a direct application of the seeds in a pond, to restrain the growth of algae by re-moving phosphate is developed.

Australia

Following successful laboratory trials, the *Sydney Water Board and the Australian Department of Industry financed* *building of a pilot reactor at Warriewood in 1994* (Angel, 1999). The methodology used was that of a fluidised bed, where an amorphous calcium phosphate was encouraged to precipitate around MgO particles, which thus acted as seeds and, via their dissolution, as the pH control. However the pilot trials failed to reproduce the laboratory results: despite high P-removal (>95%) the phosphate levels in the product were low, and this had an impact on reagent utilisation and the over-all economics of the process. The problems of scaling up from laboratory to pilot had mostly to do with functional differences in equipment at the two different scales, unpredictability of effluent chemistry and rigidity of the pilot construction (Angel, op. cit.). This development has since been abandoned.

Germany

Laboratory experiments and a full scale unit (treating 160 m^3 per hour) at a *Mercedes motorcar fac-tory in Gaggenau* using stirred reactor have been performed recently (Donnert and Salecker, 1999). The main novelty of the trials was the use of calcite as a seed, which the investigators believed en-hanced calcium phosphate nucleation (but see above). The full-scale operations continued for at least a year. The outflow effluent had consistently concentrations of P < 2 mg/l. The precipitated sludge was found to be amorphous, but to crystallise HAP, struvite and whitlockite, after heating at 900°C.

5. Future research needs

The above discussion shows that a lot of progress has already been made; however, further scien-tific and technical work is necessary to achieve low-cost universally accepted technology. This sec-tion aims to point towards the less well-studied or understood issues relevant to phosphate recovery for recycling from wastewater.

Firstly, the precise influence of all ions present in wastewater on phosphate nucleation and/or growth requires full investigation. This is to develop a better ability to predict precipitation in sewage works regardless of geographical location or technology used. Also, to better our ability to precipitate recyclable phosphates. The competitive formation of calcium phosphates and struvites has never been considered: it may be that the formation of one or the other is triggered selectively, although how sensitive this trigger to solution composition may be is as yet unknown.

Regarding precipitation inhibitors, it is necessary to consider the effect of species such as magnesium-ammonium (on calcium phosphates), calcium (on struvite), and carbonate and organic ligands, with a view to assess their effect on nucleation onset and kinetics. There is evidence that magnesium and carbonate inhibits crystallisation of calcium phosphate, but this has not been tested in wastewater type solutions. The combined presence of ammonia and magnesium may favour formation of struvite rather than calcium phosphates. Organic species commonly found in wastewater (small molecules such as acetic, oxalic and citric, or large humic species) might influence phosphate nucleation. Finally the partitioning of trace metals from solution into the phosphate phases needs to be considered.

Further studies on nucleation would also be important. It is now understood that *initial* phosphate pre-cipitation can be enhanced if an appropriate substrate is present, which will act as a template for nuclea-tion. After formation of the first monolayer on the seed, further influence by the seed will depend on whether it becomes completely armoured by the precipitate, and also by compatibility between the seed and the precipitate. Testing a range of phosphate substrates (phosphate rock, bone char, recycled phosphate) should be carried out. Phosphate seeds would have the added advantage of producing a more phosphorus-rich and hence more recyclable product. Other variables such as particle size and volume of seeds would need to be considered.

Better characterisation of scale deposits from sewage works from around the world would be beneficial, as it is often the case that any deposit is automatically considered to be struvite; however other crystalline or amorphous phases may be common, but remain uncharacterised. Such studies will enhance our ability to predict optimum precipitation conditions for phosphates, particularly if coupled with study of key analytes (phosphate, calcium, ammonia, magnesium, pH) in associated wastewaters.

In terms of technical work, perhaps the most important issue is reactor design. Most of the tested technology involves fluidised bed reactors, but it is unclear whether this is the most efficient way of removal/recycling of phosphates, or simply a historic influence. Finally, a lot more work needs to be done to address where and how phosphorus recycling will fit within wastewater works, and how it can complement and perhaps even improve (in places where scale formation is a problem) operations.

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Recent scientific and technical developments :

Struvite precipitation

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1. Introduction

Struvite in wastewater treatment plants was identified as early as 1939. Whilst studying digestion Rawn (1939) found crystalline material identified as struvite, in the digested sludge supernatant lines. Problems with struvite formation date back to the 1960s when it was noticed at the Hyperion treatment plant, Los Angeles (Borgerding, 1972). Operators at the plant noticed crystalline deposits on the underside of post digestion screens. The digested sludge stream was diluted and it was thought the problem was solved, until five years later when the normal gravity flow of digested sludge had decreased to such a stage that pumping was required. The pipeline had diminished in size from twelve inches in diameter to six (Borgerding, 1972). Similar instances of pipe blockages have been reported elsewhere (Pitman et al., 1991, Mohajit et al., 1989, Webb and Ho, 1992, Mamais et al., 1994).

The blockage of pipes leads to an increase in pumping costs ; as the diameter of the pipe is reduced, more energy is required to move the sludge. Also the time taken for the sludge to be moved from one place to another increases. The pipelines can be cleared by flushing through with 10% sulphuric acid and leaving to soak for at least 24 hours (Williams, 1999). Sometimes the extent of fouling is so bad that there is no option but to replace the pipework. At the Sacramento Regional Wastewater Treatment Plant, California, 5.6 km of pipework had to be replaced due to struvite formation (Ohlinger et al., 1998). Replacing pipework is not only an expensive procedure, it can also be extremely disruptive -especially if most of the pipework is located below ground. It is not only pipes that are affected by struvite deposits; pumps, centrifuges and aerators are also prone to contamination (Mohajit et al.,1989).

The impact of struvite formation on pump performance (page 16) has been shown by Bernisch (2000). The thin line (B) represents a glass-lined ductile iron pipe (6", C=100), conveying 570 gpm of 3 percent digested sludge at 6.5 ft/s. The thick line (A) represents the same pipeline but with a 0.5 inch struvite deposit. The deposits result directly in a 30 percent cross-section reduction. The struvite formation leads to the pump operating outside of its normal range such that the pump life can be significantly reduced.

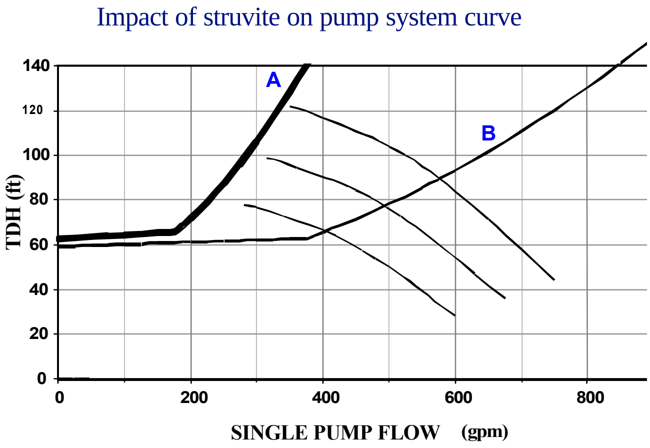


Figure 1. Effect of struvite formation on pump efficiency (Bernisch et al., 2000)

Most plants which have a struvite problem, incorporate a time consuming maintenance programme into the normal operation of the plant. For example at the Ponggol Pigwaste plant, Singapore, floating aerators are regularly cleaned resulting in the loss of 8-10 man hours each time (Mohajit et al., 1989). At Slough STW in the UK, struvite deposits are manually chipped from the centrifugal pump casing on a regular basis, resulting in an estimated time loss of 10 man hours. The manual process of removing struvite is laborious and time consuming, but at present seems to be the most effective method (Williams, 1999).

Whilst struvite can be a problem in wastewater treatment plants it has potential use as a fertiliser. Natural sources of struvite include guano deposits and cow manure and it has been shown to be a highly effective source of nitrogen, magnesium and phosphorus for plants foliage and soil applications. Struvite can be recovered from wastewater and sludges etc. if the chemical constituents of the sludge are such that the K_{sp} value is exceeded. A number of processes have been evaluated at bench, pilot and full using fluidised bed reactors and pellet reactors In all of these processes the precipitation is achieved by either (i) pH changes or (ii) concentration changes

Whilst this review focuses on wastewater treatment struvite has appeared in scientific journals concerned with the veterinary industry (Osbourne et al., 1999; Ross et al., 1999; Markwell et al., 1998), the medical profession (Dewan et al., 1997), the food and beverage industry (Austermann et al., 1997) and industrial wastewaters produced by the fertiliser, leather and chemical manufacturing in-dustries (Tunay et al., 1997). Yet common trends can be drawn from the literature published. The chemical composition and the pH of these solutions determine the potential for struvite precipitation (Borgerding 1972) and it is these factors which are common to the industries mentioned.

2.Chemical principles of Struvite

2.1 Struvite solubility

Struvite is a white crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations ($MgNH_4PO_4.6H_2O$). Struvite forms according to the reaction shown below.

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4(H_2O)_6$$

Struvite has a distinctive orthorhombic crystal structure, Figure 2, and can be identified via X-ray diffraction (XRD) by matching the intensity and position of the peaks produced to a database for the crystal structure. The crystal habit and polarity are discussed in detail elsewhere (Abbona et al., 1984). Other forms of struvite can exist including K^+ and Ni^{2+} although they are not covered in this review.

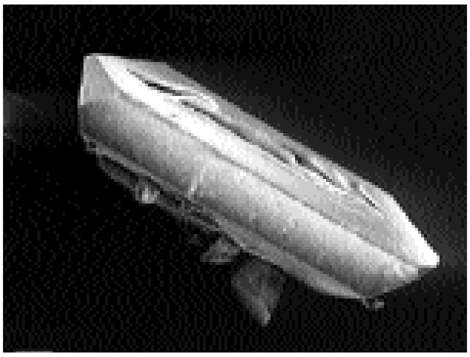


Figure 2. Crystal of struvite precipitated from sludge liquors (Doyle et al., 2000).

Struvite solubility can be separated into two stages: nucleation and growth. Nucleation occurs when constituent ions combine to form crystal embryos. Crystal growth continues until equilibrium is reached (Ohlinger et al., 1999). In systems continuously replenished with struvite constituents; e.g. wastewater treatment plants, crystal growth continues indefinitely.

Struvite precipitation is controlled by pH, supersaturation, temperature and the presence of impurities such as calcium (Bouropoulos and Koutsoukos, 2000) and can occur when the concentrations of Mg^{2+}, NH_4+ and phosphate ions PO_4^{3-} exceed the solubility product (K_{sp}) for struvite. The K_{sp} is given by the following expression:

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

The relationship between K_{sp} and pH indicates that struvite solubility, in mg/l, decreases with increasing pH, which in turn leads to an increase in the precipitation potential of a water (Figure 3 below). A number of chemical equilibrium based models have been developed and allow reasonable prediction of struvite precipitation (Lowenthal et al., 1994; Musvoto et al., 2000).

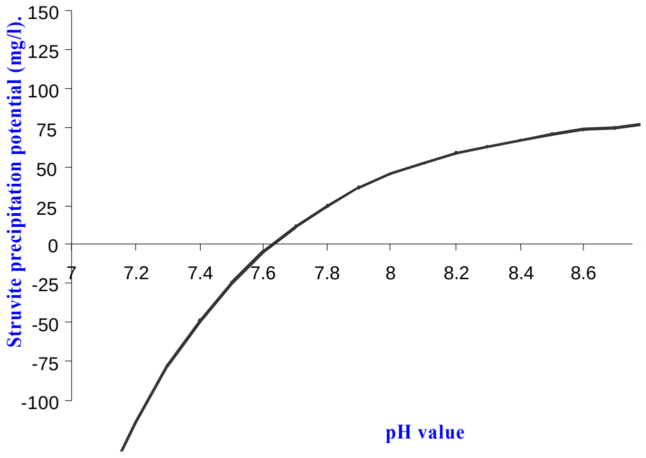


Figure 3. Effect of pH on struvite precipitation potential

2.2 Struvite Precipitation

The formation of crystals (ie. nucleation) usually occurs spontaneously (homogeneous nucleation) or can be aided by the presence of suitable nuclei, which may be either solid impurities in suspension or sites on the pipe walls (heterogeneous nucleation). The time taken for nucleation to occur (often termed the induction time) has been investigated to identify what controls the formation of a precipitate and hence what control scaling. Bouropoulos and Koutsoukos (2000) and Ohlinger et al., (1999) showed how the nucleation is inversely proportional to the solution supersaturation (Ω). A clear change from heterogeneous to homogenous precipitation was identified when Ω = 2. No change in crystal habit was identified over the range of Ω investigated at the pH of 8.5.

The effect of temperature and pH has also been reported to effect induction time where increasing pH and temperature lead to a reduction in the induction time (Abbona et al., 1982). In systems where the pH is below 8 struvite precipitation is very slow and can take a number of days (Battistoni et al., 1997). Momberg and Oellermann (1992) showed how the induction time for struvite precipitation from an anaerobic digester supernatant fell from days at pH 7 to less than 1 hour at pH 8.5.

Ohlinger et al., 1999 showed how the induction time is affected by turbulence where a doubling in mixing speed led to a halving of the induction time. Increased turbulence leads to CO_2 liberation, an increase in pH and hence an increase in struvite precipitation. Comparing stirred and static experiments shows that mixing a batch solution of sludge liquor containing struvite at 500 rpm has the same effect on induction time as a 1.5 pH unit rise, Table 2.

Reference	**pH**	**W**	**Mixing speed (rpm)**	**Induction time (s)**	**Scaling rate (g/m^2.day)**
Ohlinger *et al.,* 1999	6.9	2.1	500	60	5.6
Bouropoulus and Koutsoukos, 2000	8.5	2.0	static	50	-
Battistoni *et al.,* 1997	7.2	1.0	static	2 days	-
Doyle and Parsons (unpublished)	7.4	5.0	150	-	48

Table 2. Comparison of induction time in static and mixed systems.

2.3 Scale Formation

The level of supersaturation effects not only the induction time but also the scaling rate. A comparison of the scale formed during the mixing of anaerobic digestion sludge liquor showed that the rate of scale accumulation on stainless steel increased from 5.6 g/m^2.day for a sludge liquor with a Ω of 2 (Ohlinger et al.,1998) to 48 g/m^2.day for a Ω of 5. Ohlinger also showed that the rate of accumulation of scale was greater in the splash area around a tank rather than on an aerator, Figure 4.

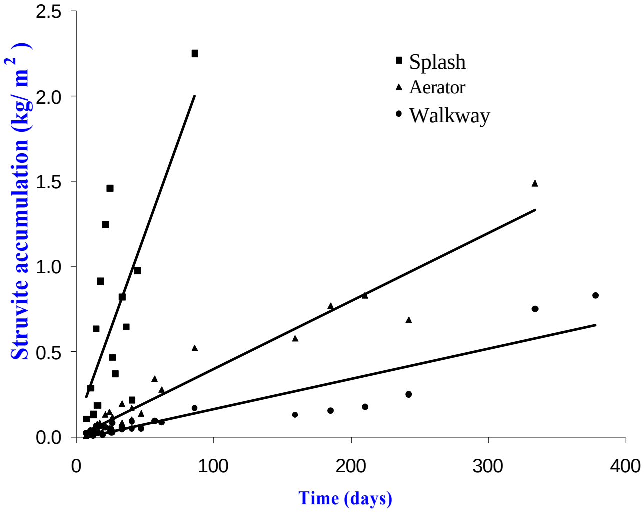


Figure 4. Struvite scale accumulation (Ohlinger et al., 1998

The surface roughness of the pipeline or equipment can effect the rate of deposition. If a surface is rough it provides ideal sites for crystal nucleation on which crystals can then grow rapidly. Surface roughness can also lead to localised turbulence and increase local mixing (Ohlinger et al., 1998).

Pipe material can also have a significant influence on scaling rate. It has been shown that smooth PVC pipes do not foul as readily as steel pipes (Borgerding, 1972, Ohlinger et al., 1998). Mohajit et al., (1989) found that acrylic pipes were better than PVC for suppressing the deposition of struvite. In a test conducted over a period of 24 days there was no deposition of struvite in the acrylic pipe, com-pared to 10.6 mm deposition of struvite in the PVC pipe.

3.Struvite Control

Struvite deposition can be ameliorated by both chemical and biological methods. Chemical controls fit into three main categories: those that affect solubility, those that alter the growth mechanisms of the crystals and those that act as dispersants. **Since struvite formation is based upon equilibria, most treatments have been based upon either forming other phosphate containing salts or reducing the pH to a value where struvite formation is less prevalent.** Buchanan et al., (1994) considered 20 potential inhibitors of struvite formation and went on to rank the chemical based upon the cost of use and the risk their operational use posed.

Seven chemicals were identified which they were considered to actually reduce struvite deposition. One of these chemicals was ferric chloride. Dosing with iron(III) salts to remove the phosphorous is the most commonly reported treatment process although this produces large quantities of sludge and has poor molar removal of phosphate per mole of chemical added. Ratios ranging from between 0.38 and 0.48 removal of phosphate per mole of iron added have been reported. Recent research by Hill et al. (1999) involved the use of silicates to reduce the magnesium concentrations in the sludge liquors. The addition of silicates resulted in the formation of a magnesium silicate which was less tenacious than struvite and easily dispersible.

Novel methods of attempting to alleviate struvite formation include the application of non-chemical treatment devices based on the use of magnetic and electrical fields. Reports are varied as to the success of these treatments and the paucity of systematic studies of the phenomenon (Williams 1999, Scalewatcher 1998) and the lack of recorded design criteria have prevented acceptance of the method.

4.Struvite Recovery

Recovery experiments have typically been undertaken with sludge liquors. Jaffer et al., (2001) compared liquid and sludge streams from Slough STW, UK. They identified those streams that had the greatest potential for struvite formation (page 19). Whilst the digested sludge and centrifuge cake had the highest potential they contain mainly solids making recovery very difficult. The digested sludge liquors were chosen to be the best option for recovery. An evaluation of digested sludge liquors from seven STW was undertaken by Wall (2000) who identified 4 out of the seven works consistently had the potential to form over 100 mg/L of struvite.

A range of processes have been investigated to recovery struvite, page 20. Experiments have been undertaken on bench, pilot and full scale and precipitation is usually encouraged by changing the pH by either dosing base in the form of NaOH or $MgOH_2$ or by aeration of the liquors to degas the solution. The second method to initiate precipitation is to increase the concentration of one of the constituent ions, usually Mg, so that the driving force for precipitation in promoted.

Some authors have used magnesium hydroxide as a source of magnesium ions and to raise the pH. Salutsky et al., (1972) achieved 90% phosphorus recovery with magnesium

Stream	P-PO_4 mg L^{-1}	NH_4 mg L^{-1}	Mg mg L^{-1}	Ca mg L^{-1}	Alk mg L^{-1}	pH	Temp mg L^{-1}	SPP mg L^{-1}
Thickened SAS	14.2	389	482	NA	50.7	6.9	18.3	-21
Belt Liquor	14.2	1.6	11	121	285.8	7.3	17.2	-342
Digested Sludge	154	1166	153	NA	98.8	7.3	26.8	198
Centrifuge Liquor	94.9	615	44	56	2580	7.6	24.1	140
Centrifuge Cake	94.9	4477	1049	NA	482	7.0	NA	420
Crude Sewage	5.7	16.1	8.9	118	360	7.9	14	-341
Settled Sewage	5.7	23.9	8	111	356	7.7	14	-352
Effluent C	5.6	0.8	8.1	109	199	8.2	13.4	-276
Effluent A	0.6	1.4	6.7	112	268	7.6	13	-440

Table 3. Comparison of sludge and liquor streams at Slough STW, UK (Jaffer et al., 2001)

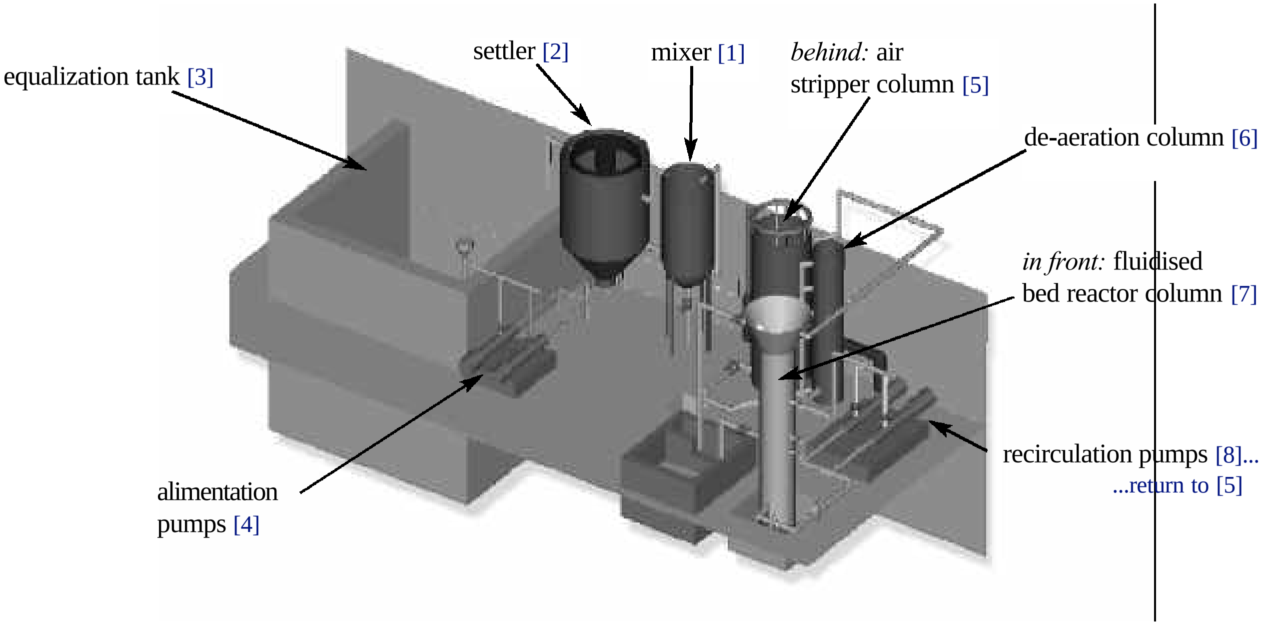
hydroxide addition, but at a temperature of 25°C. Munch and Barr (2000) also used magnesium hydroxide as a dual function chemical and obtained an average of 94% phosphorus removal as struvite.

However, using magnesium hydroxide to serve both functions means that the magnesium dose or the pH can not be optimised independently of each other. The Phosnix process uses magnesium hydroxide, but also has sodium hydroxide addition to control the pH. The sodium hydroxide requirement is less with magne-sium hydroxide, than with magnesium chloride (Taruya et al., 2000). An advantage of using magnesium chloride over magnesium hydroxide is that magnesium chloride disassociates faster than magnesium hydroxide, resulting in shorter reaction times. A shorter reaction time means a smaller full-scale reactor can be constructed as the hydraulic retention time can be reduced.

Some authors have managed to crystallise phosphorus from wastewater without the addition of any chemicals. Battistoni et al., (1997) removed 80% of phosphorus from belt press liquors, from a treatment plant that had nitrification, denitrification and anaerobic digestion. The liquors were aged and air stripped to remove carbon dioxide. The pH was raised from 7.9 to 8.3-8.6 and the phosphorus was removed as struvite. The liquor had a very high Mg:P ratio of 3.7 : 1, so did not require magnesium addition. However, when the work was repeated with centrate liquor from a biological nutrient removal plant, phosphorus removal was achieved as a mixture of struvite and hydroxyapatite. The Mg:P ratio had decreased to 0.22:1 and was no longer sufficient to exclusively form struvite (Battistoni et al., 1998). Recently 10% seawater (contains 1250 mg Mg/L) has been used as the magnesium source at pilot-plant (Matsumiya et al., 2000).

Typical processes used are fluidised bed reactors (FBR) or pellet reactors, where the material is collected as small solid pellets. The design of these processes has been covered in depth elsewhere (see Environmental Technology Volume 20:(7)). There are a number of full scale plants operating across the world, the largest of which are in Japan. The three main plants operating are situated at Shimane Prefecture (500 m^3/day), Fukuoka Prefecture (170 m^3/day) and at Osaka South Ace Centre (266 m^3/day). They each use magnesium addition (magnesium hydroxide or chloride) and pH adjustment (to pH 8.1 - 8.9) to cause struvite precipitation. The fine crystals of struvite formed are grown to 0.5-1 mm granules by air stirring or recirculation stirring over an average 10 day residence time. The extracted granules are separated (fine crystals are returned to the reactor) and either left to stand or air-dried down to 10% water content. The Shimane Prefecture reactor removes 90% of soluble phosphates from the treated liquors. The recovered struvite is sold as a quality fertiliser for 1 - 200,000 Euros/tonne.

In Treviso, Italy, a full scale FBR is being used to treat dewatering liquor from the belt press treating anaerobic digester sludge from an 85,000 pe sewage works. The plant has recently been commissioned. P removal as high as 86% have been reported using just aeration (Battistoni et al., 2000) - see process diagram page 20.



Full-scale struvite recovery installation at Treviso municipal wwtp, Italy (Battistani et al).
(with order of process flow)

Reference	Scale	Source	Method	P removal
Waki *et al.*, 1987	-	digester liquor	aeration	88% after 120 mins
Somiya et al., 1989	bench	synthetic digester liquors	aeration /pH	>90% at pH 9.5
Grace Dearborn, 1969	bench	digester liquor	pH only + degassing	93% 97%
Ohlinger *et al.*, 2000	bench FBR	digester liquor	aeration + seed crystals	>80%
Kabdasli *et al.*, 2000	bench	textile waste	aeration	~90% removal of NH_3
Lind et al., 2000	bench	human urine	adsorption on to zeolite	65-80% removal of NH_3
Webb and Ho 1992	bench	piggery waste	$MgSO_4$/NaOH	-
Munch and Barr, 2001	pilot reactor	dewatering liquors	aeration /pH/ $MgOH_2$	94%
Matsumiya *et al.*, 2000	pilot scale reactor	belt liquors	seawater	>70%
Battistoni *et al.*, 1998	pilot FBR	belt press liquors	aeration	80%
Yamamoto *et al.*, 1988	pilot reactor	digester liquor	NaOH/$MgCl_2$	>90%
Okumora *et al.*,	pilot reactor	digester liquor	aeration	Granules of struvite after 3 days
Suigimori *et al.*, 1995	pilot reactor	digester liquor	NaOH/$MgCl_2$	~90% removal at 1.5 Mg:P
Battistoni *et al.*, 2000	full scale FBR	belt press liquors	aeration	61.7–89.6 % removal of PO_4^{3-}
Taruya *et al.*,	full scale FBR	dewatering liquors	$MgCl_2$/$MgOH_2$ 1-2 Mg:P	>90%
Susckha *et al.*, 2000	bench/full scale	dewatering liquors	aeration	-
Jaffer *et al.*, 2001	bench FBR/full scale	centrifuge liquors	NaOH/$MgCl_2$	97%

Table 4 Examples of P.recovery at bench, pilot and full scale.

5.Struvite recovery : future research needs :

Whilst much of the recent research has focussed on recovering struvite little has been undertaken on the nucleation and precipitation of struvite. The previous chapter highlights that considerably more is known about calcium phosphates than about struvite. Before recovery can be truly optimised more information on what influence other ions and organics have on formation is required and how best to precipitate struvite.

One of the major issues with struvite is the formation of a hard scale. Detailed studies are required to find out how and why the scale forms, what interferes with its formation, what effect material has on growth and how best to control it. Most studies so far have used control chemicals developed for other scale such as calcite rather than specifically developing methods for struvite.

Better information on nucleation, precipitation and scaling will allow more reliable models to be developed. Current models are based on equilibrium and whilst they can predict that there is a potential for formation they are unable to predict where and when and how much. There is an obvious need for a model to predict where and when a struvite scale might form.

There are a number of treatment processes that have been used to recover struvite at both pilot and full scale. Recent data from Japan and Italy have shown the potential of these plants to recover struvite under different conditions. As with calcium phosphates most are based on fluidised bed reactors but it is unclear if this is the best method. Whilst these acts as very useful demonstration sites for this type of technology there is a need to compare a range of technologies and precipitation methods (seeding, chemicals, aeration, vacuum etc.) to identify optimum conditions for recovery.

Whilst much of the current research has focussed on recovery of struvite little has been done to identify a market for the recovered struvite. This must be shown before recovery will become a viable option for many water companies.

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Pilot-scale struvite recovery reactor

Brisbane, Australia

A 143 litre struvite crystallisation reactor, based on the Phosnix process of Unitika Ltd. Japan, was constructed and tested on anaerobic sludge digester centrate from a sewage works. An economic assessment suggests the process could break even or be significantly profitable, because the resulting struvite product may be marketed as a slow-release fertiliser.

Struvite crystallisation was tested as a method for removing phosphates from sludge digester return streams. A pilot plant was tested for three months at the Oxley Creek municipal waste water treatment plant in Brisbane, Queensland, Australia, using as influent the liquids from the dewatering centrifuges treating anaerobically digested primary and thickened waste activated sludge.

This is a conventional activated sludge plant, without phosphorus removal. The objective of the work, however, was to investigate the removal of nitrogen and phosphorus from digester return streams, in order to improve the efficiency of biological nutrient removal, in the context of objectives set by Brisbane City Council to reduce nutrient levels in discharges from the city's eleven wastewater treatment plants.

The pilot plant was based on the same principles as the Phosnix process of Unitika Ltd, Japan (Katsuura, 1998). It was a plexi-glass reactor consisting of two concentric columns (diameters 0.3 and 0.6 m, liquid height 1.365 m, see diagram) with an influent pumped and compressed air injection at the reactor base to maintain the seed crystals in suspension. Influent flow rate was around 40 l/h and air flow rate around 420 l/h.

This air flow was sufficient to ensure that the struvite particles remained in suspension, without air bubbles reaching the top of the outer cylinder, and without excessive foaming developing on top of the inner cylinder.

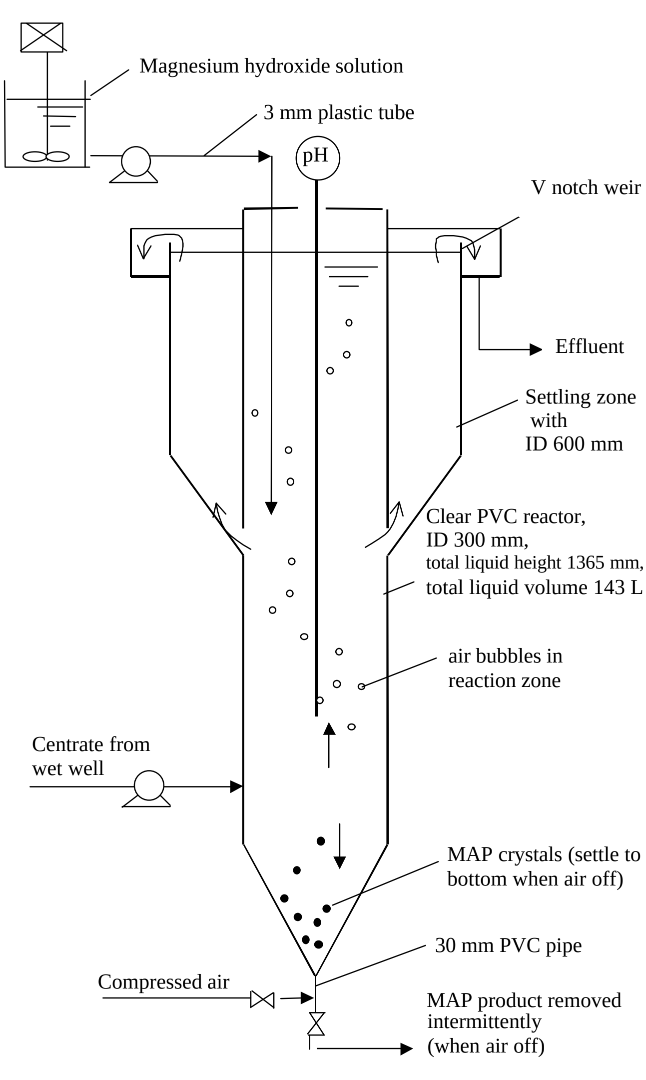


Figure. 1 Diagram of pilot-scale struvite reactor with ancillary equipment. (Reprinted from Water Research vol. 35(1), 2000, page 154, with permission from Elsevier Science).

Magnesium hydroxide slurry was used to give both magnesium dosing, necessary to supply magnesium up to stoichiometry with soluble phosphates, and to increase pH in order to facilitate struvite crystallisation. This has the disadvantage that magnesium addition and pH cannot be adjusted separately, but is the cheapest way to add magnesium. The use of a commercially-available 55% $Mg(OH)_2$ 42% water slurry had the advantage that it did not have to be stirred and is non-hazardous.

The reactor influent had a pH of around 7.7, suspended solids of around 160 mg/l, NH_4 around 790 mg/l, soluble magnesium around 11 mg/l and soluble phosphorus (PO_4-P) around 61 mg/l. Magnesium hydroxide slurry was added in order to maintain a Mg:P ratio of 1.3 (30% higher than the stoichiometry of struvite) as this ratio had been identified by previous authors as ensuring good phosphorus crystallisation rates. This resulted in an effluent pH of around 8.5

94% phosphorus removal.

Once initial teething problems had been sorted out, the reactor reliably removed 94% of influent soluble phosphate, with a reactor effluent concentration of around 4 mg/l PO_4-P.

Experiments demonstrated that this could be achieved with a hydraulic residence time of 1-2 hours only, and that longer residence times up to 8 hours did not significantly improve performance.

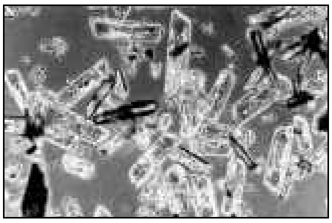
At the start of experiments, the reactor was seeded with 500g of crushed and 1mm sieved struvite from a pipe deposit. During operation, the struvite slurry had a volume of around 12 litres when allowed to settle. Every 5 days some 2-4 litres of struvite slurry were removed from the base of the reactor (after allowing settling by stopping the air flow). The reactor thus produced around 320g/day of dry struvite, in close agreement with the value calculated from the phosphorus removed (expected struvite production 327 g/day) - only around 0.2% of the struvite production was being lost as suspended particles in the reactor effluent.

If phosphorus was added to the struvite process (to also remove nitrogen from the wastewater), then significantly more struvite could be produced, but probably with significant chemical costs for the phosphate addition.

Easily dried struvite product

This recovered struvite slurry was 84% water on removal, but dried in a few days (by standing at room temperature and the supernatant being decanted) to 39% water (struvite is in fact magnesium ammonium phosphate hexahydrate and so has a theoretical water content of 44%). The final product was a fine, non-odorous grey-white powder.

The recovered struvite was analysed under the microscope (see photo) showing typical trapezoid struvite crystal structures. X-ray diffraction suggested that >90% of the product was indeed struvite. Laser analysis showed that the median size of the recovered struvite particles was 110 µm, with a 10-90% volume range of 28-215 µm. This is significantly smaller than the particles produced by full scale reactors in Japan, for example 2-3.8 mm for the Kurita process (Abe, 1995).



Photomicrograph of liquor from reaction zone of struvite reactor (100 times magnification). Reprinted from Water Research, vol. 35(1), 2000, page 157, with permission from Elsevier Science.

Fertiliser value

The recovered struvite from the Oxley Creek municipal waste water treatment plant was analysed for cadmium, lead and mercury content. These were undetectable in a majority of samples, with maxima of 5.5 mg/kgP for cadmium, 6.9 mg/kg-product for lead and 0.2 mg/kg-product for mercury (compared to 350 mg/kgP, 100 mg/kg-product and 5 mg/kg-product being the legal limits for fertilisers in Queensland, respectively).

The authors quote an number of authors who indicate that struvite is a useful and marketable slow-release fertiliser for which fertiliser burn is not a problem, even at high application rates (in particular Bridger et al., 1961), and has been used successfully on turf, tree seedlings, ornamental plants and vegetables. They indicate that Unitika Ltd., Japan, sell recovered struvite for around 276 US$/tonne and estimate a price on the Australian market (determined from preliminary market research) of 198-330 US$/tonne.

Process profitability ?

The Oxley Creek municipal wastewater treatment plant has an average dry weather flowrate of around 55 million l/day and a flowrate for the sludge dewatering centrifuge centrate of around 5 litres/second. With a hydraulic residence time of 1-2 hours, a full scale reactor would require a volume of 27,000 litres.

On the basis of a cost of round 330 US$/tonne for the commercial magnesium hydroxide slurry, the authors estimate the operating economics for a full-scale process at Oxley Creek (not including capital costs) between US$ 8,600/year loss through to US$ 98,000/year profit, depending on magnesium hydroxide costs, struvite sale prices, reactor efficiency achieved and on possible higher soluble phosphate levels in digester centrates if enhanced biological phosphorus removal is introduced to the sewage works.

Summary prepared by SCOPE Newsletter of the article: "Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams". Water Research, vol. 35, n° 1, pages 151-159, 2000, with permission of Elsevier Science

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Industrial requirements for recyclability of recovered phosphates.

There are a number of routes possible for the re-use of phosphates recovered from waste streams. These include re-use as a raw material (in substitution for mined phosphate rock) in the phosphate industry, re-use directly as a fertiliser (without further processing other than packaging and conditioning) or chemical processing to manufacture higher-value fertiliser products.

The article below addresses the requirements and constraints applicable if recovered phosphates are to be used as a raw material in the thermal phosphorus production process operated by Thermphos International at Vlissingen on the Dutch coast. The phosphate or fertiliser industry also uses phosphate rock as a raw material at a number of other sites in Europe (e.g. France, Spain, Belgium, Poland, Finland) but the at all these sites the "wet-acid" process used to generate phosphoric acid is completely different from the thermal route used by Thermphos for the production of elemental phosphorus, so that the constraints applicable to recovered phosphates will be different.

At these "wet-acid" process sites, certain limitations will be comparable to those identified by Thermphos below; in particular, iron is a problem in both cases. In order to enable its transport and reuse to be viable, the recovered phosphate product will always need to have a reasonable P-content and a limited water,. Aluminium is not compatible with the "wet-acid" process at any significant percentage (maximum 1-2%), whereas it does not pose any problems in the thermal phosphorus process. On the other hand, it may be easier to deal with copper and zinc in the "wet-acid" process than in the thermal phosphorus process.

Where recovered phosphates are to be re-used either directly or after processing as fertilisers, rather than in industrial processes, other limitations will apply. These will concern the agronomic value (plant availability) of the phosphates and other nutrients, processing and storage properties, granule size, etc…

Levels of cadmium and lead in recovered phosphates are likely to be significantly lower than those in mined phosphate rock and so are unlikely to be an issue for fertiliser applications.

Phosphate recycling in the Dutch phosphorus industry :

constraints for recovered phosphate materials.

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Introduction

Interest in phosphate recycling is steadily increasing in the Western world. There are large amounts of phosphate available in waste streams from e.g. agriculture, sewage treatment and from industrial side streams. Since regulations for discharge into the environment are becoming increasingly strict, these phosphate streams pose an increasing problem. The easiest solution, landfill, is increasingly inaccessible because of regulatory, social or economic pressures in most Western countries. Therefore, other possibilities have to be explored to dispose of these secondary phosphates.

The phosphate content of these streams make them potentially interesting for bulk users of phosphate rock, such as the fertiliser industry. It is generally possible to recycle phosphate waste streams in fertilisers, provided the phosphate content is not too low and the impurities level (heavy metals) is not too high.

Another bulk user of phosphate rock, albeit not on the same scale as the fertiliser industry, is the elementary (white) phosphorus industry. The only phosphorus producer in Western Europe is Thermphos International, a facility formerly owned by Hoechst, located in Vlissingen, on the coast of The Netherlands. Since the management buy-out in early 2000, Thermphos has decided to replace 40 kt/year of their P_2O_5 intake (17.5 kt P) by recovered materials. It is expected that this will bring advantages to both the supplier of the recovered material, and Thermphos: there will be disposal cost savings for the supplier, and raw material savings for the phosphorus producer. Our company has decided to play an active role in making phosphate recycling feasible.

This article will present a review of the possibilities for phosphate recycling in the phosporus process at Thermphos. The most important limitations will be discussed, and ways forward will be suggested.

The phosphorus process

The Thermphos phosphorus process is depicted in fig. 1. It starts with a granulation step for the phosphate rock (calcium apatite, $Ca_5(PO_4)_3OH$), where a binder (clay) is added as a slurry on a rotating disc, together with ground rock. The pellets which are obtained in this way are then dried and sintered at 800 °C. This rock treatment is necessary to prevent blocking further downstream. The rock pellets are then mixed with cokes (reducing agent) and pebbles (SiO_2, for slag formation) and fed into a furnace. The furnace is heated to 1500 °C by passing a large current through three carbon electrodes in the furnace.

At this elevated temperature, phosphate is reduced to P_4. This leaves the furnace as a gas, together with the by-product CO and some dust. This dust is removed in an electrostatic precipitator and recycled into the process. The P_4 is then condensed. The resulting CO gas stream is used as fuel for the sinter and other on-site processes. The calcium oxide which is left in the furnace after the phosphate has reacted, combines with the SiO_2 to from a liquid slag. This slag is then cooled and crushed. It is used for e.g. road construction.

Trace amounts of iron are also reduced in the furnace. These form a separate slag, ferrophosphorus, which is roughly 75% Fe and 25% P. It is sold as a steel additive.

Possibilities for phosphate recycling in the phosphorus process

The usual route for phosphate recycling is to mix the material with the rock before the grinding stage.

The high-temperature phosphorus process is generally seen as a robust process. **In practice, however, the quality requirements for the raw materials can be strict. Certain types of impurities in particular can lead to large problems. The main restrictions are:**

•1 The material should contain a sufficient amount of phosphate,

•2. The amount of certain impurities should not exceed a critical value

•3. It should be obtainable as a dry material (in principle)

•4. It should not contain large amounts of organic material or ammonium

•5. It should not interfere with the granulation and sintering process

These restrictions are discussed in some detail below.

Phosphate content

The typical P_2O_5 content of phosphate rock is 30-40% (= 13-17.5% P) The phosphate content of waste streams is usually lower. If the remainder is made up by compounds that lead to more slag per tonne of P_4, then this will affect the energy efficiency of the process negatively. The heat in slag is lost since it requires a special cooling process in order to make it suitable for civil engineering purposes. The slag takes up a substantial amount of the total electricity consumption of the process; therefore extra slag should be avoided if possible.

On the other hand, if the remainder of the secondary stream consists of SiO_2 ,this has no effect on the energy balance since the process requires the addition of SiO_2 anyway. Aluminium compounds replace SiO_2 in slag formation, so that recovered aluminium phosphates would make a good raw material for the process.

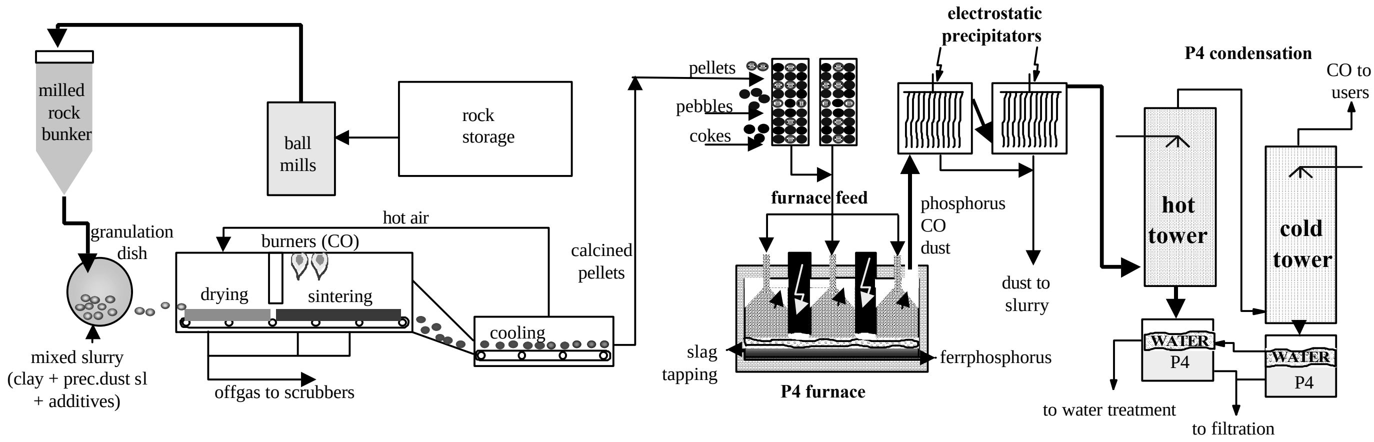

Figure 1 : The Thermphos phosphorus process

Impurities

Since the phosphorus furnace is a reduction process, it also reduces every (trace) element present which is more easily reduced than phosphorus. The most notable are:

- Iron : this forms a separate slag and effectively removes phosphorus from the process. This poses P-depreciation and capacity problems
- Zinc : this metal is volatilised in the furnace and subsequently precipitated on the furnace dust. Since this is recycled, zinc tends to build up in the system. This makes (costly) purges necessary. **Similar problems are expected with other volatile metals, such as lead, cadmium and tin**.
- Chloride : causes corrosion damage to the sintering plant, where metal parts are exposed to the raw materials at high temperatures.
- Copper : ends up in the ferrophosphorus. A significant increase in the copper content may limit the application potential of this side stream.

Water content

Phosphate rock is usually supplied as a dry material. A considerable number of waste treatment processes generate wet "sludges" of inorganic phosphates. The Thermphos process cannot use wet material on a large scale because of technical limitations (mixing, milling, interference with internal sludge processing capacity). Drying materials on-site could solve this problem, but there is no waste (low-grade) heat source available, so that drying would involve energy purchase and consumption and so be costly; also, **it is economically and ecologically undesirable to transport materials with a high water content**.

Organic material and ammonium

The presence of significant amounts of organic material lead to a decreased pellet strength after sintering. This will seriously limit the capacity of the plant, which is unacceptable. **Therefore, the material should consist of inorganic phosphates only (max. 5% carbon)**.

Also, **nitrogen present in recovered materials would cause a serious emission or gas scrubbing problem** in the sintering stage, since NH_3 will be volatilised and oxidised to nitrous/nitric oxides. This would be a major obstacle to the use of recovered struvite (magnesium ammonium phosphate) as a feed material for the process.

Pellet strength

If the presence of a secondary material leads to decreased pellet strength, this will limit the plant capacity (see under Organic material)

Currently available sources of secondary phosphates

Thermphos' work towards phosphate recycling has so far concentrated on finding inorganic phosphate streams which are dry. The most notable such streams are at present animal manure incinerator ash, and sewage sludge incinerator ash. In the future, however, new processes may be developed and installed in waste treatment facilities to recover phosphate in a recyclable form.

Manure ash

In countries with intensive livestock agriculture, such as the Netherlands, animal manure storage and disposal pose a large problem wherever production exceeds agricultural spreading limits fixed by regulators to protect water quality. It is not possible to use the full amount as natural fertiliser.

Therefore, several projects have been started to incinerate manures. When the manure is not too wet, it may be incinerated, and the released energy may be converted to electricity. Amongst other projects, a large scale plant for *poultry manure* incineration in Moerdijk, the Netherlands, is currently being engineered.

The residue of this process is a dry product containing a high proportion of calcium phosphate. Unfortunately, the zinc and copper content are relatively high, which at present prevents use of large amounts of this material by Thermphos. *Pig manure* poses the same problem. Copper and zinc originate from animal feeds; we are currently discussing possible reductions in metal levels in animal feed with the relevant industries. Since these metals are also becoming increasingly problematic for other manure applications, such as agricultural spreading, it is expected that the Cu and Zn content in manure ash will decrease in the future.

The total yearly amount of P in Dutch pig and poultry manures is 86 kt. In theory, Thermphos could recycle a considerable amount of this phosphate. An advantage of this is that the phosphate is taken out of the agricultural P-cycle which is encouraged by the Dutch environmental government policy. Unlike agricultural spreading of manures, Thermphos can take recovered phosphates all year round, avoiding manure storage problems.

Sewage ash

In the Netherlands, by the end of the 1990's, about 60% of the sludge from communal sewage treatment plants was incinerated and this proportion is expected to rise. The ash contains a significant proportion of dry iron- calcium- and/or aluminium phosphates, alongside silicates, with up to 16% P_2O_5 (7% P) **The large** iron **content of this ash, up to 10%,**

currently prevents use in the phosphorus process, since the amount of ferrophosphorus formed would exceed the processing capacity and the re-use application potential for this stream (phosphate rock typically contains only 0.4-1% of Fe). Iron originates mainly from the phosphate precipitation step in sewage treatment plants using chemical P-precipitation. The use of iron in sewage works P-removal can be replaced by calcium or aluminium, which would make ash processing at Thermphos much more feasible. At present, the use of aluminium is more costly and calcium use in existing sewage works processes can cause sludge handling problems; it has to be evaluated whether the positive effect on the ash side will compensate for this. The general, government-induced tendency away from landfilling and towards recycling may be helpful here. A discussion between Thermphos and the central organisation of Dutch sewage plants STOWA has been started.

Unfortunately, sewage ash also contains considerable amounts of zinc **and** copper which are difficult to avoid, as they come from sources such as water piping and foods. Just as is the case with manure ash, the amounts of zinc and especially copper pose a serious limit on the recycling capacity of this material in the Thermphos process.

The total amount of P in sewage ash in the Netherlands today is 5 kt/y. In theory, Thermphos could recycle all of the P in sewage in the Netherlands, provided that it is supplied as ash with a low Cu and Zn content.

Precipitation of recoverable phosphates within sewage works

In some sewage works it may be possible to precipitate phosphates from a liquid stream in a specific process, rather than transferring them into the sewage sludge and then into ash. This is most likely to be attractive in works equipped with biological phosphorus removal and/or sludge digestion. Phosphate precipitation in a side stream (using Al or Ca,) will produce a material which is very suitable for recycling by Thermphos, since high phosphorus contents can be achieved and most of the Cu and Zn will be absent from the phosphate material (these metals usually enter the main sludge stream).

Industrial and food industry waste streams

Many industries produce phosphate waste streams, for example food and dairy product processing, metal treatment, electronics manufacturing and other processes that use phosphorus, phosphoric acid or phosphates. A large variety of phosphate-containing wet and dry materials result from the treatment of these waste streams . In The Netherlands these contain approx 5 kt/y (as P). Thermphos is currently considering the construction of an on-site dryer for slurries and wet cakes. A large problem in getting secondary phosphates from other countries is the waste legislation. It is usually not permitted to transport waste across the border, especially when the material does not originate from our clients. What is needed here is a less rigid legislation and regulation on national and European scale, especially regarding the difference between waste materials and recyclable raw materials. This should prevent landfill of valuable materials. The current legislation creates barriers which discourage or prevent recycling.

Outlook and conclusions

From the above, we can conclude that the potential for P recycling in the phosphorus process is high, but there are many practical difficulties to be overcome. These make recycling at present economically difficult. **Thermphos has chosen a proactive role in investigating and trying to develop suitable streams of recovered phosphates. We expect that over the next decade, this will lead to quality improvements of recovered phosphate materials, making recycling more viable. For this, an integral P chain approach is needed. Adaptations in legislation may accelerate these developments**.

Other possible pathways for P-recycling and CEEP-funded research underway

Phosphorus can be recovered from sewage and from other waste streams by a number of routes. The pathway involving precipitation of phosphates from liquid effluent streams is explored in depth in this Newsletter (previous pages) because, in a number of specific circumstances, this pathway seems most likely to rapidly reach industrial application and economic feasibility. In other circumstances, other routes are likely to develop.

One significant possible route for phosphorus recovery is from sewage sludges and from sewage sludge incineration ashes. Where phosphorus removal is installed in sewage works, sludges contain significant phosphorus contents, and sludge incineration concentrates this phosphorus to even higher levels in incineration ash. Phosphorus levels in sludge incineration ashes are around 50% those in currently available mined phosphate rock (though the P content of rock is continuing to fall as the better quality seams are consumed) - but see the article by Thermphos in this Newsletter concerning other technical limitations to the use of ash as a raw material by the phosphate industry.

So even if phosphate recovery by precipitation develops in a variety of sewage works and waste streams, there will still be many situations where it is not economic or appropriate (small sewage works, trickling filter works …) and so sludges and sludge incineration ashes will continue to offer significant potential opportunities for phosphorus recovery.

One major question concerning phosphorus recovery from sewage sludges is that of iron. Most authors consider that iron phosphates are not a useful fertiliser because the phosphorus is not plant available; and there are no significant industrial outlets for recovered iron phosphates today. One possibility would be to develop biological processes for recovering a useful phosphate product from iron phosphates/iron containing sludges, using sulphur reducing bacteria. A brief presentation of this possibility is included in this section below.

This section also summarises work currently financed by the West European phosphate industry (CEEP) into other possible pathways for recovering phosphates from waste streams: ion-exchange (REM-NUT®) which might allow recovery from dilute phosphate solutions (such as main-stream effluent from sewage works, whereas precipitation processes are likely to only be efficient in concentrated side-streams); biologically inducted phosphate precipitation (using micro-organisms in sewage sludges); reversible adsorption onto fly ash, etc...

Phosphorus recovery from sewage sludges :

Research and experiences in Nordic countries

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Swedish policy now requires phosphorus to be recycled and, because agricultural sewage sludge re-use is increasingly limited, this is putting pressure on cities to develop P-recovery systems. In an number of cases, authorisation to construct sludge incinerators is being given with the condition that phosphorus must be recovered. Different processes are therefore being developed to recover phosphorus for recycling through the process of sludge fractioning.

Swedish goal of 75% phosphorus recovery

The Nordic countries have a long tradition of phosphorus removal in sewage works by use of chemical precipitation, although biological phosphorus removal is increasingly used and is now common in Denmark. **A national goal has recently been proposed in a report to the Swedish government that at least 75% of phosphorus from wastewater and other biological wastes should be recovered at latest by 2010** without risks for health and environment. Sludge incineration should therefore include technology to either recover phosphorus before incineration or from the produced ashes.

Phosphorus recovery by spreading sludge on agricultural land has been stopped to a high extent due to resistance from the farmers' organisation (LRF) and food industries. Disposal of organic material to landfill will be forbidden in 2005. Difficulties to use earlier routes of final sludge disposal have led to a great interest in fractionation of sludges followed by recovery of different products and transfer of toxic materials into a small stream.

Two systems for phosphorus recovery

Much research on phosphorus recovery has been directed towards the use of biological phosphorus removal, release of the phosphorus under anaerobic conditions into a small stream followed by precipitation as calcium or magnesium phosphates. If chemical precipitation is used for phosphorus removal other technologies must be used for the recovery.

Two systems for phosphorus recovery from sludges from biological and chemical treatment have been developed in the Nordic countries, Cambi/Krepro and Bio-Con.

The two systems have in common that thermal treatment is used of the sludge for removal of organic material, dissolution of phosphorus compounds and metals by use of sulphuric acid and a system for recovery of precipitation agents and phosphorus. However, there are also many dissimilarities (see Table page 31). Process schemes for Cambi/Krepro and Bio-Con are shown in Figure 1 and 2 below.

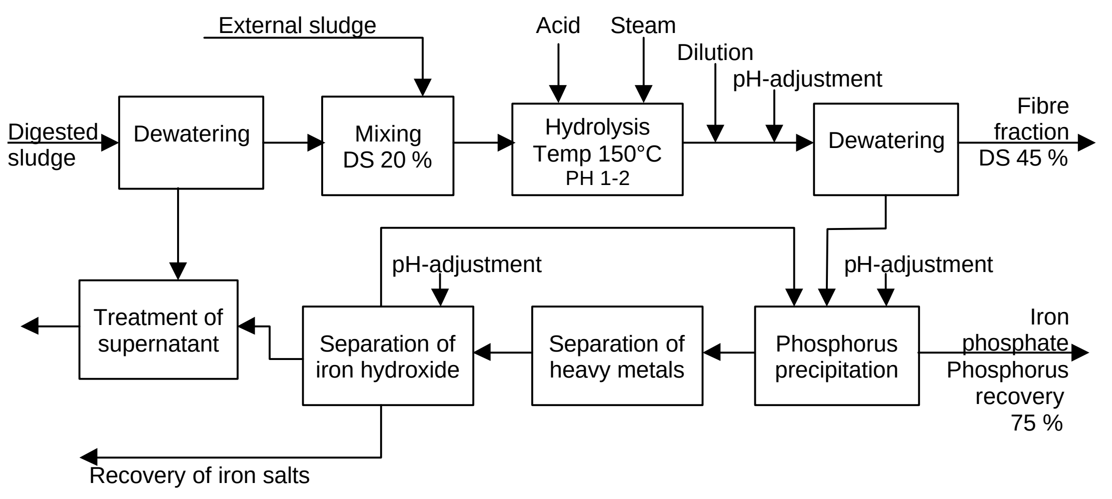

Figure 1. Process scheme for Cambi/Krepro

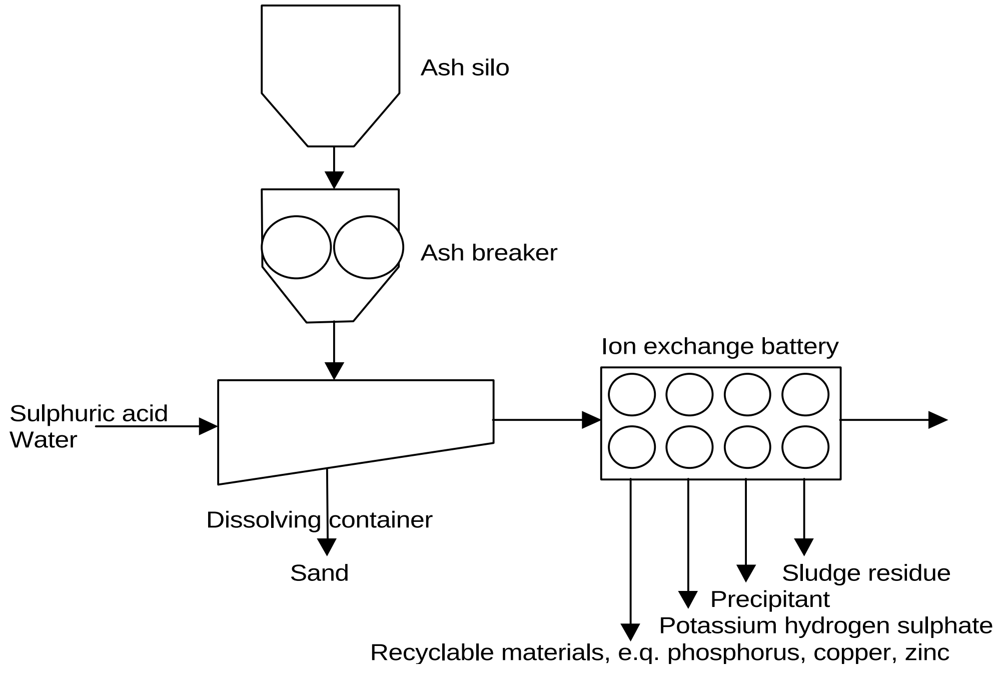

Figure 2. Process scheme for Bio-Con

Process function	Cambi/Krepro	BioCon
Removal of organic material	Thermal hydrolysis of dewatered sludge, incineration of rest sludge, biological oxidation of soluble hydrolysed organic material	Heat drying and incineration of dewatered sludge
Dissolution of phosphorus and metals	Use of sulphuric acid treatment of dewatered sludge	Use of sulphuric acid treatment of ashes from incineration
Phosphorus product and recovery technology	Ferric phosphate obtained in chemical precipitation	Phosphoric acid obtained by use of ion exchange
Transfer of heavy metals in a small stream	Precipitation as metal sulphides	Concentration by use of ion exchange
Recovery of precipitation agents	Partial recovery by solution by acids(part of the precipitation agent is used to produce ferric phosphate)	Concentrated and recovered by use of ion exchange

Table 1. Comparison of Cambi/Krepro and Bio-Con systems

The Cambi/Krepro and Bio-Con processes

The Cambi/Krepro process is a combination of earlier developed systems by Cambi and Kemira/Alfa Laval, respectively. The idea of Cambi was to use steam as a heat source directly into pre-dewatered sludge and then digest it. The process was commissioned 1996 in full scale in Hamar in Norway. Later on plants have been commissioned in Naestved south of Copenhagen, in Chertsey (west of London) and an additional plant is planned for Aberdeen (Weisz et al., 2000). A full-scale sludge recovery pilot plant with the Krepro system has been in operation since autumn 1995 at Helsingborg wastewater treatment plant in Sweden and with a maximum capacity of 500 kg TS/h (Hansen et al., 2000 ; see also the following article in this Newsletter), . The project has partly been supported by the Swedish EPA.

Although the combined system Cambi/Krepro has not been tested in full scale, the different process units have been extensively studied. A consortium comprising of Purac, Cambi, Kemira and Alfa Laval are now offering process guaranties of the system and the city of Malmö in Sweden has far reaching plans to install a modification of the Cambi/Krepro process.

Bio-Con is a Danish company that has developed a system for heat drying of sludge and incineration. As a third part of the BioCon sludge handling a system has been developed to recover resources from ashes by leaching with sulphuric acid and recovery of resources by ion exchange. The last part has been studied in pilot plant scale at a wastewater treatment plant near Aalborg in Denmark. The company is now offering the treatment system and in Sweden far reaching plans exist to install the system in the city of Falun.

The two developed systems are in the stage to be implemented in full scale but there is still a need for a careful evaluation of the function of the systems under different conditions.

Alternatives and possible improvements of the systems

The systems according to Cambi/Kemira and Bio-Con have as a disadvantage the need to dissolve precipitated iron compounds by use of sulphuric acid. Chemicals are also needed in the Krepro process to precipitate ferric phosphate and in the Bio-Con process to regenerate the ion exchangers.

The use of systems like Cambi/Kemira and Bio-Con would benefit much if the dosage of precipitation chemicals could be diminished. One obvious way is to partly substitute precipitation with iron salts with biological phosphorus removal. A combined system with phosphorus recovery from biologically bounded phosphorus followed by a system as Cambi/Kemira or Bio-Con to recover chemically bound phosphorus might have advantages, but has not yet been studied.

The Cambi/Krepro system consists of many process steps and they might be substituted by other steps such as sludge dissolution and disintegration by mechanical or chemical means. Selective removal of phosphorus from the sludge without dissolving iron is possible by use of treatment of the sludge by sulphides. Part of the dissolution and disintegration of the sludge may be performed before the digester.

References

Hansen B., Karlsson I., Cassidy S. And Pettersson L. (2000) Operational experiences from a sludge recovery plant, Water Sci. & Techn., Vol. 41, No 8, pp. 23-30.
Weisz N., Kepp U., Norli M., Panter K. And Solheim O.E. (2000) Sludge disintegration with thermal hydrolysis - case from Norway, Denmark, and United Kingdom, 1st World Water congress of IWA, Paris 3-7 July 2000, Conference Preprint Book 4, pp 288-295

For information : Swedish cities currently subject to requirements to recover phosphorus or planning to install P-recovery processes *(information provided by the Swedish Environmental Protection Agency Naturvärtsverket)*

- Eskilstuna : application has been made for a permit to incinerate sludge and the Swedish EPA has asked that P be recovered. The application is still pending.

- Falun : the town intends to apply for a permit for sludge incineration with phosphorus being recovered from the incineration ash.

- Halmstad : a permit for sludge incineration was granted in 2000 specifying that the local authority should take a decision concerning P recovery

- Malmö : authorisation has been given for sludge incineration including P-recovery, and the city is expected to build a plant using the Krepro process (see article above), but this remains to be confirmed

- Södertälje : the local garbage combustion plant Igelstaverket has obtained a permit to incinerate sludge. From the year 2002 P must be extracted before incineration.

- Stockholm : sludge incineration is planned at the Högdalen garbage combustion plant. The question of P recovery has not yet been raised but is expected to come up.

the KREPRO process :

Successful pilot operation of sludge treatment process at Helsingborg, Sweden

The KREPRO high temperature acid hydrolysis process enables energy recovery from sewage sludge and produces a relatively pure iron phosphate "paste" A paper by Kemwater (Kemira Kemi AB) presents the successful operating experience of the first full-scale pilot KREPRO sludge treatment plant at Helsingborg sewage works, Sweden (150,000 pe, 500 kg dry solids/hour of sludge). The plant enabled the recovery from sludge of energy (production of biofuel), organic feed stock) for the biological nutrient removal process) and an iron phosphate syrup.

The plant was **automated for continuous operation**. The use of hasteloy steel pumps, Teflon lined pipes and a glass lined hydrolysis reactor, enabled efficient operation in the corrosive and abrasive operating conditions : presence of sand particles in sewage sludge, high temperature, acid environment. Clogging of equipment by fibres present in sludge was avoided by maceration/shredding of the influent sludge. The risk of odours (hydrogen sulphide and organics) was prevented by enclosure of all equipment in buildings where the air was pumped (4000 m^3/hour) and treated

These design features enabled the plant to operate according to requirements and specifications.

Biofuel pellets and iron phosphate "paste"

The KREPRO process
- treats sludge by acid hydrolysis at high temperature (pH < 2, temperature 140°C, pressure 3.6 bars for around 1 hour),
- then separates out insoluble organic material to be made into a biofuel pellets,
- precipitates out heavy metals with sodium hydroxide,
- finally precipitates out phosphorus with iron salts.

Dissolved iron salts and hydrolysed organics (now soluble) were returned to the head of the waste water treatment plant : the iron salts used in the Krepro process thus contributed to phosphorus removal in the plant (significantly reducing addition of such products in the sewage works itself by 90-95%) and the soluble organics improved the functioning of biological nutrient removal in the sewage works.

The insoluble organics after hydrolysis (mainly cell membranes and cellulose) were removed from the KREPRO process as sludge which, after centrifuging and being left to dry for 12 hours at ambient temperatures produced **a solid biofuel with a dry solid content of 50%, an ash content of 20-30% DS and an energy content of around 8 MJ/Kg.** This material contained some heavy metals and sulphur (figures not given in the paper), but these are generally not considered a problem for installations using such products for energy production as these are equipped with gas cleaning installations.

The energy content of the biofuel produced from 1 tonne of wet sludge was around 2000 kWh, compared to the energy used in the process of 800 kWh.

Process inputs and products generated

The treatment of one tonne dry solid (DS) equivalent of influent digested sludge (DS content of 2.7 - 3%, increased to 5% by preliminary centrifuging) used (dry weights)
Process inputs and products generated

The treatment of one tonne dry solid (DS) equivalent of influent digested sludge (DS content of 2.7 - 3%, increased to 5% by preliminary centrifuging) used (dry weights)
- 200 kg sulphuric acid
- 200 kg sodium hydroxide
- 12 kg magnesium hydroxide (pH adjustment of phosphate precipitation)
- 390 kg ferric chloride
- 2 kg polymers

From this one tonne DS equivalent of sludge input, the process produced approximately (dry solid DS equivalents) :
- 500 kg of biofuel
- 350 kg of soluble organics
- 200 - 350 kg of ash and inorganics (sand)
- 180 kg of iron phosphate

The soluble organics were returned to the head of the sewage works and provided a valuable sub-strate for the biological nutrient removal process.

The 180 kg DS of iron phosphate (ferric phosphate) produced corresponded to nearly all the phosphorus in the sewage works inflow. It was produced as a "syrup" with a 35% DS content.

What use for iron phosphate ?

Organic micro-pollutants are so low as to be scarcely detectable in the ferric phosphate produced by the process. **The heavy metals content was relatively low** : 20-100 x lower than in conventional sewage sludge and **significantly lower for all metals except mercury than in most mineral fertilisers** (expressed as g metal / gP). In particular, cadmium, which can be a problem contaminant in mineral fertilisers, was significantly lower (2.6 mg/kgP cadmium in the KREPRO product).

The authors suggest that ferric phosphate can be used as a phosphate fertiliser and state that pot and field trials indicate that the phosphorus is available for crops. Results of (unpublished) barley pot trials are shown in the quoted paper (details of experimental method not published), and the authors state that these suggest that the ferric phosphate offers comparable efficiency to conventional NPK fertilisers.

However (Scope Newsletter editor's note), in the barley pot trials shown, the addition of iron alone gives similar results to that of ferric phosphate or NPK fertiliser, making the results difficult to interpret. Other sources suggest that ferric phosphate is not generally considered to be a useful fertiliser, and that it is not currently useable in existing fertiliser or phosphate industry processes. This suggests that further research would be useful to adapt the KREPRO process to produce a marketable and re-usable phosphorus product instead of iron phosphate.

The iron phosphate produced at the Helsingborg KREPRO plant was spread on agricultural land. Its "syrup-like" consistency (at the 35% dry solids content resulting from the process) necessitated further processing before spreading and it was mixed with coconut flour for spreading.

Following the pilot plant experience at Helsingborg, the city of Malmö is now planning a full scale KREPRO sludge processing plant.

This text is a review, written by the SCOPE Newsletter editors and updated with data supplied by Kemwater, of the following published article : "Operational experiences from a sludge recovery plant". Water Science and Technology, vol. 41, n°8, pages 23-30, 2000.
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P-recovery from iron-containing sludges

A possible route for recovering phosphates in a useful form

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Many municipal sewage treatment plants use iron salts for phosphorus removal (chemical P-stripping). Sometimes it is the only phosphates removal process, in other cases iron salts are added in addition to biological processes. Most of the phosphorous precipitated as iron salts are not available for plants and therefore such sewage sludge has a very limited use as a natural fertiliser. Also, iron content is an obstacle to industrial re-use or recovered phosphates.

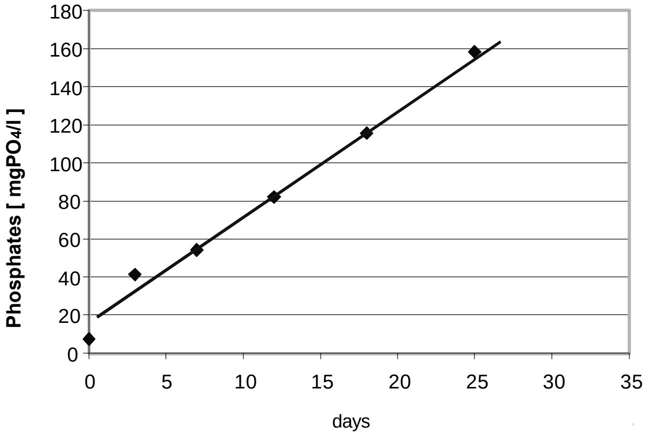
One possible route for phosphorous recovery from such iron containing sludges **could be through converting iron salts to iron sulphide by biological processes** (sulphur reducing micro-organisms). This is to some extend based on natural occurring process in the environment and could possibly be achieved with little or no input of chemicals and energy. The phosphates would then be released into a soluble form, available for precipitation as useful and recyclable products (eg. calcium phosphates).

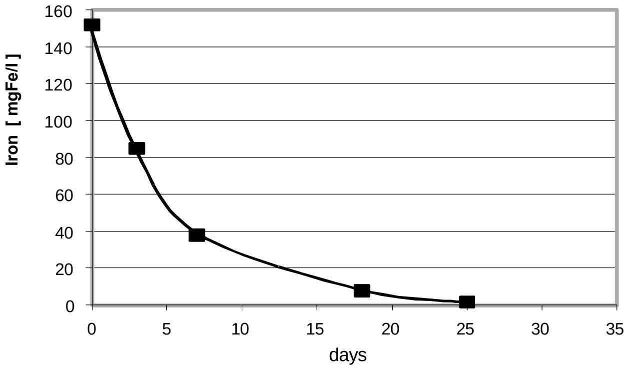
Some initial experiments have been carried out in Bielsko Biala by adding waste water treated anaerobically with the aim of sulphates reduction (containing high concentrations of sulphides and around 100 ppm hydrogen sulphide) to sewage sludge including precipitated iron phosphates from a municipal sewage treatment plant. The sulphide rich waste water contains SRB (Sulphur Reduction Bacteria) which are expected to participate in the process of iron sulphides production. Iron has a higher affinity to sulphur than phosphates (PO_4).

Results of a first test experiment are shown in the figures below. **These show that such a biological phosphorus release process is feasible.**

Further work is now necessary to establish whether the process can be developed, by selection of the micro-organisms and adaptation of the medium conditions, in order to achieve phosphorus release in much shorter periods more compatible with application of the process at an operational scale.

This could be attempted by isolating the SRB bacteria and cultivating them on a medium chosen to serve as a constant source of easy biodegradable carbon (sodium lactate) and by the addition of different concentration and rate of sulphate cation - $XSO_4 . XH_2O$ or $X_2SO_4 . XH_2O$. The experiments should allow evaluation of the process under different C/S ratio, and finally determine the optimal sulphate reduction coefficient before testing the cultivated SRB in iron-rich sludges.





Biological phosphate release from iron containing sludges

Ion exchange
followed by struvite precipitation

Adapting the REM-NUT® process for P-recovery

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REM NUT® (see Fig.1) is a resource-conservative process developed in the 1980s for removing both ammonium and phosphate ions from wastewater and recovering ithem in the form of a slow release fertiliser, struvite $MgNH_4PO_4$. The process is based on the use of NH_4-selective natural zeolite and P-selective commercial anion exchanger able to remove nutrient ions from sewage down to the dis-charge limits in force. Both ion exchangers are regenerated by closed-loop recirculation of neutral 0.6M salt solution (NaCl) from which, after stoichiometric addition of Magnesium and Phosphate to give a $Mg:NH_4:PO_4$ ratio of 1:1:1 molar ratio, struvite is precipitated.

Although passing successfully several demonstrations with civil and animal sewage, municipal sludge digestor liquids etc. in Europe and USA, the REM-NUT® process did not reach full scale application yet due essentially to the following limitations:

- unbalanced N:P ratio in most sewage (generally around $NH_4:HPO_4$ = 5:1 in municipal effluent), requiring expensive addition of P, as well as Mg, to achieve the stoichiometry for the precipitation of struvite
- relatively undemanding P-discharge limits in some EU Countries (e.g., 10 to 20 mgP/L in Italy)
- poor attitude of (waste) water industry toward technological innovation.

Planning and financial approvals were obtained for a full scale plant at Manfredonia, Italy, in 1998. The economics in this case were positive because a nearby fertiliser factory agreed to purchase the recovered struvite. This project, however, was not finally constructed because of closure of the fertiliser factory.

At CEEP's initiative, Bari Polytechnic University, Italy, is currently revising the REM-NUT® process to configure the process for phosphorus recovery rather than for ammonium removal. This new "P-driven" REM NUT® layout is included in Fig. 2 : the selective ion exchange/chemical precipitation scheme for struvite recovery is in this case designed on a 1:1 = N:P molar ratio, based on the P content of sewage

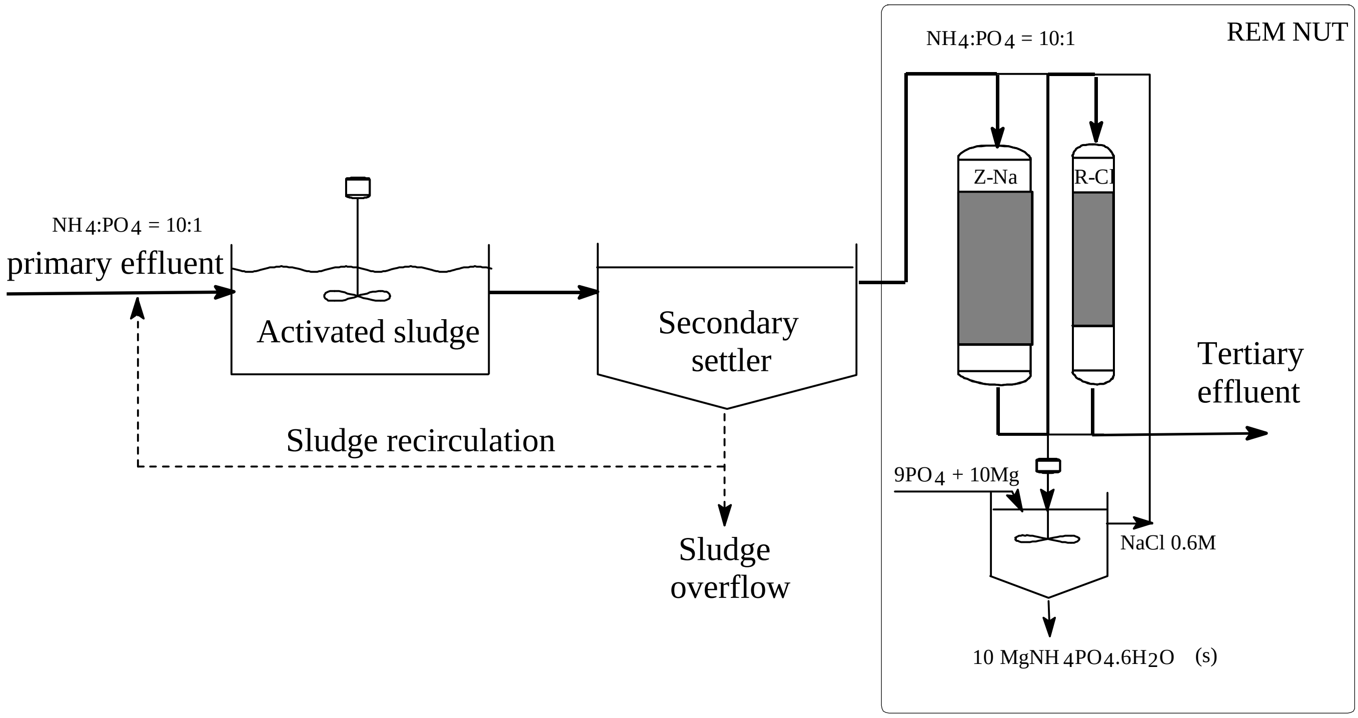

Figure.1: REM NUT® process layout applied to municipal wastewater treatment
(Z-Na = NH_4-selective zeolite in Na-form; R-Cl = P-selective anion resin in Cl-form)

(rather than on the ammonium content which is some 5x higher), thus significantly reducing equipment size, capital costs, operating and chemical costs. In particular, the addition of phosphorus is completely avoided.

Different solutions can be applied for removing the excess ammonia. These could include combining the P-driven REM-NUT® process with conventional biological nitrogen removal systems or use new technologies currently being investigated, such as batch adsorption by zeolite followed by biological nitrification-denitrification of this latter (Fig.2)

The paper presents preliminary experimental results of the "P-driven" REM-NUT® process with some technological and economic details.

A paper to be presented at the Noordvijkerhoot phosphorus-recovery conference will present the conclusions of the preliminary technical and economic assessment of the revised REM-NUT® process configured for to allow phosphorus recovery from the main-stream discharge of conventional secondary-biological sewage works or from other effluents such as sludge digester supernatants.

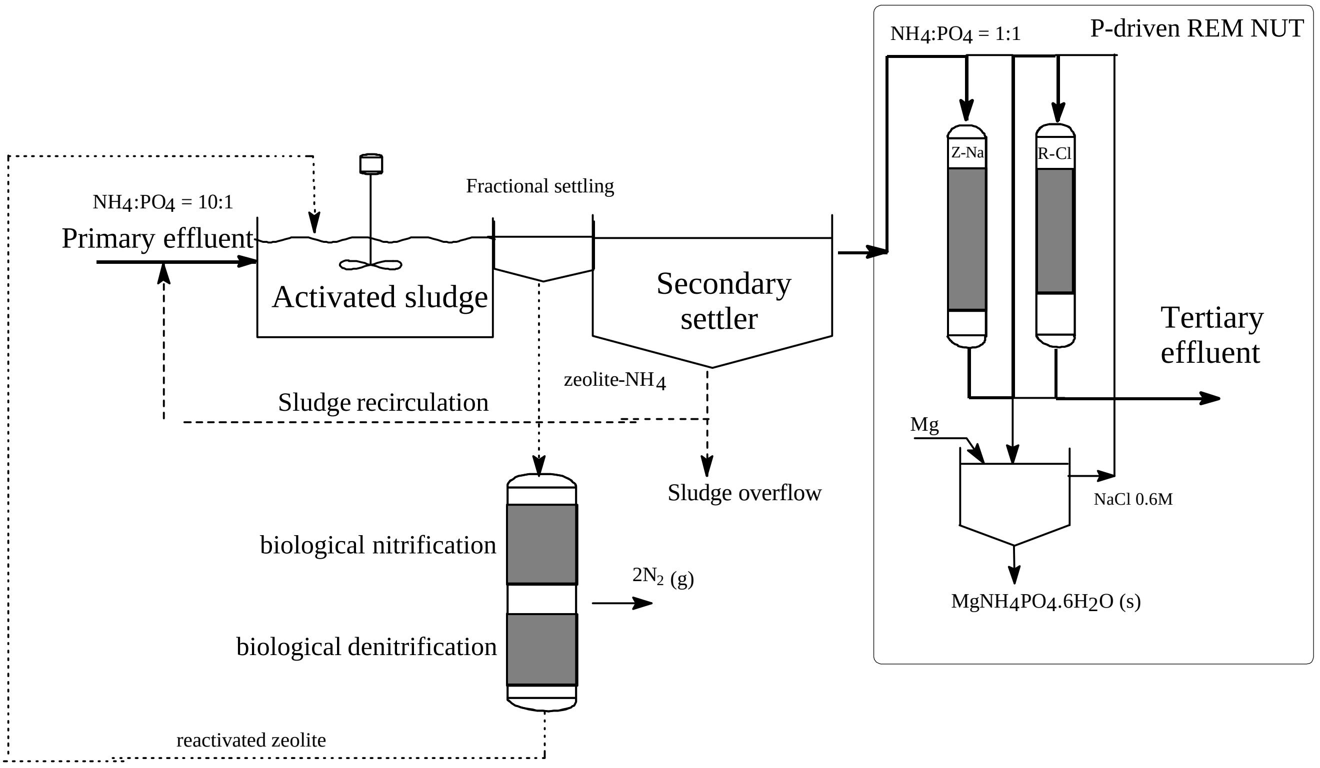

Fig.2 P-driven REM NUT® process layout with fractional sedimentation and biogeneration of the NH_4-loaded zeolite

Bath University, UK

An Integrated Biological/Adsorption Process for Phosphorus Recovery

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Adsorption is one of the technologies which is potentially attractive (technically and economically) for the recovery of phosphates from waste waters. The advantages of adsorption are that no additional sludge is produced, reagents are not needed to overcome high alkalinity, and wastewater pH is unaffected.

Proposed process:

In work partly funded by CEEP, Bath University is investigating a waste water treatment process using an anaerobic membrane bioreactor followed by phosphorus adsorption onto fly ash.

The aim is to design and test a novel, integrated process (Figure page 38) for recovering phosphates from sewage liquors in a form appropriate for industrial or fertiliser recycling. The process comprises:

- anaerobic membrane bioreactor to release soluble phosphorus in the permeate in a concentrated solution;
- energy generation from combustion of the methane, and residual solids disposal;
- adsorption column, using fly ash, to adsorb and recover phosphorus;
- desorption/separation system to release and recover phosphate product.

Fly ash is a residue that results from the combustion of coal in power plants. Research shows that fly ash is a good adsorbent for the removal of heavy metals from wastewaters [1]. Fly ash is also a good conditioner and it has been shown that sewage sludge conditioned with fly ash can be considered as non-hazardous, so that it can be landfilled or used for land application [2].

One of the main advantages of phosphorus removal using fly ash, compared to the phosphorus stripping by chemical dosing, is that it does not produce any excess sludge. The combination of high pH and readily available calcium in fly ash favours rapid precipitation of calcium phosphates that could be separated then recycled to the fertiliser industry. Further, the abundance of fly ash, and its ready availability, makes it a strong candidate in the investigation of an economical way to recover phosphorus.

An anaerobic membrane reactor has the advantages of being able to operate under small hydraulic residence times. The biomass is retained inside the reactor behind the membranes and the resulting high sludge ages give the potential benefit of a high efficiency of phosphorus release and increased organic matter biodegradation and methane generation. This should result in lower residual solids for disposal and a higher energy yield when the methane is put to power generation. Furthermore a submerged membrane bioreactor is attractive because of its low power costs in comparison with a system with an external recycle [3].

A University of Bath Research Studentship and a grant from CEEP BIT fund the project. Orion Research Inc and National Power have donated analytical instruments and fly ash samples respectively. The work is being carried out in close contact with related work underway at the BBSRC Institute of Grassland and Environ-mental Research, North Wyke, UK. It also runs alongside a major EPSRC project on "Membrane Bioreactors for Wastewater Treatment" involving the University of Bath, Cranfield University, Imperial College of Science, Technology & Medicine, and seven of the water utility companies in the UK.

References

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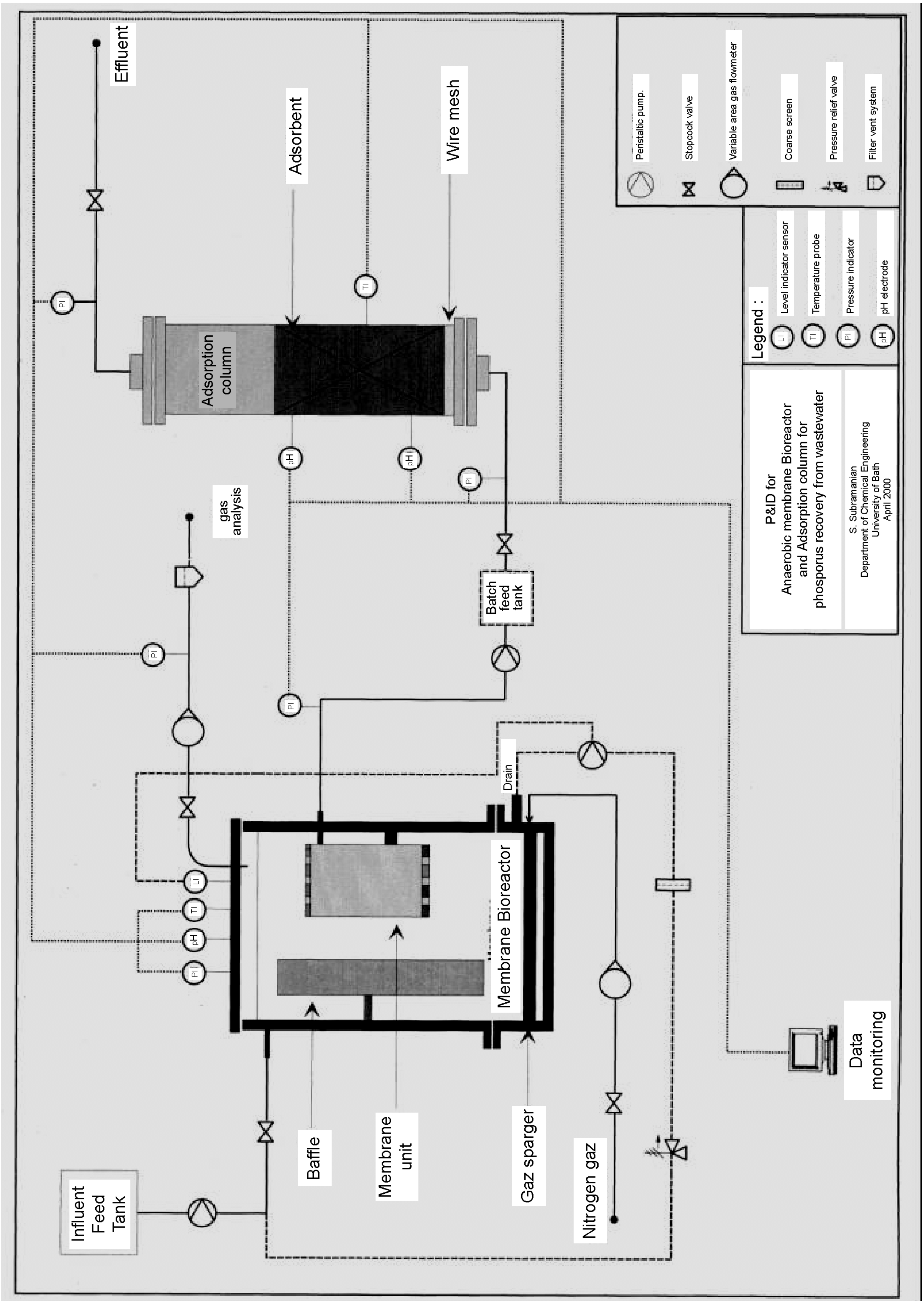
Figure 1 : Bath University :a schematic diagram of the process



Queen's University, Belfast

Biologically-driven phosphate precipitation

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In work partly funded by CEEP, Queen's University Belfast/the Questor Centre are looking at the possibility of developing phosphorus recovery by inducing phosphate precipitation onto the cell surface of sewage sludge micro-organisms by local biological-chemical mechanisms.

In a number of biological systems including wastewater sludges, bacteria can act as a seed for crystallisation and precipitation reactions. Research on heavy metal removal by Lynne Macaskie's group in the University of Birmingham has shown that the cellular efflux of phosphate during organic phosphate degradation or inorganic polyphosphate hydrolysis can promote metal phosphate precipitation on cell surfaces(1,2). The formation of insoluble metal-phosphate complexes at the cell surface is driven by the concentration gradient of phosphate around the cell, inducing crystal formation and growth.

Why not apply this technique to achieve phosphorus recovery in biological P-removal sludges ? So just how would this work? A cellular efflux of phosphate occurs under anaerobic conditions during Enhanced Biological Phosphorus Removal. The objective of this research is to use the biologically induced local conditions on the cell membrane surface to achieve phosphate precipitation without the need to manipulate the pH or chemical conditions of the whole liquid stream (thus avoiding chemical reagent addition and/or enabling phosphate precipitation to be achieved from relatively low phosphate concentration solutions).

Precipitation could perhaps be optimised to form crystalline phosphates on the surface of phosphate-releasing cells by adding calcium ions during the anaerobic release of phosphate from polyphosphate. If the cycle was repeated with sludge recycling, then significant quantities of calcium phosphates could be precipitated onto sludge organism cell surfaces, and these could then be recovered.

Recent research(3) has shown experimental calcium phosphate precipitation with formaldehyde-inactivated sludge below pH 8.0. During anaerobic phosphate release, the pH and conductivity of the wastewater also rise: these conditions, and the gradient of phosphate around the cell, may create the right conditions to drive the equilibrium to favour the formation of calcium phosphates when conditions in the bulk solution are less favourable. The objective should perhaps be to add sufficient calcium to precipitate only a proportion of the phosphate. This may help to minimise the voluminous nature of the sludge associated with chemical phosphate precipitation, and reduce the excess of calcium normally added.

In the following aerobic period, in which the bacterial cells reform their quotient of stored polyphosphate, the potential for biological uptake of phosphate from the wastewater would be enhanced as much of the phosphate previously released is now sequestered as a precipitate. In subsequent anaerobic periods, the efficiency of crystal formation would be increased as nucleation has already occurred.

To test the feasibility of this approach, a fill-and-draw reactor with an operating volume of 4 litres has been set up in the laboratory and seeded with sludge from a full scale EBPR municipal waste water treatment plant. Initial efforts have concentrated on establishing a stable phosphate cycle in the sludge, and in understanding the changes in the relevant chemical species during anaerobic/aerobic periods. Excess sludge will be used for batch experiments before calcium is introduced as a precipitant into the regime.

Should this approach be successful, sludge containing two independent forms of phosphate, polyphosphate and precipitated phosphate salts, would be formed. The amount of polyphosphate in the sludge at the end of each cycle should be relatively constant (typically 9% P for EBPR sludges); the proportion of additional phosphate precipitate present would increase with sludge age.

Assuming that all this is possible, there still remains the problem of how to recover the phosphorus from the sludge. Research has shown that sludge incineration followed by water elution(4) can extract biologically-sequestered polyphosphate from EBPR sludges. However, the additional presence of calcium phosphates would likely require chemical extraction. Thermal treatment could also be used to eliminate the organics leaving a material with a relatively high calcium phosphate content. Other suitable methods are likely to depend on the phosphorus content achievable and the concentration of metals present in the sludge.

Queen's University Belfast: proposed operation of biologically driven phosphate precipitation. In initial cycles crystal nucleation is likely to be the rate-limiting step; in subsequent cycles precipitation will be more rapid. The goal is to produce a compact sludge containing precipitated phosphates in addition to biologically sequestered polyphosphate with a total phosphorus content higher than would be possible with either biological or chemical phosphate removal alone (figure below).

References
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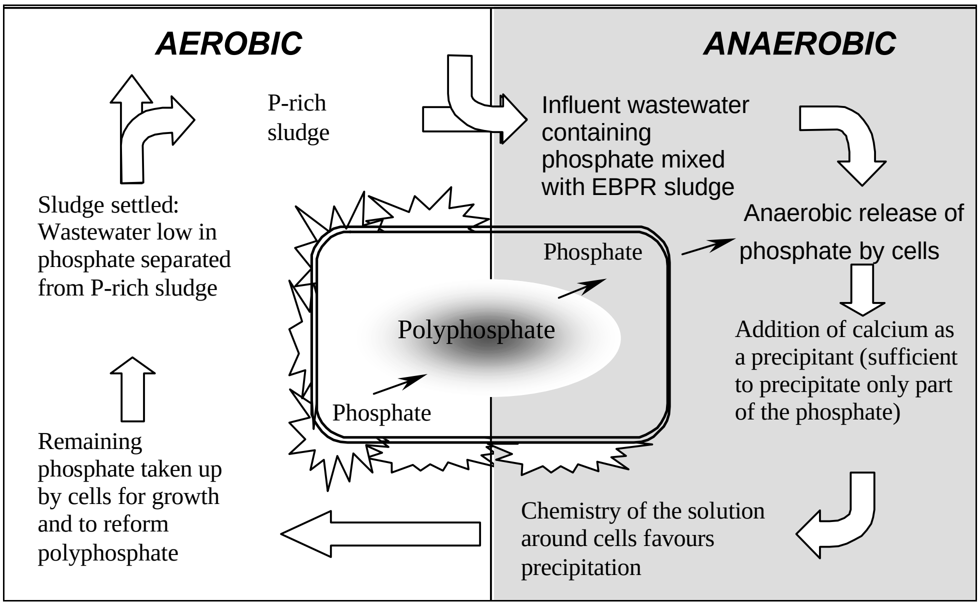

A summary of key published papers relevant to P-recovery

Abbona F., Lundager Madsen H.E. & Boistelle R. (1988). The final phases of calcium and magnesium phosphates precipitated from solutions of high to medium concentrations. Journal of crystal growth, vol. 89, pp. 592-602

This paper discusses the formation of calcium and magnesium phosphates in simple batch systems at 25°C and P concentrations: 0.050 * [P] * 0.500M. It is shown that initial precipitation was followed, in some cases, by phase transition due to formation of a more stable phase with time. Early calcium phosphates precipitated were brushite ($CaHPO_4*2H_2O$) and monetite ($CaHPO_4$). Newberyite ($MgHPO_4*3H_2O$) and struvite ($MgNH_4PO_4*6H_2O$) were the magnesium phosphates identified. **A key observation of this study was that the phases precipitating first were not those most supersaturated, but those that nucleated faster.**

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

The paper investigates the possibility of removing phosphate from a carbon-nitrogen wastewater treatment plant, via the precipitation of struvite. Experiments using anaerobic supernatant from the treatment plant (85,000 equivalent inhabitants) showed satisfactory P removal at low P concentrations (30-60 mg PO_4/l), in the form of struvite and struvite/hydroxyapatite, without Mg or Ca addition. **The process involved use of quartz sand, and crystallisation occurred in about 100 minutes. Only CO_2 stripping with air was sufficient to increase the pH to an operative value.**

A summary of key published papers relevant to P-recovery

Borgerding J. (1972). Phosphate deposits in digestion systems. Journal of the water pollution control federation, vol. 44, pp. 813-819

This is an investigation into crystalline buildup (struvite, $MgNH_4PO_4*6H_2O$) in pipes of a wastewater treatment plant. The in-situ solubility of struvite was determined to be $3.9*10^{-10}$ which is much higher than the solubility determined in pure water ($2.5*10^{-13}$). The causes given for the precipitation are high surface: volume ratio in pipes, roughness of the interior of the pipes, increase in energy by vibration of the sludge screens and a pressure decrease at bends causing CO_2 release followed by a rise in pH.

Christoffersen J., Christoffersen M.R. & Kjaergaard N. (1978). The kinetics of dissolution of calcium hydroxyapatite in water at constant pH. Journal of crystal growth, vol. 43, pp. 501-511.

The dissolution rate of synthetic hydroxylapatite was measured in pure water at a temperature of 25°C at a constant pH in the range 6.6-7.2, using a pH stat method. **On the basis of the results it was suggested that dissolution rate is process controlled by the rate of release of the components from the crystal surface, rather that the rate of diffusion of these components into the solution**.

De Rooij J.F., Heughebaert J.C. & Nancollas G.H. (1984). A pH study of calcium phosphate seeded precipitation. Journal of colloid and interface science, vol. 100, pp. 350-358.

This is a study of the influence of pH on the formation of calcium phosphate on octacalcium phosphate seed crystals at 37°C, using a constant composition method. **It was found that in the pH-range 5-5.5 dicalcium phosphate dihydrate ($CaHPO_4*2H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6*5H_2O$) formed, whereas in the range 5.5-7 octacalcium phosphate was the only phase formed. At higher pH (7.4-8) octacalcium phosphate and hydroxylapatite-like ($Ca_5(PO_4)_3OH$) crystals formed.**

Eggers E., Dirkzwager A.H. & Van der Honing H. (1991). Full-scale experiences with phosphate crystallisation in a crystallactor. Water science and technology, vol. 23, pp. 819-824.

The results of a full-scale phosphate removal plant running for a year are discussed. Phosphate is removed from wastewater by means of a fluidised bed with sand grains as seeding material. The process works with a maximum carbonate concentration of 2 mmol/l and a pH between 10-10.5. **It was possible to reduce P-levels to 0.5 mg/l**.

Heughebaert J.C., Zawacki S.J. & Nancollas G.H. (1990). The growth of non-stoichiometric apatite from aqueous solution at 37°C: Methodology and growth at pH 7.4. Journal of colloid and interface science, vol. 135, pp. 20-32.

The precipitation of non-stoichiometric apatite using a hydroxylapatite seeding material was studied at a temperature of 37°C, pH of 7.4, using a method of constant composition. It was concluded that the apatite formed under these conditions is calcium deficient with a Ca/P molar ratio of 1.57 and a molecular formula of $Ca_{9.43}(HPO_4)_{0.57}(PO_4)_{5.43}(OH)_{1.43}$.

Hirasawa I. (1996). Study on the recovery of ions in wastewater by crystallization. Memoirs of the School of Science & Engineering, Waseda University, vol. 60, pp. 97-119.

The article reviews Javanese research on recovery of ions, after wastewater treatment. The topics considered include the efficiency of seeding by a range of materials (marble, calcium carbonate, activated carbon, bone char and phosphorus rock) as a function of mass, experimental work on the crystallisation of magnesium ammonium phosphate, crystal properties of the precipitate as a function of composition and phosphorus removal using iron.

Inskeep W.P. & Silvertooth J.C. (1988). Inhibition of hydroxyapatite precipitation in the presence of fulvic, humic and tannic acids. Journal of the american soil science society, vol. 52, pp. 941-946.

The precipitation of hydroxylapatite ($Ca_5(PO_4)_3OH$) is studied using a pH-stat method in the presence of different acids. It was concluded from the results that the presence of large acids (high atomic weight) like fulvic, humic, tannic and citric acids decreases the rate of precipitation.

Joko I. (1984). Phosphorus removal from wastewater by the crystallisation method. Water Science and Technology, vol. 17, pp.121-132.

In this paper the concentrations of calcium, phosphate and pH appropriate for the precipitation of calcium phosphates was studied in batch experiments. **It is shown that in a seeded flow through pilot plant using sewage effluent the concentration of phosphorus can be decreased to low levels**.

Katsuura H. & Ueno, Y. (1998). Phosphorus recovery technologies from sewage treatment plant: phosphorus resource recovery system, granule forming phosphorus removal process. Environmental Conservation Engineering, vol. 27, pp. 397-402.

The problem of clogging due to struvite deposit formation in wastewater pipes was studied. A method of early struvite precipitation, following addition of Mg was proposed, and the separation of struvite crystals from the suspended solids was investigated. Agitation by aeration of the suspension in a vessel was found to produce large composite granules of recoverable quality.

Kibalczyc W. (1989). Study of calcium phosphate precipitation at 37 °C. Crystal research and technology, vol. 24, pp. 773-778.

The precipitation of calcium phosphate has been studied at a temperature of 37°C and a pH of 7.4. The initial Ca/P ratio in the experiments were 1.33 and 1.67, sufficient for the precipitation of ocatcalcium phosphate (OCP) and hydroxylapatite (HAP). **The precipitation of calcium phosphate occurs through a fast precipitation of an amorphous calcium phosphate called ACP1 which quickly transforms into another precursor called ACP2**. The transformation is through dissolution (which causes a change in solution pH) and flocculation of the ACP2. In time, ACP2 will transform to the more stable hydroxylapatite.

A summary of key published papers relevant to P-recovery

Koutsoukos P., Amjad Z., Tomson M.B. & Nancollas G.H. (1979). Crystallisation of calcium phosphates. A constant composition study. Journal of the american chemical society, vol. 102, pp. 1553-1557.
The crystallisation of calcium phosphate onto seeding material was studied using a constant composition method. **At low supersaturation direct precipitation of highly crystalline hydroxylapatite was observed.**

Koutsoukos P.G. & Nancollas G.H. (1981). The morphology of hydroxyapatite crystals grown in aqueous solution at 37°C. Journal of crystal growth, vol. 55, pp. 369-375.
The crystallisation of hydroxylapatite (HAP) is studied within the pH range of 5-8.5 with a constant composition method. In these experiments direct precipitation of HAP onto HAP seeding material was observed. The morphology of the formed HAP changed when pH was increased. **In a more acidic environment HAP precipitates in a plate-like form while at higher pH HAP precipitates in a needle-like form**.

Liberti L., Limoni N., Lopez A. and Passino R. (1986). The RIM-NUT process at West Bari for removal of nutrients from wastewater: first demonstration. Resources and conservation, vol. 12, pp. 125-136.
The first demonstration of a new process developed to remove N and P from wastewater and in a demonstration plant is discussed. In the process ammonium and phosphate is recovered from wastewater by ion exchange using natural zeolites and a basic anion resin. The resin is then regenerated and the regeneration eluates are mixed and magnesium is added. This reaction results in the formation of struvite, which is separated from the solution. The struvite can be used as a fertiliser. **The results show that N and P are removed down to acceptable levels**.

Maekawa T., Chung-Min Liao & Xing-Dong Feng. (1995). Nitrogen and phosphorous removal for swine wastewater using intermittent aeration batch reactor followed by ammonium crystallization process. Water Research, vol. 29, pp. 2643-2650.
The optimal conditions for ammonium phosphates crystallisation are given. This process is used to remove NH_4-N and to bring up the C/N ratio but it does not remove phosphorus. After an aeration period the BOD, T-N and NH_4-N are removed to lower concentrations. **PO_4-P is removed by flocculation and precipitation by adding $CaCl_2$.**

Matsumiya Y., Yamasita T. & Nawamura, Y. (2000). Phosphorus removal from sidestreams by crystallisation of magnesium ammonium phosphate using seawater. J. CIWEM, vol. 14, 291-296.
A pilot study of phosphorus removal as struvite, at the Hiagari sewage works. The plant is operating biological phosphorus removal, and the study involved addition of 9-10% seawater to the digester sludge dewatering liquor. The tests were carried out in an aeration stirred 1100 litre pilot reactor. 70% P-removal was achieved with a reactor residence time of 10-12 minutes (at pH 8.03) or 29 minutes (at pH 7.77) at levels ranging from 64-110 mg P/l and without seeding.

Meyer J.L. (1983). Phase-transformations in the spontaneous precipitation of calcium phosphate. Croatica chimica acta, vol.56, pp. 753-767.
The paper describes experiments carried out to determine precursor phases to the precipitation of hydroxylapatite (HAP). It has been shown that the precipitation of HAP in a pH-range of 7-9.25 proceeds through two stages. First an amorphous calcium phosphate is precipitated this then undergoes an amorphous-crystalline transformation to an octacalcium phosphate like phase which undergoes a crystalline-crystalline transformation into HAP.

Momberg G.A. & Oellermann R.A. (1992). The removal of phosphate by hydroxyapatite and struvite crystallization in South Africa. Water Science & Technology, vol. 26, pp. 987-996.
Phosphate removal by hydroxylapatite (HAP) and struvite crystallisation is studied in lab-scale experiments. A pond effluent was used as influent and parameters such as pH, Ca and Mg concentration were adjusted to optimise P-removal. **The experiments indicate that optimum conditions for effective P-removal are: pH > 9.5 and the addition of calcium for HAP crystallisation and pH > 8.0 and addition of magnesium for struvite crystallisation**.

Muro S., Abe S. & Yamasaki M. (1994). MAP (Magnesium ammonium phosphate) process pilot test. JSWA Conference, pp. 500-503 (in Japanese).
The paper describes the wastewater treatment programme developed by Fukuoka City, to prevent eutrophication of Hakata Bay. The treatment plant performs P-removal using anaerobic/aerobic activated sludge and MAP removal at full scale (25,000 m^3 equivalent). MAP precipitation takes place in a fluidised bed, and is assisted by introduction of air and addition of NaOH and MgCl.

Nancollas G.H., Amjad Z. & Koutsoukos P. (1979). Calcium phosphates - speciation, solubility and kinetic considerations, in: Chemical modelling in aqueous systems, pp. 475-497.
An overview is given of research that has been carried out into the influence of foreign ions on the kinetics of precipitation of calcium phosphates. **Foreign ions such as magnesium and strontium will inhibit precipitation while fluoride ions accelerate precipitation by formation of fluorapatite**.

Nancollas G.H., Lore M., Perez L., Richardson C. & Zawacki S.J. (1989). Mineral phases of calcium phosphate. The anatomical record, vol. 224, pp. 234-241.
In this study a constant composition method was used to investigate the crystallisation/precipitation of calcium phosphates. The first phase to be formed was dicalcium phosphate dihydrate (DCPD). DCPD then dissolved and re-nucleated as octacalcium phosphate (OCP), which subsequently transformed into hydroxylapatite (HAP). **It was found that the hydroxylapatite formed was not stoichiometric**.

A summary of key published papers relevant to P-recovery

Ohlinger K.N., Young T.M. & Schroeder E.D. (2000) Postdigestion struvite precipitation using a fluidised bed reactor. Journal of environmental Engineering, pp. 361-368.

The possibility to precipitate struvite from postdigestion was studied using a pilot scale fluidised bed reactor. The removal of phosphate through precipitation of struvite was effective and was made more efficient by using an elevated pH and struvite seed material.

Pavan P., Battistoni P., Bolzonella D., Innocenti L., Traverso P. & Cecchi F. (2000). Integration of wastewater and OFMSW treatment cycles: from the pilot scale experiment to the industrial realisation - the new full scale plant of Treviso (Italy). Water Science & Technology, vol. 41, 165-173.

The paper discusses scientific developments following recent legislation in Italy, encouraging separate collection of organic fraction of municipal solid waste (OFMSW). **The results from pilot scale experiments investigating the possibility to integrate organic waste and wastewater treatment cycles, via using the light organic fraction produced from the anaerobic fermentation of OFMSW as readily biodegradable organic carbon source for biological nutrient removal**. The addition of this effluent from the fermentation unit to wastewater under treatment achieved nitrogen and phosphorus removal of about 70-80%. A full scale plant at Treviso (70,000 EI) has been operating since July 1999 and a simulation of the plant is presented using the AMS_2 model.

Seckler M.M., Bruinsma S.L. & Van Rosmalen G.M. (1996). Phosphate removal in a fluidized bed-1 and 2. Water research, vol. 30, pp. 1585-1596.

In this paper the results are shown of a study into phosphate removal with a fluidised bed reactor. Phosphate is precipitated as an amorphous calcium phosphate ($Ca_3(PO_4)_2$). **Phosphate removal rates of 50-65% were achieved in the absence of carbonate and magnesium. A conversion of 80-95% was achieved when carbonate and magnesium were present possibly indicating a co-precipitation of $CaCO_3$ and $Mg_3(PO_4)_2*22H_2O$.**

Somiya I., Tsuno H. and Yoahino M. (1989). Study on phosphorus and nitrogen removal by struvite recovery. 26th annual conference of Japan sewage works association, pp. 400-402.

An artificial solution, simulating anaerobic sludge digestion liquor, was investigated for struvite recovery in batch experiments. Parameters such as pH, experimental time and mixing strength were investigated.

Waki N., Kondo H. & Nishida M. (1987). Study on phosphorus removal from digester supernatant by aeration. J. of water and wastewater, vol. 29, pp. 10-14 (in Japanese).

The authors report on observations of precipitation of struvite, as a result of CO_2 release due to aeration of wastewater from sludge digestion.

Yokoyama K., Iida Y. & Sagai M. (1988). Treatment and disposal of phosphates by recovery of struvite from sludge containing concentrated phosphorus. Japan Society of Civil Engineers Annual Conference Abstracts II, vol. 43, pp. 1074-1075 (in Japanese).

The paper reports on batch treatment tests for struvite recovery from the wastewater treatment plant of Kobe City. The effect of Mg dosing and pH were investigated. At a dosing rate of 1:1 magnesium:phosphate, more than 90% of phosphate is removed at pH over 9.

Zoltek J. (1974). Phosphorus removal by orthophosphate nucleation. Water pollution control federation, vol. 46, pp. 2498-2520.

This publication investigated a method of phosphate removal from secondary wastewater. Results are given from both batch and column experiments. **In the column experiments wastewater was led through a column of phosphate rock, operating as seeding material**. The phosphate concentration of the effluent was monitored. The influence of temperature, pH, magnesium and carbonate on the rate constant were also studied. The paper concluded that the method appeared promising although the surface area of the used seeding material must be increased up to 100 m^2/g.

The SCOPE Newsletter is produced by the CENTRE EUROPEEN D’ETUDES DES POLYPHOSPHATES, the phosphate industry’s reserach association and a sector group of CEFIC (the European Chemical Industry Council).

The SCOPE Newsletter seeks to promote the sustainable use of phosphates through recovery and recycling and a better understanding of the role of phosphates in the environment.

The SCOPE Newsletter is open to input from its readers and we welcome all comments or information. Contributions from reader are invited on all subjects concerning phosphates, detergents, sewage treatment and the environment. You are invited to submit scientific papers for review.

Articles and information concerning P-Recovery available on request from CEEP

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- ☐ "Environmental Technology" Magazine, edition devoted to phosphorus recovery, July 1999, 140 papers
- ☐ First International Conference on Phosphorus recovery for Recycling, Warwick University, UK, May 1998, summary of discussions
- ☐ Phosphorus recovery brochure produced by CEEP, 1998
- ☐ An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertiliser markets" Gaterell, Gay, Wilson, Gochin & Lester, Environmental Technology vol.21, n° 9, September 2000
- ☐ Phosphorus recovery from animal manure - the possibilities in the Netherlands", 1998
- ☐ Summaries of published work concerning phosphorus recovery published in previous numbers of the SCOPE Newsletter:
  - ☐ Sweden - phosphorus and nitrogen recovery from urine - SCOPE 40
  - ☐ Italy - studies on struvite precipitation and full-scale reactor recovering struvite by aeration at Treviso
  - ☐ Municipal sewage works - SCOPE 39, 35, 33, 28
  - ☐ struvite fertiliser value - SCOPE 38, 37
  - ☐ struvite precipitation chemistry and experimentation in the USA - SCOPE 38, 36
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