PHOSPHATE FIXATION IN WASTE WATER BY MEANS OF CONTROLLED STRUVITE FORMATION

PROJECT 250

by

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EXECUTIVE SUMMARY

BACKGROUND

In 1988, as a result of work done by the Division of Water Technology on "Phosphate crystallization in activated sludge systems" (Project 215), the Water Research Commission appointed the Division of Water Technology to investigate the fixation of phosphate in wastewater by means controlled struvite formation. This work was run in parallel with Project 215 and its primary objective was to investigate the feasibility of immobilizing dissolved orthophosphate arising from biological removal from municipal effluents by means of magnesium ammonium phosphate removal (or struvite) formation. Treatment of liquors arising during anaerobic digestion of the phosphate-rich sludge produced in biological nutrient removal plants as well as phosphate enriched mixed liquor within the modified activated sludge plant itself. The research approach, techniques and apparatus utilized in both projects were similar, but were not seen as an overlap since the struvite process was envisaged as having mainly an off-stream application while the calcium process was essentially as a mainstream operation.

MOTIVATION

The uncontrolled precipitation of the mineral struvite, which essentially consists of magnesium ammonium phosphate, is a major problem in many wastewater conveyance and treatment systems. Heat exchanger surfaces in digester systems and pipe networks utilized in treatment plants employing such processes are particulary prone to scaling and clogging as a result of struvite precipitation when ammonium, magnesium and phosphate are present in sufficient quantities. The premise of this project is that struvite formation, which is normally experienced as a serious operational problem, can be turned into an effective method of phosphate immobilization, provided the process is properly engineered and controlled. While the process can be used directly to treat raw or settled domestic sewage in activated sludge or other plants, the most promising applications pertain to enhanced phosphate removal plants and particulary the treatment of anaerobic digester effluents. In the case of direct application, struvite crystallization could be used to immobilise part or all of the phosphate which is primarily concentrated and then released by the microbial biomass in the anaerobic stage of nutrient removal plants, thus enabling consistently lower effluent phosphate concentrations to be obtained. In addition, stoichiometry shows that the ammonium load on the nitrification stage, and hence also the aeration requirement, would be proportionately reduced.

AIMS OF THE PROJECT

The specific objectives of the research were the following:

- Verification, or development where necessary, of the kinetics of struvite formation in digester liquors and activated sludge mixed liquor
- Development of design and operating criteria for a struvite precipitation/crystallization system

- Pilot-scale evaluation of struvite formation
- Technology transfer by compiling a document which can be issued to consultant engineers and other interested parties by the WRC.

MAIN FINDINGS

Scaling as a result of struvite formation can be a serious problem in many wastewater treatment systems. Problems are often encountered in the treatment of animal wastes, especially in piggeries. It is possible, however, to turn struvite formation into a method of phosphate immobilization. Effluents containing high phosphates, such as anaerobic digester effluents or the anaerobic stage of biological nutrient removal plants, have been identified as potentially suitable.

A literature survey indicated that, in addition to inorganic formation or precipitation of struvite, a large number of bacteria are responsible for struvite formation in microbial environments.

Laboratory-scale and pilot scale tests have indicated struvite formation in anaerobic digester effluents after dosing with $MgCl_2$ and adjusting the pH to more than 8. Phosphorus fixing of up to 90% was obtained.

Struvite crystallization was studied on a laboratory scale in fluidized bed reactors. Supplementation of anaerobic digester effluents with both $MgSO_4$ and K_2HPO_4 enhanced struvite formation. With pH adjustment to 9,5, 99% of phosphate could be removed in a continuous flow reactor as a result of both struvite and hydroxyapatite formation.

Effective struvite formation can contribute significantly to phosphate removal and will depend on four major parameters :

- The presence of sufficient magnesium and ammonia
- The presence of sufficient phosphate
- An alkaline enviroment
- Suitable seed material

The required mass ratio (complying with the 1 : 1 : 1 molar ratio) for effective and efficient struvite formation is 1,71 Mg : 1 N : 2,21 P. While most sewage effluents contain large amounts of ammonia, there is usually a deficiency of magnesium and phosphate. Supplementation with these components was necessary to establish conditions in the effluent which were conducive to struvite formation.

The use of quartz sand as a seed material proved to be suitable, as it did not intefere with the struvite formation and provided an inert surface on which crystallization could take place.

Precipitation patterns can be complex in liquors or effluents with many components, but it is possible to predict the types of precipitates that may be expected from chemical modelling.

Potentially the most rewarding application of struvite formation, however, is to be found in the treatment of effluents arising from the anaerobic digestion of excess phosphate accumulating sludge withdrawn from nutrient removal plants. These liquors contain high concentrations of ammonia and phosphate. Recycling such effluents to the head-of-works would simply create a closed loop and thus another means of phosphate disposal or elimination needs to be found. Harnessing struvite formation in a controlled environment presents itself as one of the best ways to immobilise not only the dissolved phosphate but also an equivalent mass of ammonia. The troublesome problems of disposing phosphate- and ammonia-rich effluents, and the indiscriminate precipitation of struvite on surfaces where it is highly detrimental, can both be solved if the precipitation/crystallisation can be made to occur under controlled conditions in a reactor designed for that purpose.

The controlled formation of struvite by means of crystallisation in effluents from anaerobic digesters will have the following advantages:

- enhance biological phosphate removal in activated sludge plants
- reduce anaerobic digester maintenance costs by reducing scaling problems in pipelines and pumps
- quantitatively reduce phosphate concentrations in effluents to levels which are more compatible with the environment
- make phosphates, ammonia and magnesium available to the agricultural sector as a slow release fertiliser for plant growth.

This study did not go into design or operating criteria for a struvite crystallization/precipitation system, since these aspects have been dealt with in a companion report entitled 'Phosphate crystallization in activated sludge systems'. Struvite formation is nevertheless seen as a potentially useful method for phosphate reduction as part of a side-stream process in a sewage treatment plant.

A technology transfer document has been compiled to transfer the findings of the project, thus providing an additional tool to local authorities, consultants and industrialists involved in enhanced biological phosphate removal in modified activated sludge systems.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

1.1 Motivation

The uncontrolled precipitation of the mineral struvite, which essentially consists of magnesium ammonium phosphate, is a major problem in many wastewater conveyance and treatment systems. Heat exchanger surfaces in digester systems and pipe networks utilized in treatment plants employing such processes are particulary prone to scaling and clogging as a result of struvite precipitation when ammonium, magnesium and phosphate are present in sufficient quantities. The premise of this project is that struvite formation, which is normally experienced as a serious operational problem, can be turned into an effective method of phosphate immobilization, provided the process is properly engineered and controlled. While the process can be used directly to treat raw or settled domestic sewage in activated sludge or other plants, the most promising applications pertain to enhanced phosphate removal plants and particulary the treatment of anaerobic digester effluents. In the case of direct application, struvite crystallization could be used to immobilise part or all of the phosphate which is primarily concentrated and then released by the microbial biomass in the anaerobic stage of nutrient removal plants, thus enabling consistently lower effluent phosphate concentrations to be obtained. In addition, stoichiometry shows that the ammonium load on the nitrification stage, and hence also the aeration requirement, would be proportionately reduced.

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1.2 Phosphate removal from treatment plants and anaerobic digesters

1.2.1 *Biological phosphorus removal*

Enhanced biological phosphorus removal has been incorporated in many South African municipal wastewater systems in an effort to control eutrophification in receiving waters. Phosphate removal to effluent levels < 1,0 mg/ℓ is required in all the so-called sensitive catchments of the country, which has highlighted the need to develop improved techniques of dealing with the increased amounts of phosphorus retained in various parts of the treatment process.

Sludge from biological phosphorus removal plants contains much more phosphorus than their conventional counterparts. A feature of such plants is that the excess of the accumulated phosphorus may be released into the environment again when left under anaerobic conditions for a sufficiently long time. The effluent from such plants is usually returned to the biological phosphorus removal process. The increased phosphorus mass in the return water makes it increasingly difficult to achieve overall effluent concentrations of 1,0 mg P/ℓ or less. There is a need, therefore, to either prevent or lessen phosphorus release from sludge and to recover released phosphorus.

1.2.2 *Treatment of anaerobic digester effluents*

(a) The potential of struvite formation

The treatment and safe disposal of the phosphate-rich sludge from anaerobic digester plants is environmentally a sensitive, as well as an expensive, operation in that chemical treatment by means of dosing with $FeCl_3$ or $FeSO_4$ is becoming more and more costly. Phosphates, however, also can be immobilized by means of a controlled crystallization process.

Phosphates form many virtually insoluble, or completely insoluble, compounds which facilitate their chemical precipitation from wastewater. Among the inorganic nitrogen compounds there are no insoluble nitrites or nitrates, while ammonium forms a number of insoluble compounds. Of these, only the salt $MgNH_4PO_4{\cdot}4H_2O$, is applicable in sewage treatment technology. An advantage of this salt is that it contains valuable constituents which are not toxic to plants. Magnesium-ammonium-phosphate is a white crystalline powder. Mineralogically it is known as struvite and is found, for example, in guano. In MAP, the three elements P,N and Mg are present in a molar ratio of 1 : 1 : 1, whereas communal wastewater generally contains a surplus of ammonium compared to the other two elements. It is therefore necessary to add additional phosphate and magnesium to effect the precipitation of struvite. In principle, commercial alkali phosphates and magnesium salts. e.g. Na_2PO_4 and $MgCl_2$ can be used in the precipitation process but the resulting reaction produces large quantities of neutral salts, such as NaCl, which increase the salinity of the water. To avoid this, technical grade phosphoric acid (H_3PO_4) and magnesia (MgO) may be used instead (Schulze-Rettmer, 1991).

It must be noted that, even given optimum precipitation conditions, certain residual concentrations of ammonia and phosphate remain dissolved in the water. By the law of mass action, the solubilities of the ammonium and phosphate ions, together with that of the third ion, magnesium, are interrelated with one another. Schulze-Rettmer (1991), for example, found in a pilot test at a pH of 8,5 that 9 mg/ℓ NH_4-N and 20 mg/ℓ PO_4 remained in solution after precipitation. These concentrations are too high for the wastewater to be released into a water body. It is therefore proposed that the struvite process ideally should be applied as an intermediate purification process followed by post-treatment. The struvite process has only a minor influence on the organic compound content. In the case of organically polluted wastewater, struvite formation should therefore be followed by a biological treatment process. Taking these constraints into account, a number of combined biological and chemical treatment processes are available (Schulze-Rettmer 1991).

b) Anaerobic digestion

The traditional method of stabilizing primary and waste activated sludges is anaerobic digestion. These sludges can contain 7 to 8 % nitrogen and 2 - 5 % phosphorus (on a dry mass basis), and in the digestion process considerable solubilization of these nutrients occurs. For example, more than half of the organic nitrogen is broken down to ammonia while organic and other particulate phosphorus compounds are partially solubilized to orthophosphate. Depending on the concentration of solids in the digester feed, anaerobic liquors can contain up to 1000 mg ammonia-N/ℓ and 100 mg orthophosphate-P/ℓ in solution as well as considerable quantities of soluble chemical oxygen demand (COD). The recycling of these liquors to nutrient removal plants could limit their ability to produce high quality effluents.

The phosphate content of digester liquors is responsible for other operational problems. For example, at Johannesburg's Northern Works, phosphate scales have occurred on heat exchanger tubes through which digesting sludge was recirculated. Deposits also occur on walls of supernatant liquor conditioning tanks and in transfer pipes between these tanks. The most serious problem is the scaling up of rising mains conveying digested sludge and conditioned liquors to holding dams. Hard deposits on a 300 mm pipe between the Northern Works and a holding pond one kilometre away became so serious that sections near the delivery side of the pump were reduced to an effective diameter of 80 mm. Pumping capacity and valve operation were so impaired that the system had to be cleaned out with hydrochloric acid. This treatment proved successful but had to be repeated on a number of occasions at considerable cost, after regrowth of the scale. Deposits are also known to occur in supernatant liquor conditioning tanks at the Southern Works and on occasion blocked a tank outlet pipe at Klipspruit. Similar problems have been reported from the Western Cape where anaerobic digesters are used to treat wine industry effluent. On the settling tanks following these digesters, phosphate scales have accumulated on overflow weirs and other mechanical plant components have also been encrusted with deposits. These scales were particularly hard and had to be removed by manual chiselling (Pitman, 1973; 1982).

(c) Presence of participating ions in anaerobic digester mixed liquor

Conditions in the anaerobic digestion process can create an environment which is ideal for the formation of phosphate scales. During digestion solids are solubilised to high ammonia and phosphate concentrations. The presence of magnesium at concentrations of 20 - 50 mg/ℓ and calcium at concentrations of 50 to 150 mg/ℓ lead to the formation of various phosphate precipitates. If the feed sludge is more concentrated, a greater concentration of these ions in solution will occur. Experience has shown that phosphate scales do not usually form inside digesters, only making their appearance once the liquid has left the digester and comes into contact with the outside environment. The equilibrium pH of most mesophyllic digesters is in the range 7,0 to 7,2 with the high concentrations of CO_2 producing a considerable bicarbonate alkalinity which buffers the system into this pH range. A slight precipitation probably does occur in digesters but the action is retarded by the relatively low pH and higher than ambient temperature (Pitman, 1973; 1982).

(d) Carbon dioxide evolution

Once the liquid has left the digester, precipitation conditions quickly improve due to the liquid coming into equilibrium with the outside environment. Two important changes occur : -

- Carbon dioxide gas is evolved to the atmosphere which causes a weakening of the bicarbonate buffering and the pH tends to rise
- The temperature decreases, eventually reaching ambient levels

Agitation will accelerate the cooling and CO_2 stripping will cause a more rapid pH rise. The combination of these two changes forces the solubility equilibrium into the solid phase and precipitation of phosphate occurs. This will either happen immediately or progress gradually over a period as the system moves slowly into ranges where precipitation occurs. A super-saturated state is also possible where precipitation will not happen until seeding or disturbance of the liquid occurs (Pitman, 1973; 1983).

(e) Considerations in respect of phosphate removal from digester liquors

The necessary cations are present in digester liquors in quantities that could theoretically precipitate up to 75% of the phosphate present, so that only a relatively small supplementation would be necessary to remove additional phosphate. In hard water areas sufficient cations may be present to ensure 95% phosphate removal. However, in soft water areas, supplementary magnesium may have to be added to ensure improved removal. It is preferable to add magnesium rather than calcium as this causes some ammonia to be co-precipitated and a better product is formed. The choice would obviously depend on the chemical costs involved (Pitman, 1973; 1982).

In general, two basic systems can be used to enhance struvite formation:

- The addition of a magnesium salt, viz. $MgSO_4$, and caustic soda in sufficient quantities to raise the pH of the liquor to 9,0 or 9,5. Only 40% of the stoichiometric requirement of magnesium may have to be added to achieve 94% phosphate removal due to the simultaneous precipitation of calcium phosphates.

- In the second process, liquor is heated to 70° C and magnesium salts such as $Mg(OH)_2$ and $MgCO_3$ are added. The high temperature causes the decomposition of bicarbonate buffers, CO_2 is evolved and the pH rises from 8,8 to 9,2 which, together with the added Mg^{2+}, causes the precipitation to occur. This precipitation at elevated temperatures probably explains why phosphate scales have occurred in digester heat exchangers. The evolution of CO_2 can also be accelerated if a vacuum and/or rapid stirring is applied. A temperature of 50° C is suitable if a vacuum of 700 mm Hg is applied. The elevated temperature has an added advantage that ammonia is also stripped from the liquor (Pitman, 1973; 1982).

Both processes produce good reduction in COD, suspended solids and total Kjeldahl Nitrogen (TKN) of the liquors. Also, at pH levels above 9,0 the nitrogen content of the precipitates decreases, indicating the formation of $Mg_3(PO_4)_2 \cdot 4H_2O$ at higher pH values. Similarly, when calcium concentrations are relatively high, the precipitate also contains $Ca_3(PO_4)_2$ as well as organic debris. Thus, the product obtained is not a pure magnesium ammonium phosphate but is nevertheless an excellent fertiliser containing 8,8% P and 2% N (Pitman, 1972; 1983).

The main factor causing the precipitation of phosphate from digester liquors is the increase in pH due to CO_2 evolution. Air-stripping can be used to remove CO_2 and elevate the pH to the point of phosphate crystallization. This has a number of advantages:

- It is cheaper than heating and vacuum application

- The CO_2 can be stripped to equilibrium in a short time

- Rapid cooling of the liquor occurs which lowers the temperature into ranges where precipitation is improved and digestion inhibited

- The addition of oxygen suppresses further anaerobic digestion and hence gas evolution. This prevents additional CO_2 going into solution and assists the settling of sludge when required at a later stage (Pitman, 1973; 1982).

1.3 Struvite formation in animal wastes

The problem of struvite formation is not unique to sewage plants, it has also occurred in several types of animal wastes (Westerman *et al.*, 1985). It has been identified in cattle liquid manure (Fordham & Schwetmann, 1977), on aerator paddles in an in-house cage rotor swine aerobic treatment system in Italy and on floating aerators in a modified anaerobic lagoon in Singapore (Kirkby, 1979). Struvite deposits also proved to be a major problem in a piggery waste plant in Singapore (Mohajit *et al.*, 1989). Struvite is also a major component of kidney stones. Inhibition of struvite formation has been achieved by the neutralisation of the urease enzyme which cleaves the urea molecule, releasing ammonia and thereby increasing pH and favouring struvite formation (Miller, 1979; Miller & Opher, 1974). Whether urease activity is a factor in struvite formation in swine and poultry recycle flush systems has not been studied.

Flushing systems for swine, poultry, dairy and beef facilities have become popular because labour, odour, and possibly health problems can be reduced by this approach. Recycling lagoon water for flushing is normally conducted to reduce fresh water consumption and to minimize liquid input to the lagoon. However, the buildup of crystalline material in pumps and pipes of the recycle systems of swine and poultry farms have caused serious problems in several states of the USA as indicated in survey responses reported by Safley *et al.* (1982). Many of the present recycle systems have pipes installed underground and sometimes embedded in concrete, and thus cleaning or replacement of valves, elbows, tees and couplings where the crystalline buildup is worst is often a major task. The amount and rate of crystalline buildup seems to vary from system to system, and apparently beef and dairy systems have had few if any problems with crystalline buildup (Westerman *et al.*, 1985).

1.4 Bacterially-induced struvite formation

Although the 'mechanical' induction of struvite precipitation, as in digester supernatant circuits, is of obvious importance in studies of the topic other mechanisms may contribute significantly to the problem. Among these is the role of bacteria in the formation of exocellular struvite.

The involvement of bacteria in the formation of exocellular crystals is well known. Hutchison (1961) reported on the occurrence of crystals within bacterial colonies of *Staphylococcus aureus*, which had previously been considered to be calcium carbonate. In cultures of *S. aureus*, grown on horse blood agar at room temperature, multiple crystals in a curious circular distribution typically occurred within the colonies after 2 to 4 days or longer. The crystals were some complex form of calcium phosphate and a variety of solid media which supported good *S. aureus* growth would also give good crystal formation. Cultures grown anaerobically, where growth is restricted, yielded no crystals. It was thought that the crystals were the result of alkaline conditions produced by *S. aureus* when grown in infusion or digest media, or the product of inorganic phosphates liberated from organic compounds by phosphatases produced by these organisms, or by both mechanisms.

Experimentation confirmed that the pH rise was the primary mechanism accompanying crystal formation. The 'fairy ring' arrangement of crystals was readily explained by the pH gradient between the centre of the growing colonies (pH about 8,8) and the surrounding medium (pH about 7,4). Between these extremes a relatively sharp rise in pH takes place in the short distance between the edge and centre of the colony. If Ca^{2+} and PO_4^{3-} ions diffuse from the medium into the colony, a point in pH will be reached on this gradient at which calcium phosphate will be thrown out of solution to form crystals. If the pH gradient is sharp enough, all available ions will be deposited in a circular zone, corresponding to the critical pH, before the centre of the colony is reached.

The occurrence of struvite in material rich in organic matter was reported long ago. For example, Robinson (1889) identified such crystals and suggested "... that the microorganisms produce the ammonia from nitrogenous organic matter in which they are growing and that it then combines with the magnesium phosphate present ...." Later, Beavon and Heatley (1962) identified crystals which occurred within colonies of *S. aureus* growing on nutrient agar as struvite and reported that other organisms, all of them increasing the pH of the medium during growth, formed similar crystals. They also found that the nature of the colonial crystals might vary with the ions available in the medium derived from different agars, nutrients, or tap water and drew the following conclusions:

- Apparently identical crystals may appear in the nutrient agar as well as, or instead of, in colonies.
- Crystals are larger and/or more numerous, the larger the amount of Mg added (as sulphate) to the medium.
- The addition of Ca (as chloride) decreases, or in higher concentration prevents, the formation of extra- or intra-colonial crystals, presumably due to removal of some of the phosphate as insoluble calcium phosphate, which can be detected as a slightly increased opalescence in the medium in the higher concentrations used.
- When nutrient agars of different ionic composition are exposed to ammonia vapour large numbers of crystals form within the agar in a few minutes. They are larger in media which contain added Mg and scantier or absent altogether when extra Ca is present.
- When the same media is re-exposed to triethylamine vapour, the agar becomes alkaline as quickly as with ammonia, but only after an hour or two are any crystals seen, and they are very scanty or, when Ca has been added, absent.
- Intra-colonial crystals form more readily in rich media when colonies grow fast to a large size. Presumably the local concentration of ammonia is higher in such colonies than in smaller ones. Ammonia is readily detectable when such plates are opened, both by odour and the effect on litmus paper.

- Organisms other than the *Staphylococcus* spp., e.g. *Pseudomonas pyocyanea*, *Proteus* spp. and *Escherichia coli*, will form intra-colonial crystals; within any group those strains which form alkali the more readily are those in which crystals appear earlier and more abundantly.

- Crystals were also formed by the *Staphylococcus* in fluid media, possibly because the organisms tended to sediment and presumably caused a higher local ammonia concentration.

Shinano and Sakai (1975) obtained crystals of struvite (magnesium ammonium phosphate) and studied the effect of Mg^{2+} ion concentration on the type of $CaCO_3$ crystal that is precipitated by *Pseudomonas calciprecipitans* by raising the concentration of magnesium in proportion to the calcium content in culture media. They observed that struvite precipitated on the media, beside the crystallization of calcite ($CaCO_3$) and calcium carbonate monohydrate (CCM).

Increases in magnesium ion concentration relative to calcium caused a change in crystal form from $CaCO_3$ to CCM to struvite. The crystal formation itself was ascribed to the production of carbon dioxide and alkalinization as a result of bacterial metabolism, such as respiration and decarboxylation or deamination of nitrogenous substances.

Rivademeyra *et al.* (1983) investigated the conditions under which struvite is formed, what kinds of bacteria produce it and to what extent Mg^{2+} and Ca^{2+} ions influence its formation. Results showing the identities of 96 strains tested are given in Table 1.

Table 1. **Genera of bacterial strains capable of producing exocellular struvite**

Strain	**Total number of strains**[a]	**Number of positive strains**[b]
Acinetobacter sp.	5	1
Alcaligenes sp.	1	-
Arthrobacter sp.	18	3
Bacillus sp.	42	5
Brevibacterium sp.	2	1
Corynebacterium sp.	4	1
Flavobacterium sp.	2	1
Kurthia sp.	3	2
Micrococcus sp.	3	-
Listeria sp.	3	1
Pseudomonas sp.	12	5
Staphylococcus sp.	1	1

[a] *Number of strains tested belonging to the same genus.*
[b] *Number of strains producing struvite.*

They found that the number of struvite-producing strains increased as the amount of calcium acetate in the growth medium decreased. Ammonia was produced by all the strains that formed struvite. However, 75% of the strains that did not produce struvite also produced ammonia during their growth. Handschuh and Orgel (1973) found more struvite than apatite to be precipitated when phosphate was added to seawater containing more than 0,01 M NH_4^+. Therefore it is possible that in the experiments of Rivademeyra *et al.* (1983) the exocellular precipitation of struvite due to bacterial growth in media containing $P0_4^{3-}$ and Mg^{2+} ions took place as a consequence of the liberation of NH_4^+. However, the formation of ammonia by nonstruvite-producing strains indicates that the formation of ammonia by such bacteria is certainly not the only factor causing precipitation of struvite, although it may influence it. There must be other factors involved.

Strains found consistently able to produce large amounts of struvite were identified as belonging to the genera *Arthrobacter*, *Flavobacterium*, *Listeria* and *Pseudomonas*. However, 15 other strains of *Arthrobacter*, one of *Flavobacterium*, two of *Listeria*, and seven of *Pseudomonas* failed to produce struvite, which seems to indicate that there is no correlation between the production of these crystals and the taxonomic identify of strains capable of producing them. Struvite formation was influenced by Ca^{2+} ion concentration, and the number of crystals produced was strain-dependent. For a given microorganism a slight increase in the number of crystals formed was observed when less calcium acetate was supplied in the culture medium. This suggests that Ca^{2+} ions hindered the biological production of struvite, although an inhibitory effect by acetate cannot be excluded. Acetate may also affect the solubility of struvite.

In summary it may be concluded that struvite formation in microbial environments occurs readily and it may be induced by a variety of organisms. The predominant requirements for struvite formation are that the participating ions (Mg^{2+}, PO_4^{3-}, and NH_4^+) should be present and that the pH of the environment should be such that the solubility of the product is exceeded.

Microbial cultures can induce struvite precipitation in several ways. One route is via the excretion of ammonia, which may trigger struvite formation either directly or via the concomitant pH rise or by both such mechanisms.

The relationship between Mg and Ca seems to be an important factor controlling the formation of struvite in pure culture media. Struvite occurs readily when the Mg^{2+}:Ca^{2+} is 4 or higher.

In nutrient removal activated sludge and associated anaerobic digestion systems the propensity for struvite precipitation is enhanced by the biological phosphate and release mechanisms, especially because magnesium is accumulated and released together with phosphate, resulting in relatively high liquid phase concentrations.

2. THERMODYNAMICS AND KINETICS OF STRUVITE CRYSTALLIZATION

Magnesium ammonium phosphate has a molecular mass of 254,3. According to Borgerding (1972) the struvite crystal is composed (on a mass basis) of 9.8% magnesium, 7.3% ammonium, 38.8% phosphate, 44.1% water and organic compounds. Furthermore, concentrations of magnesium, ammonium and phosphate required for precipitation at $K_{sp} = 3.9 \times 10^{-10}$ are 17,5; 13,1; and 69,5 mg/ℓ, respectively. Borgerding (1972) hypothesized that the factors which may be responsible struvite formation are :

- relative surface to volume ratio. Crystal growth may be enhanced when the sludge is not being withdrawn and the fluid in the pipeline is in a quiescent state
- interior surface roughness aids crystalline growth, and the increase in energy caused by vibration or turbulent flow and the raising of pH when CO_2 is released as a result of pressure decrease also contribute to struvite formation.

Struvite has a low solubility in water, is highly soluble in dilute acidic solutions and highly insoluble in alkaline solutions. To form MAP the reactants must be present in the ratio 1,71 Mg : 1,0 N : 2,21 P. Thus, if digester liquor contained 100 mg/ℓ dissolved phosphate, 77 mg/ℓ and 45 mg N/ℓ (as ammonia) will be required to remove it all by the precipitation of this compound. In a typical liquor however, ammonia is present in excess quantities and magnesium is deficient. However, calcium can also take part due to the simultaneous precipitation of calcium phosphate ($Ca_3(PO_4)_2$ and thus needs to be considered as well.

Four crystalline species are possible in pure solutions containing Mg^{2+}, NH_4^+ and PO_4^{3-}: -

- Struvite or magnesium ammonium phosphate (S): $MgNH_4PO_4 \cdot 6H_2O$
- Newberyite or magnesium hydrogen phosphate trihydrate (N): $MgHPO_4 \cdot 3H_2O$ and trimagnesium phosphate in two states of hydration:
  - $Mg_3(PO_4)_2 \cdot 22H_2O$
  - $Mg_3(PO_4)_2 \cdot 8H_2O$

Following Abbona *et al.* (1982) the presence of trimagnesium phosphate was ignored in the pH range (3-9) for which the calculations were performed. In order to simplify the calculations the concentrations of the high pH species PO_4^{3-} and low species H_3PO_4 were neglected.

It must be stressed that the discussion which follows is for pure solutions and the presence of Ca^{2+}, SO_4^{2-} and other ions in real solutions will interfere, probably quite severely, with the crystallization processes. Furthermore, it is not clear whether amorphous solids analogous to calcium phosphate can form.

The thermodynamics of crystallization of S and N are discussed in 2.1. This gives the domains of stability of these two species. The kinetics of crystallization are briefly discussed in 2.2.

2.1 Thermodynamics of struvite crystallization

Two crystalline species are considered

1.	Struvite	$MgNH_4PO_4.6H_2O$	(S)
2.	Newberyite	$MgHPO_4.3H_2O$	(N)

The following solubility product constants are available in the literature (for 25 °C):

$$(S)MgNH_4PO_4\ (s) \overset{Ksp}{\rightleftarrows} Mg^{2+}(aq) + HPO_4^{2-}(aq) Ksp = 1.15x10^{-10}M^2 \cdots\cdots (1)$$

$$(N)MgHPO_4\ (s) \overset{Ksp}{\rightleftarrows} Mg^{2+}(aq) + HPO_4^{2-}(aq) Ksp = 3.09x10^{-6}M^2 \cdots\cdots (2)$$

Equations 1 and 2 lead to the following equations for solubility products

$Ksp\ (S) = f_{mg}\ [Mg^{2+}]\ f^{''}\ [HPO_4^{2-}]\ [NH_3]$ .... (3)

$K_{sp}\ (N) = f_{mg}\ [Mg^{2+}]\ f^{''}\ [HPO_4^{2-}]$ .... (4)

Where:

f_{mg} is the activity coefficient of Mg^{2+}
$f^{''}$ is the activity coefficient of HPO_4^{2-}
[ ] represents molar concentration.

The activity coefficient of NH_3 is assumed to be unity, because it is a neutral species.

Only one phosphate equilibrium is considered (Bates & Acree, 1943):

$$H_2PO_4^- \overset{K_2}{\rightleftarrows} + H \ (5) \quad K_2 = 6.339 \times 10^{-8}M \cdots\cdots\cdots\cdots \quad (5)$$

In addition the ammonia equilibrium must also be considered (Bates and Pingching, 1949):

$$NH_4^+ \overset{K_N}{\rightleftarrows} NH_3 + H^+ \quad K_N = 5.675 \times 10^{-10}M \cdots\cdots\cdots\cdots \quad (6)$$

Equations 5 and 6 lead to the following equations for the acid dissociation constants: -

$$K_2 = \frac{(H^+)\ f''\ [HPO_4^{2-}]}{f'[H_2PO_4^-]} \cdots\cdots\cdots\cdots\cdots\cdots \quad (7)$$

$$K_N = \frac{(H^+)\ [NH_3]}{f_N\ [NH_4^+]} \cdots\cdots\cdots\cdots\cdots\cdots \quad (8)$$

Where: (H^+) is the activity and $(H^+) = 10^{-pH}$
f' is the activity coefficient of $H_2PO_4^-$
f_N is the activity coefficient of NH_4^+

The total dissolved phosphate (P_T) and ammonia (N_T) concentrations are:

$$P_T = [H_2PO_4^-] + [HPO_4^{2-}] \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (9)$$

and

$$N_T = [NH_4^+] + [NH_3] \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (10)$$

Combining equations 9 and 7 yields:

$$P_T = \frac{(f'' (H^+)}{(f'K_2)} + 1) \; [HPO_4^{2-}] \; \cdots\cdots \; (11)$$

$$P_T = \gamma[HPO_4^{2-}] \quad \text{where } \gamma = \frac{f''(H^+)}{f'K_2} + 1 \; \cdots\cdots \; (11)$$

so

$$[HPO_4^{2-}] = \frac{P_T}{\gamma} \; \cdots\cdots \; (12)$$

and combining equations 10 and 8 yields

$$N_T = \frac{((H^+) + K_N f_N)}{(K_N f_N)}[NH_3] \; \cdots\cdots \; (13)$$

$$\epsilon[NH_3] \quad \text{where } \epsilon = \frac{(H^+) + K_N f_N}{K_N f_N}$$

$$\text{so } [NH_3] = \frac{N_T}{\epsilon} \; \cdots\cdots \; (14)$$

Combining equations 3, 12 and 14 and 4 and 12 yields

$$K_{sp}(S) = \frac{f_{mg} f'' \; [Mg^{2+}] \; P_T \; N_T}{\gamma\epsilon} \; \cdots\cdots \; (15)$$

so

$$[Mg^{2+}] = \frac{K_{sp}(S) \; \gamma \; \epsilon}{f_{mg} f'' \; P_T N_T} \; \cdots\cdots \; (16)$$

$$K_{sp}(N) = \frac{f_{mg}f'' \, [Mg^{2+}] \, P_T}{\gamma} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (17)$$

so

$$[Mg^{2+}] = \frac{K_{sp}(N) \, \gamma}{f_{mg}f'' \, P_T} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

Thus the concentrations of Mg^{2+} required can be determined if the activity coefficients are known.

The extended Debye-Hückel theory can be used to calculate activity coefficients:

$$-\log f_i = \frac{A \, Z_i^2 \sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

f_i is the activity coefficient of the ion of type i
A is a constant, $A = 0{,}522 \; M^{-1/2}$ for H_2O (Manov *et al.*, 1943)
Z_i is the charge on the ion of type i
μ is the ionic strength of the solution
B is a constant. $B = 0.331 \times 10^8 \; M^{-1/2} \, cm^{-1}$ (Manov *et al.*, 1943)
a_i is a constant relevant to the i th ion

$$a_{Mg^{2+}} = 8x10^{-8} \text{ cm}; \; a_{H_2PO_4^-} = a_{HPO_4^{2-}} = 4x10^{-8} \text{ cm}; \; a_{NH_4^+} = 2.5x10^{-8} \text{ cm}$$

(Kielland 1937).

Thus if the ionic strength of the solution is known, the activity coefficients can be calculated.

Ionic strength is defined as:

$$\mu = \tfrac{1}{2} \sum_i M_i \; Z_i^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

Where M_i is the molarity of the solution in ion of type i.
The concentrations of counterions will depend on the nature of the phosphate, ammonia and magnesium species used. In this case K_2HPO_4 is the phosphate species, $MgCl_2$ is the ammonia/ammonium species used. It is further assumed that HCl is used to adjust pH and that $[H^+] = [H_2PO_4^+] + [NH_4^+]$ so that the concentration of Cl^- counterions is $[H_2PO_4^-] + [NH_4^+]$.

The ionic strength determination is further complicated by an ion pairing equilibrium in solution, which results in a neutral species:

$$Mg^{2+} + HPO_4^{2-} \overset{K°}{\rightleftarrows} MgHPO_4 \text{ ,} K° = 490 \text{ M}^{-1} \quad (25°C) \cdots\cdots \quad (21)$$

This leads to the following equation:

$$K° = [MgHPO_4]/f_{mg}[Mg^{2+}]_F \, ''[HPO_4^{2-}]_F \quad \ldots\ldots\ldots\ldots\ldots \quad (22)$$

Where $[Mg^{2+}]_F$ and $[HPO_4^{2-}]_F$ are the concentrations of free Mg^{2+} and HPO_4^{2-} in solution, respectively.

Now the total dissolved Mg^{2+} concentration $[Mg^{2+}]$ is:

$$[Mg^{2+}] = [Mg^{2+}]_F + [MgHPO_4] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (23)$$

Substituting equation 22 yields:

$$[Mg^{2+}] = [Mg^{2+}]_F \, (1 = K° \, f_{Mg}f'' \, [HPQ_4^{2-}]_F) \quad \ldots\ldots\ldots\ldots\ldots \quad (24)$$

so

$$[Mg^{2+}]_F = \frac{[Mg^{2+}]}{1 + K° \, f_{Mg}f'' \, [HPO_4^{2-}]_F} \quad \ldots\ldots\ldots\ldots\ldots \quad (25)$$

The total phosphate concentration is:

$$P_T = [H_2PO_4^-]_F + [HPO_4^{2-}]_F + [M_gHPO_4] \quad \ldots\ldots\ldots\ldots\ldots \quad (26)$$

Substituting equations 7 and 22 yields

$$P_T = \gamma[HPO_4^{2-}]_F + K° \, f_{Mg}f'' \, [Mg^{2+}[_F \, [HPO_4^{2-}]_F \quad \ldots\ldots\ldots\ldots \quad (27)$$

Substituting equation 25 yields

$$P_T = \gamma[HPO_4^{2-}]_F + \frac{K° \, f_{Mg}f'' \, [HPO_4^{2-}]_F}{1 + K° \, f_{Mg}f'' \, [HPO_4^{2-}]_F} \quad \ldots\ldots\ldots\ldots \quad (28)$$

Rearrangement gives

$$(P_T - \gamma[HPO_4^{2-}]F)\ (1 + K^\circ f_{Mg} f''\ [HPO_4^{2-}]_F) - K^\circ f_{Mg} f''\ [Mg^{2+}]\ [HPO_4^{2-}]_F = 0$$
$$(K^\circ f_{Mg} f'' \gamma)[HPO_4^{2-}]_F^2 + (\gamma + K^\circ f_{Mg} f''\ [Mg^{2+}] - K^\circ f_{Mg} f'' P_T)[HPO_4^{2-}]_F + (-P_T) = 0$$

and a = $(K^\circ f_{Mg} f'' \gamma)$ .... (29)
b = $(\gamma + K^\circ f_{Mg} f''[Mg^{2+}] - [K^\circ f_{Mg} f'' P_T)$ .... (30)
c = $(-P_T)$ .... (31)

Solving the quadratic yields

$$[HPO_4^{2-}]_F = \frac{-b + \sqrt{b^2} - 4\,ac}{2a} \quad \dots\dots\dots\dots\dots \quad (32)$$

The ionic strength is

$$\mu = \tfrac{1}{2}\{4\,[Mg^{2+}]_F + [H_2PO_4^-]_F + 4[HPO_4^{2-}]_F + [NH_4^+] + [Cl^-]^* + [K^+]^{**} + [Cl^-]^\dagger\} \quad \dots\dots\dots \quad (33)$$

$[Cl^-]^*$ = concentration of Cl^- ions from $MgCl_2$ = $2[Mg^{2+}]$
$[K^+]^{**}$ = concentration of K^* ions from K_2HPO_4 = $2P_T$
$[Cl^-]^\dagger$ = concentration of Cl^- ions from added HCl see above.
so:

$$\mu = \tfrac{1}{2}\{4[Mg^{2+}]_F + 2[H_2PO_4^-]_F + 4[HPO_4^{2-}]_F + 2[NH_4^+] + 2[Mg^{2+}] + 2P_T\} \quad . \quad (34)$$

Once equation 32 has been solved $[Mg^{2+}]_F$ can be obtained from equation 25 and the ionic strength can be determined.

This system of equations can be solved by iterative numerical methods. These calculations are done for 150 mg ℓ^{-1} P_T and 200 mg ℓ^{-1} N_T over the pH range 3,00 to 9,00 (See Table 2).

Table 2. $[Mg^{2+}]$ as a function of pH for 150 mg/ℓ P and 200 mg/ℓ NH_3

pH	Struvite	Newberyite
	log ($[Mg^{2+}]$/M)	log ($[Mg^{2+}]$/M)
3,00	6,54	2,13
3,20	6,13	1,92
3,40	5,73	1,71
3,60	5,33	1,50
3,80	4,93	1,29
4,00	4,53	1,07
4,20	4,13	0,85
4,40	3,73	0,62
4,60	3,33	0,38
4,80	2,93	0,14
5,00	2,53	-0,11
5,20	2,13	-0,38
5,40	1,72	-0,65
5,60	1,29	-0,93
5,80	0,83	-1,20
6,00	0,31	-1,46
6,20	-0,35	-1,70
6,40	-1,13	-1,92
6,60	-1,76	-2,11
6,80	-2,23	-2,27
7,00	-2,60	-2,40
7,20	-2,92	-2,50
7,40	-3,21	-2,58
7,60	-3,46	-2,63
7,80	-3,70	-2,67
8,00	-3,92	-2,70
8,20	-4,13	-2,72
8,40	-4,33	-2,73
8,60	-4,51	-2,75
8,80	-4,69	-2,76
9,00	-4,85	-2,77

2.2 Kinetics of struvite crystallization

Little information is available on kinetics of struvite crystallization, however a number of points do emerge from the study of Abbona *et al.* (1982).

Solutions of Mg^{2+}, NH_4^+ and phosphate easily form supersaturated solutions, the metastable zone for newberyite (N) being wider than that for struvite (S). The supersaturations for S ($ß_s$) and N ($ß_N$) are given by equations 35 and 36.

$$ß_s = \frac{f_{Mg}\,[Mg^{2+}]\,f^{\cdot\cdot}\,[HPO_4^{2-}]\,[NH_3]}{K_{sp}\,(S)} \quad \ldots\ldots\ldots\ldots\ldots \quad (35)$$

and

$$ß_N = \frac{f_{Mg}[Mg^{2+}]\,f^{\cdot\cdot}\,[HPO_4^{2-}]}{K_{sp}\,(N)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (36)$$

In general, they do not nucleate in less than 200 hours (~ 9 days) at ß values below 3 and 1.3 for N and S, respectively. The induction time (time required for first crystals to form) is also generally longer for N than S; for $ß = 4$, S crystallizes in 2 days while N requires about a week. The ratio of induction times increases with increasing ß, thus at $ß = 10.5$ S and N crystallize in 4 and 20 h, respectively.

At isosupersaturations (where ß is constant, but concentrations are different, depending on pH) the induction time for N increases with decreasing pH and is independent of concentration. For isosupersaturated solutions of S at low ß values, induction time decreases with concentration, while at high ß the converse is true, since precipitation causes a decrease in pH. Increasing temperature greatly increases the precipitation domain of N at the expense of S.

When $ß_s > ß_N$, always crystallizes first, while when $ß_N > ß_s$, N crystallizes first at low NH_3 concentrations, while S crystallizes first at high NH_3 concentrations.

The kinetics of struvite crystallization are thus slow and rather complex. These effects are likely to be more important than thermodynamic factors in determining suitable conditions for S crystallization. It would seem that relatively high supersaturations and moderately high pH's are desirable for rapid crystallization. Selection of a suitable seed material may also be very important.

2.3 The seed material

In this study quartz was concentrated upon as a seed material as it was found to be the most readily available and easily accessible. Phosphate crystallisation using magnesia clinker as seed material was successfully employed when removing phosphate in the form of hydroxyapatite, although no work was done on the formation of struvite (Kaneko & Nakajima 1988). It can, however, be speculated from this work that magnesia clinker would function well as a seed material for struvite formation, since the phosphate removal property of the magnesia clinker seems to relate to the accompanying release of a slight amount of magnesium ions (approximately 10 mg/ℓ) into the solution. In so doing the magnesium concentration will be supplemented and thereby enhancing the chances of struvite formation.

Smith & Hwang (1978) indicated that serpentine [$Mg_3Si_2O_5(OH)_2$] should function readily as an excellent adsorbent for phosphate. It is available in large quantities in some parts of the U.S.A. and could easily be mined using open-cast techniques. When serpentine is added to water there is a considerable pH increase and magnesium ions are released into the water. Therefore, serpentine has the potential for removing ammonia-nitrogen because of the pH rise and the possibility of the formation of MAP as well as the possibility of adsorption of ammonium ions on silica sites on the serpentine. The best known serpentine form is chrysotile and although serpentine has been used for adsorption rather than crystallisation, it may well have potential as a seed material for the crystallisation of struvite.

3. INITIAL BENCH-SCALE AND PILOT PLANT STUDIES ON STRUVITE FORMATION USING ANAEROBIC DIGESTER LIQUORS

3.1 Phosphorus fixation by means of struvite crystallization

Anaerobic digester liquor used in this study contained 207 mg/l of phosphate, 7,0 mg/l of soluble magnesium, and 756 mg/l of ammonia nitrogen. As the molar ratio of MAP is 1(P):1(N):1(Mg) magnesium was deficient stoichiometrically to form MAP. Addition of magnesium to the supernatant to a Mg/P ratio of 1,05 caused formation of MAP crystals, increasing the phosphorus removal potential.

Solubility of MAP declines with rising pH, as Borgerding (1972) showed, and the system should be kept at pH 8 or higher, to remove MAP efficiently. The pH level of the supernatant, which was typically within a range from 7,3 to 7,5, was increased by one of four means:

NaOH, lime, $Mg(OH)_2$ and aeration

NaOH addition was found to be more effective than lime or $Mg(OH)_2$ addition. On the other hand, aeration was found to be an effective method of removing carbon dioxide dissolved in the supernatant at a high concentration, resulting in the pH level increasing to 8,4 in about 2 hours. Based on these findings, namely, that MAP can be produced efficiently by adding magnesium to the supernatant, and by increasing the system pH to at least 8 with addition of NaOH or aeration, the MAP process to continuously remove phosphorus from the supernatant was then attempted at bench-scale.

3.2 Bench-scale study on struvite formation

Supernatant was obtained by anaerobic digestion of excess sludge from a biological phosphorus removal process, mixed with primary sludge (mixing ratio 3:2). The pH of the supernatant usually was about 7,3 to 7,5 so the experiment was carried out with addition of Mg alone.

Figure 1 and Table 3 show the flow diagram of the MAP bench-scale apparatus and relevant experimental conditions, respectively.

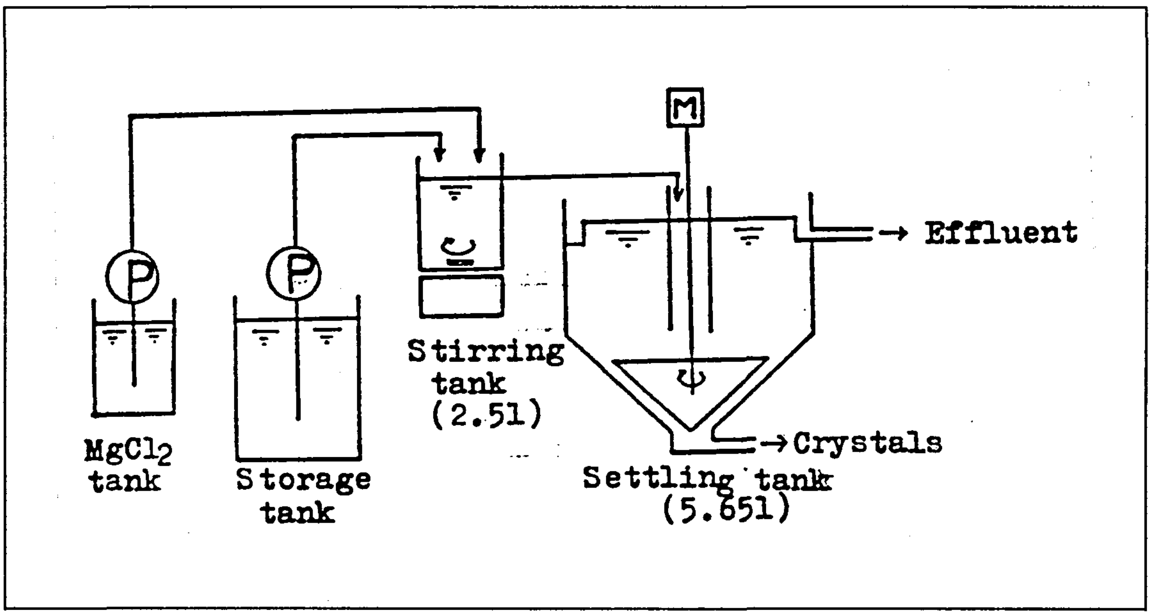

Figure 1. **Flow diagram of experimental setup to study magnesium ammonium phosphate crystallization (Fujimoto *et al.,* 1991).**

Table 3. **Experimental conditions for bench-scale magnesium ammonium phosphate crystallization**

Flow rate	102,6	ml/min
Dosage of $MgCl_2$ solution	7,3	ml/min
Molar ratio Mg to PO_4-P	2:07	
Retention time in stirring tank	23	min
Retention time in settling tank	51	min

Total phosphorus and PO_4-P were reduced from 240 mg/l to 79,8 (60%) mg/l and from 222 mg/l to 22,7 mg/l (removal ratio 90%), respectively. Composition of the precipitate obtained (Mg : N : P = 35,6 : 20,1 : 44,2 in mass percentage) was almost equivalent to MAP (35,1 : 20,2 : 44,7), therefore the precipitate was considered to be MAP and its purity was about 88%.

3.3 Pilot plant struvite crystallization - Phase 1

Figure 2 and Table 4, respectively, show the flow diagram of the pilot plant and the experimental conditions for this part of the study. NaOH solution was added automatically to the feed water, to keep a pH level in the range 8,3 to 9,0. $MgCl_2$ addition was changed in accordance with the phosphorus concentration in the supernatant. The crystalline precipitates were separated from the feed water in the settling tank, and some part of the precipitates was returned to the rapid stirring tank to serve as seed material.

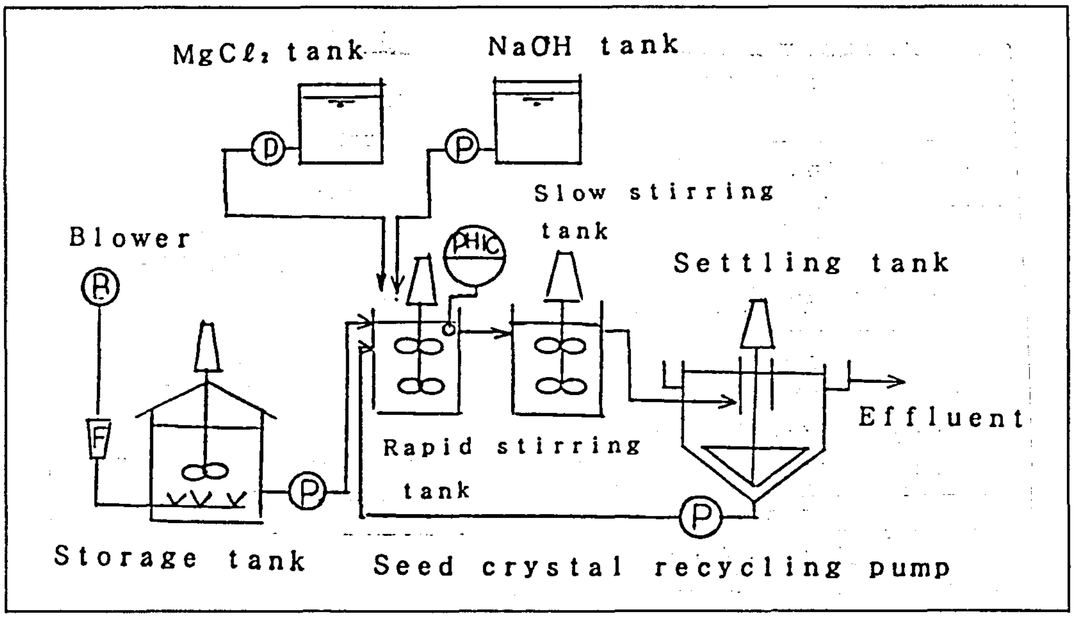

Figure 2. **Flow schematic of pilot plant magnesium ammonium phosphate crystallization process - Phase 1 (Fujimoto *et al.,* 1991)**

Table 4. **Operating conditions for pilot plant study on magnesium ammonium phosphate crystallization (Phase 1)**

Flow rate	0.5	(m^3/h)
Dosage of $MgCl_2$ solution	6	(ml/min)
Molar ratio Mg to PO_4-P	1:05	
Retention time in stirring tanks	24	(min)
Retention time in settling tank	144	(min)

Figure 3 shows the results of the pilot plant study. The influent PO_4-P concentration changed from 20 to 80 mg/l, but the effluent PO_4-P concentration ranged from 5 to 15 mg/l (10 mg/l on the average), that is, 60 to 70% as PO_4-P removal ratio. The crystals formed were very fine, mostly deposited on suspended solids surfaces, and sometimes leaked into the effluent to cause high phosphorus concentration. Recycling of the seed crystals was an effective method of increasing the size of the magnesium ammonium phosphate crystals.

The major problem observed in this study related to aeration to adjust the pH of the water in the storage tank. This frequently caused precipitation of magnesium ammonium phosphate in the storage tank, and/or decreased the purity of magnesium ammonium phosphate because the precipitated MAP was withdrawn together with the sludge out of the settling tank. Phase 2 of the study was designed to overcome this problem.

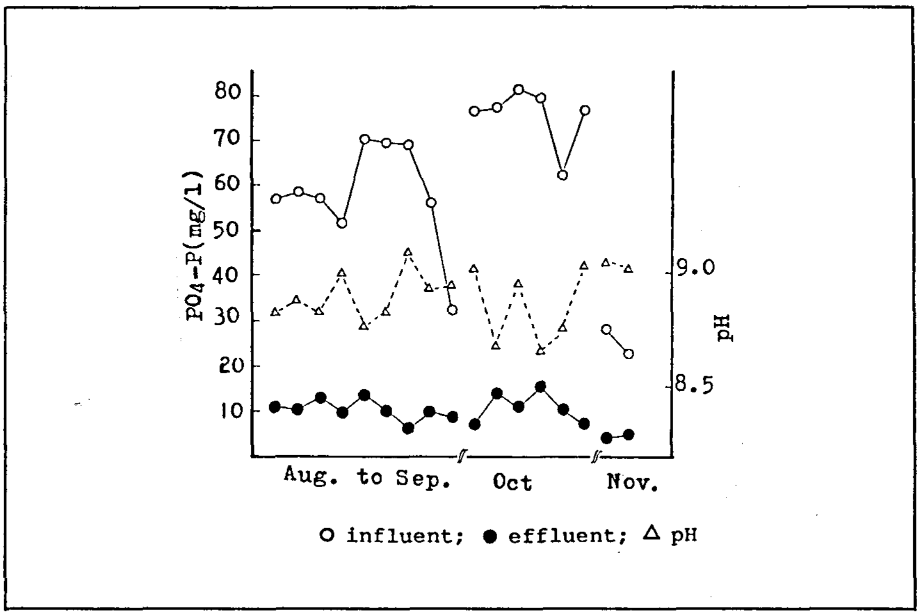

Figure 3. **Results of pilot plant struvite crystallization - Phase 1 (Fujimoto *et al.,* 1991).**

3.4 Pilot plant struvite crystallization - Phase 2

Figure 4 illustrates a pilot plant where aeration, stirring, and crystallization were carried out together in the same reactor tank. Struvite precipitates formed in the reactor are separated from suspended solids and settled by gravity. Experimental conditions were given in Table 5.

Table 5. **Operating conditions for pilot scale magnesium ammonium phosphate crystallization (Phase 2)**

Flow rate	0.3	(m^3/h)
Aeration rate	30	(ℓ/min)
Dosage of NaOH (5% solution)	60	(ℓ/d)
Dosage of $MgCl_2$ (12.5% solution)	10	(ℓ/d)
Molar ratio Mg to PO_4-P	1:1	

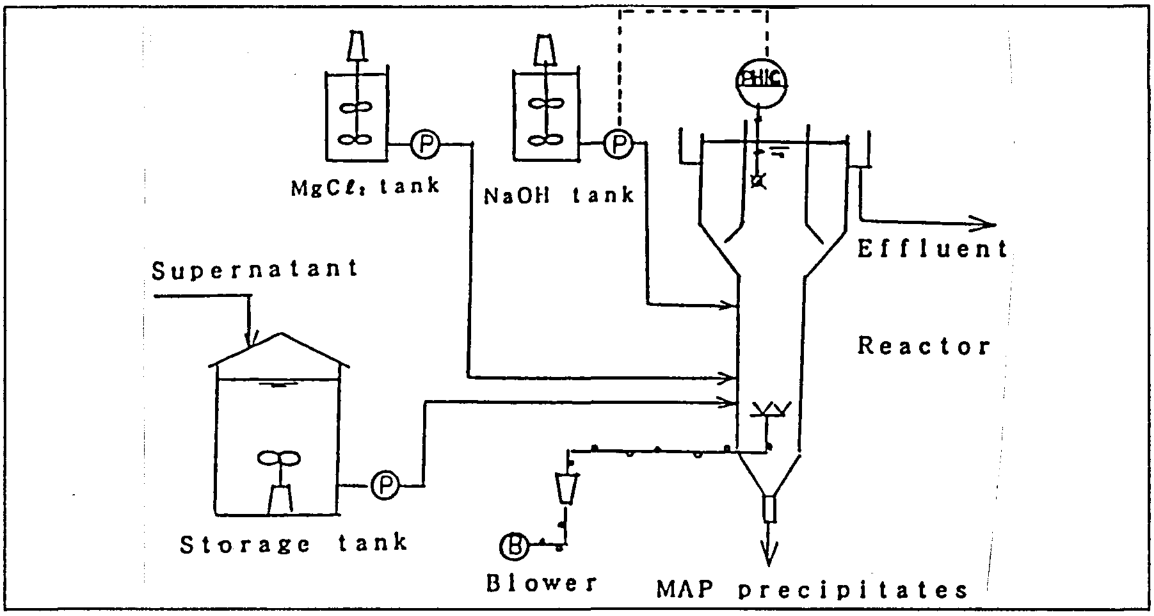

Figure 4. **Flow schematic of magnesium ammonium crystallization pilot plant - Phase 2 (Fujimoto *et al.*, 1991)**

Crystallized struvite grew to pellet size in the reactor while the struvite was moved up and down in the reactor by aeration. The phosphorus removal ratio was about 70%. The purity of obtained MAP was 88%, its size 2-3mm x 1,5 mm and its composition 10,4% P, 5,9% N and 12,9% Mg. Mercury and Cadmium were not detected in the struvite, while the Arsenic concentration was found to be 1,6 mg/Kg.

3.5 Conclusion

Phosphorus fixation of 90% or more were attained at a dosage of about 1 mol/mol. Magnesium ammonium phosphate was formed efficiently by adding magnesium to the supernatant, and by increasing the system pH to at least 8 with addition of NaOH or aeration. The phosphorus removal ratio at pilot plant experiments was 70%, and granulated struvite was produced.

4. EXPERIMENTS WITH LABORATORY SCALE FLUIDIZED BED REACTORS

The design and operation of these reactors have been described in detail in the companion report on Phosphate Crystallization in Activated Sludge (Momberg 1991) and will not be repeated here.

In the struvite precipitation experiments, the following media were used, respectively :

- Artificial media
- Anaerobic digester supernatant from Daspoort Water Treatment Works
- Anaerobic digester supernatant from Rooiwal Water Care Works

4.1 Experiments with artificial Media

In these experiments the standard procedure was to add to 14,4 ℓ tap water the following components from stock solutions (giving the final concentrations in brackets):

150 mℓ KH_2PO_4	(50,00 mg P/ℓ)
150 mℓ NH_4Cl	(29,05 mg N/ℓ)
150 mℓ $MgSO_4 \cdot 7H_2O$	(39,23 mg Mg/ℓ)
150 mℓ $CaCl_2$	(107,84 mg Ca/ℓ)

Data on NH_4^+ and Mg^{2+} utilization in artificial media (see Momberg, 1991, Table 10) gave no clear indication of struvite formation in the presence of increasing amounts of calcium. The major portion of precipitated phosphate was in the form of hydroxyapatite.

In experiments where calcium addition from stock solution was omitted struvite formation could be demonstrated by increased NH_4^+, Mg^{2+} and PO_4^{3+} utilization.

When the pH was increased to 10 or higher by lime addition in order to optimize struvite precipitation a 30% decrease in calcium concentration was observed without influencing the ammonia concentration, despite the presence of additional Mg in the reaction mixture. Formation of $CaCO_3$ and/or hydroxyapatite accounted for the disappearance of calcium.

4.2 Experiments with Daspoort anaerobic digester supernatant

In these experiments the effluent was unsupplemented and tested over a pH range of 8,9 to 9,8 to establish if there was a general pattern of struvite formation. The concentrations of relevant components in the anaerobic digester supernatant are presented in Figure 5. It has been suggested that the total and ortho-phosphate were rather low, and perhaps the reason for this was that phosphate precipitation had already occurred.

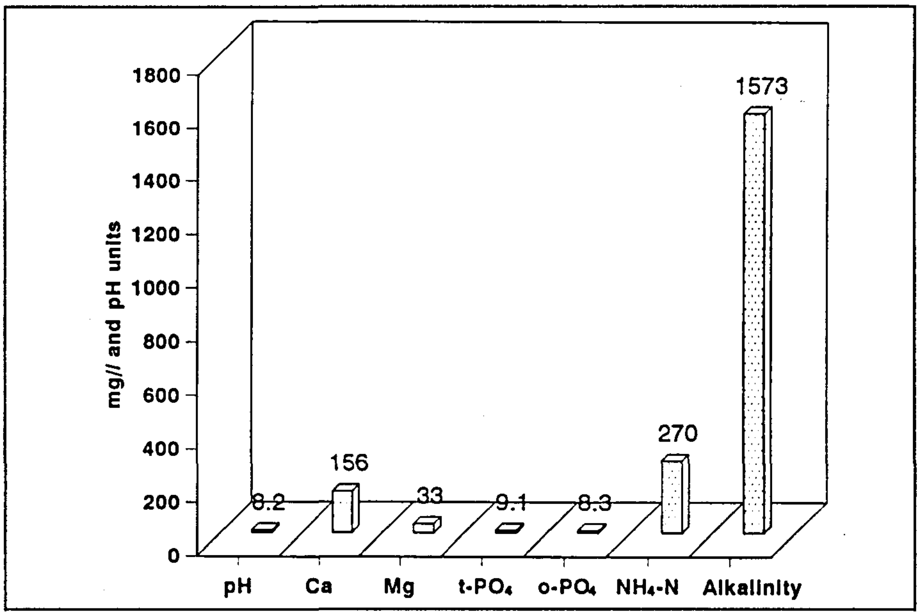

Figure 5. **Concentrations of components that may influence crystallization patterns in an anaerobic digester supernatant from Daspoort Water Treatment Works.**

Observed phosphate removal at different pH values are presented in Figure 6 and the respective Ca, Mg and NH_4 utilizations are summarized in Table 6.

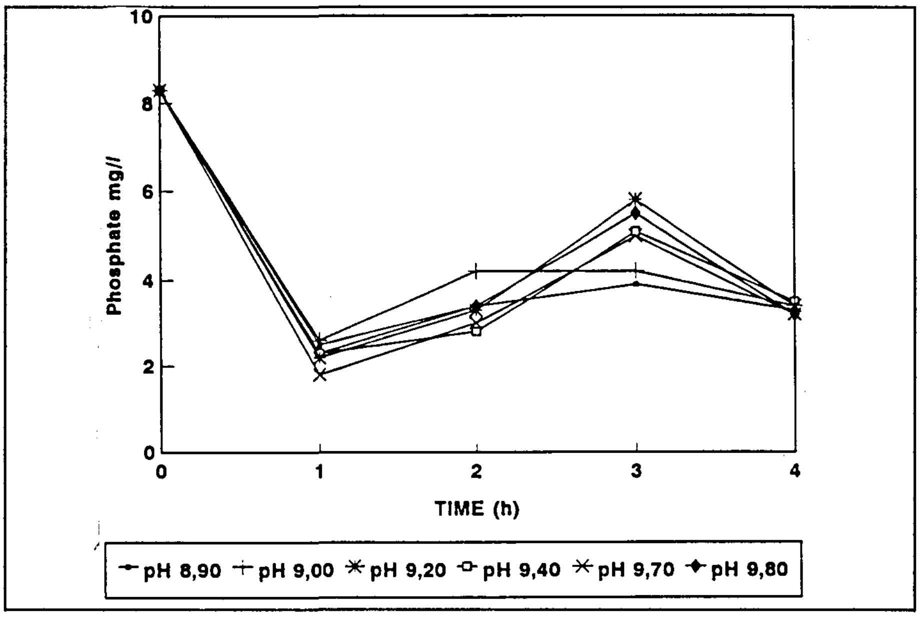

Figure 6. **Phosphate removal as a function of time at various pH levels in an anaerobic digester supernatant from Daspoort Treatment Works**

Table 6. **Summary of the experiments using unsupplemented Daspoort anaerobic digester supernatant. For initial concentrations see Figure 5**

	pH						Average
	8,9	9,0	9,2	9,4	9,7	9,8	
Av. P after treatment (mg/ℓ)	3,3	3,6	3,7	3,4	3,3	3,6	3,5
Av. P removed (mg/ℓ)	4,9	4,7	4,6	4,9	5,0	4,7	4,8
Av. P removed (%)	59	57	56	59	61	57	58
Av. Ca after treatment (mg/ℓ)	39	38	27	23	22	22	23
Av. Ca utilized (mg/ℓ)	117	118	129	133	134	134	133
Av. Ca utilized (%)	75	76	83	85	86	86	85
Av. Mg after treatment (mg/ℓ)	26	24	20	20	20	19	20
Av. Mg utilized (mg/ℓ)	7	90	13	13	13	14	13
Av. Mg utilized (%)	21	27	39	39	39	42	40
Av. NH_4 after treatment (mg/ℓ)	238	245	201	165	161	160	162
Av. NH_4 utilized (mg/ℓ)	32	25	69	105	108	109	108
Av. NH_4 utilized (%)	12	9	26	39	40	41	40

The average values in the final column for calcium and magnesium only include the pH range 9,2-9,8 and the ammonia valued only include the pH range 9,4-9,8.

The data in Table 6 indicate that both struvite and hydroxyapatite were formed on pH adjustment in the fluidized bed reactors. The high levels of calcium utilization at pH levels 9,2 to 9,8 suggest a predominance of hydroxyapatite formation under these conditions.

In efforts to increase struvite formation two further series of experiments were conducted. In both series additional Mg and PO_4 were supplemented to obtain actual concentrations closer to the molar ratio of 1 Mg : 1N : 1P found in struvite. In the first series tests were conducted over a pH range of 7,0 to 9,5 and in the second series the pH ranged from 6,5 to 11,5.

4.3 Struvite formation in Daspoort anaerobic digester supernatant supplemented with magnesium and phosphate.

4.3.1 *Supplementation and acidification*

Initial supplementation to obtain a mass ratio of 1,71 Mg : 1N : 2.21 P (complying with the 1 : 1 : 1 molar ratio) was not realized. Precipitation as well as the high alkalinity (Figure 5) were considered to be responsible for this phenomenon. The high alkalinity had already created a problem as the effluent required large amounts of NaOH to maintain the required pH levels. Figure 7 represents titration curves of 1N NaOH or 1N HCl required to obtain a desired pH level. Table 7 lists the calculated alkali requirements to raise the pH of the effluent to a required level.

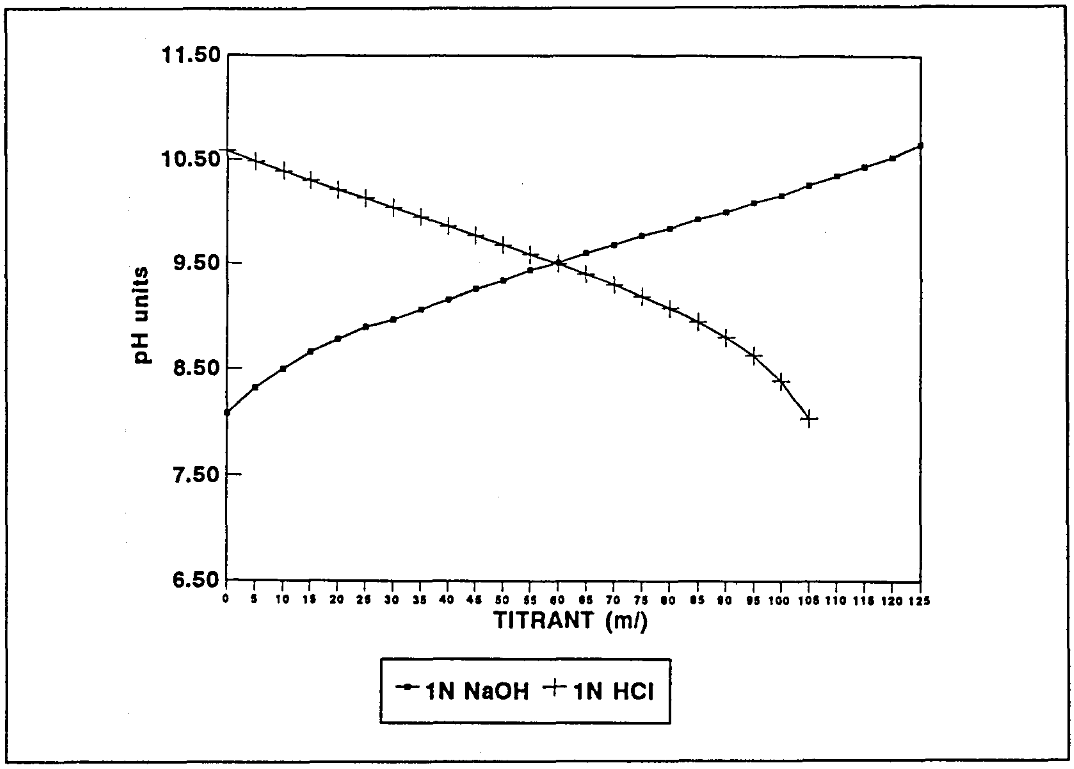

Figure 7. **Titration curves for Daspoort anaerobic digester supernatant.**

Table 7. Alkali requirement to raise the pH of Daspoort anaerobic digester supernatant to the indicated level

pH	1 N NaOH (mℓ/3ℓ)	NaOH (mg/ℓ)	$Ca(OH)_2$ (mg/ℓ)	Ca introd. (mg/ℓ)
8,08	0	0	0	0,0
8,32	5	66,7	61,7	33,3
8,50	10	133,3	123,3	66,7
8,66	15	200,0	185,0	100,0
8,78	20	266,7	246,7	133,3
8,90	25	333,3	308.3	166,7
8,97	30	400,0	370,0	200,0
9,07	35	466.7	431,7	233,3
9,16	40	533,3	493,3	266,7
9,26	45	600,0	555,0	300,0
9,34	50	666,7	616,7	333,3
9,44	55	733,3	678,3	366,7
9,51	60	800,0	740,0	400,0
9,60	65	866,7	801,7	433,3
9,68	70	933,3	863,3	466,7
9,77	75	1000,0	925,0	500,0
9,84	80	1066,7	986,7	533,3
9,93	85	1133,3	1048,3	566,7
10,00	90	1200,0	1110,0	600,0
10,10	95	1266,7	1171,7	633,0
10,20	100	133,30	1233,3	666,7
10,30	105	1400,0	1295,0	700,0
10,40	110	1466,7	1356,7	733,3
10,50	115	1533,3	1418,3	766,7
10,60	120	1600,0	1480,0	800,0
10,70	125	1666,7	1541,7	833,3

To obtain a ratio of Mg : N : P closer to the ideal the effluent was acidified to a pH of 5,5 with HCl (Figure 8) after supplementation with magnesium and phosphate. Acidification resulted in a reduction of alkalinity to 3 mg/ℓ and a mass ratio of 0,41 : 1 : 0,65 compared to the earlier ratio of 0,23 : 1 : 0,16 (derived from Figure 5).

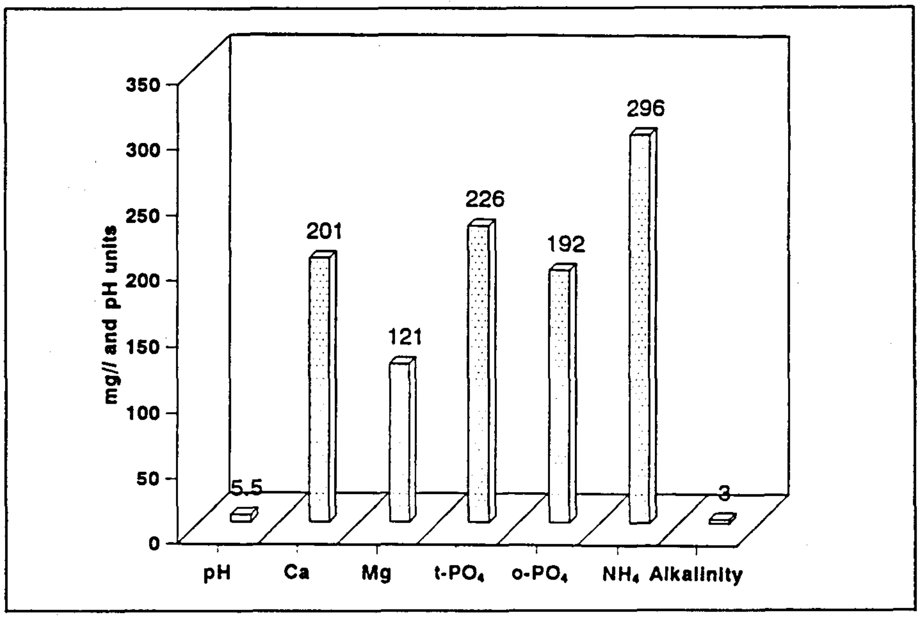

Figure 8. **Relevant components in Daspoort anaerobic digester supernatant after Mg and PO_4 supplementation and acidification.**

4.3.2 *Phosphate removal after supplementation and acidification over a pH range of 7,0 to 9,5.*

Although the supplementation and acidification procedure described above did not yield the expected calculated ratio of Mg : N : P it was found that overall phosphate removal increased after supplementation with magnesium and phosphate (Figure 9). Increased utilization of both magnesium and ammonium were observed (Table 8) even with ammonium present in excess.

It must be noted that the actual measured removals at pH 9,5 in Table 8 for Mg (103 mg/ℓ) N (101 mg/ℓ) and P (188 mg/ℓ) can be expressed as a Mg : N : P ratio of 1,01 : 1 : 1,86 (for pure struvite the ratio should be 1,71 : 1 : 2,21). The high percentages of calcium utilization at the higher pH values again indicate the formation of hydroxyapatite in addition to the struvite.

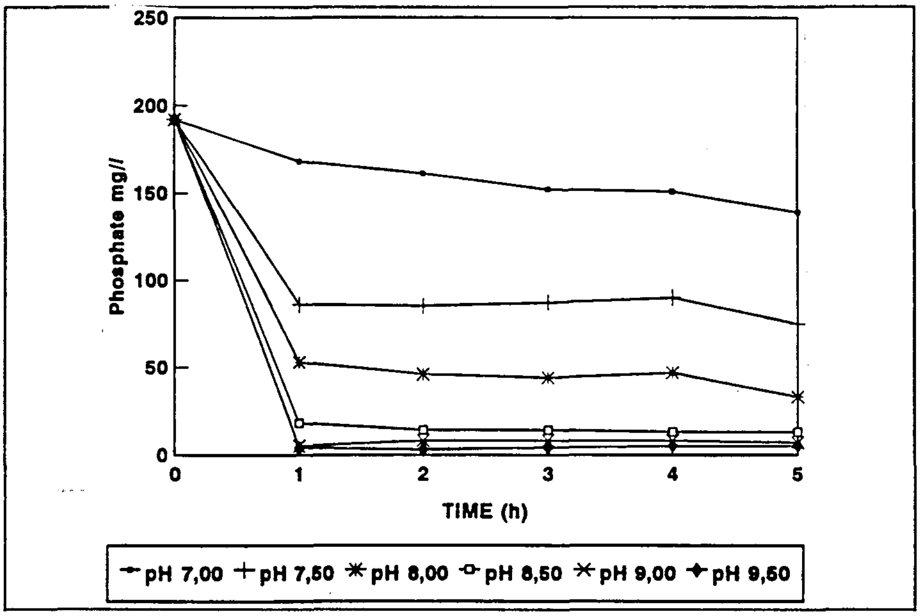

Figure 9. Phosphate removal after supplementation and acidification at pH levels ranging from 7,0 to 9,5

Table 8. Results summarizing experiments after supplementation and acidification of Daspoort anaerobic digester supernatant over a pH range of 7,0 - 9,5. For initial concentrations see Figure 8.

	pH					
	7,0	7, 5	8,0	8,5	9,0	9,5
Av. P after treatment (mg/ℓ)	154	85	45	14	7	4
Av. P removed (mg/ℓ)	38	107	147	178	185	188
Av. P removed (%)	20	56	77	93	96	98
Av. Ca after treatment (mg/ℓ)	93	56	77	93	96	98
Av. Ca utilized (mg/ℓ)	108	144	153	164	176	20
Av. Ca utilized (%)	54	72	76	82	88	181
Av. Mg after treatment (mg/ℓ)	72	62	55	36	26	18
Av. Mg utilized (mg/ℓ)	49	59	77	85	95	103
Av. Mg utilized (%)	41	49	64	70	79	85
Av. NH_4 after treatment (mg/ℓ)	276	263	252	233	219	195
Av. NH_4 utilized (mg/ℓ)	20	33	44	63	77	101
Av. NH_4 utilized (%)	7	11	15	21	26	34

4.3.3 *Phosphate removal after supplementation and acidification over a pH range of 6,5 to 11,5.*

When the experiments described in 4.2.2 were repeated over a wider pH range the initial concentrations of the relevant components after supplementation and acidification were those presented in Figure 10. The Mg : N : P ratio was 0,31 : 1 : 0,55.

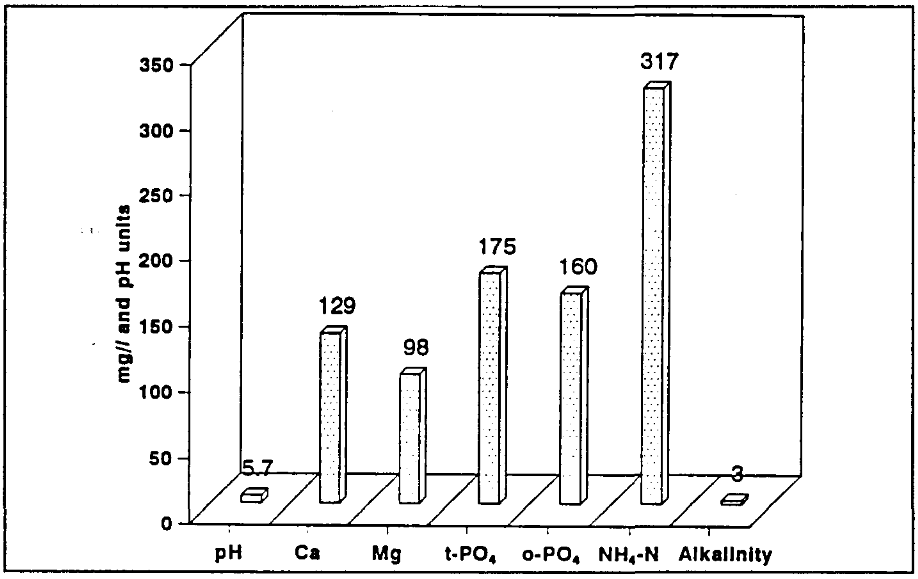

Figure 10. Relevant components in supplemented and acidified Daspoort anaerobic digester supernatant.

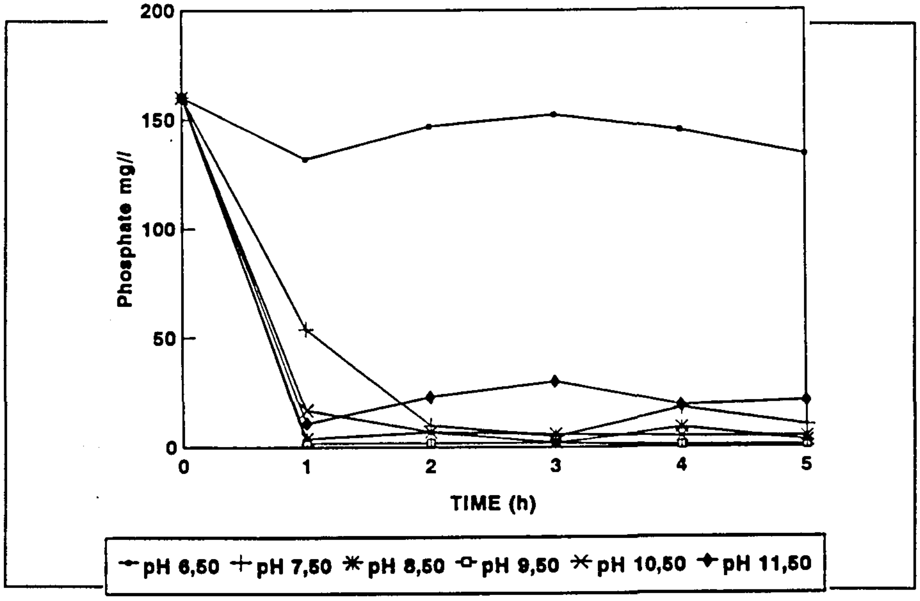

Figure 11. Phosphate removal after supplementation and acidification at pH levels ranging from 6,5 to 11,5.

Phosphate removals over the pH ranges tested are illustrated in Figure 11 and removal and utilization data are summarized in Table 9.

Table 9. **Results summarizing experiments after supplementation and acidification of Daspoort anaerobic digester supernatant over a pH range of 6,5 - 11,5. For initial concentrations see Figure 10.**

	pH					
	6,5	7, 5	8,5	9,5	10,5	11,5
Av. P after treatment (mg/ℓ)	142	20	5	2	8	23
Av. P removed (mg/ℓ)	18	140	155	158	152	137
Av. P removed (%)	11	88	97	99	95	86
Av. Ca after treatment (mg/ℓ)	110	57	44	19	3	1
Av. Ca utilized (mg/ℓ)	19	72	85	110	126	128
Av. Ca utilized (%)	15	56	66	85	99	128
Av. Mg after treatment (mg/ℓ)	15	56	66	85	98	99
Av. Mg utilized (mg/ℓ)	40	49	60	71	95	97
Av. Mg utilized (%)	41	50	61	72	97	99
Av. NH_4 after treatment (mg/ℓ)	291	241	233	207	208	200
Av. NH_4 utilized (mg/ℓ)	26	76	84	110	109	117
Av. NH_4 utilized (%)	8	24	26	35	34	37

The high levels of calcium utilization at pH levels in excess of 10,5 again indicate hydroxyapatite formation. This in combination with struvite formation resulted in a 99% phosphate removal at pH 9,5. Keeping in mind that the original PO_4-P concentration was 160 mg/ℓ after supplementation, these findings give a clear indication of the potential of crystallization technology as a tool for phosphate removal.

4.4 Struvite formation in Rooiwal anaerobic digester supernatant

4.4.1 *Unsupplemented effluent*

The composition of Rooiwal anaerobic digester supernatant (Figure 12) resembled that of the Daspoort anaerobic digester supernatant. Both effluents were characterized by high ammonia and high alkalinity. In Rooiwal the PO_4-P concentration was somewhat higher (20 mg/ℓ compared to 8,3 mg/ℓ in Daspoort) but the calcium concentration was lower (78 mg/ℓ compared to 158 mg/ℓ in Daspoort).

Phosphate removal from the unsupplemented effluent in the fluidized bed reactor was between 36 to 60% over a pH range of 8,6 to 10,8 (Figure 13) and Table 10). These results showed a great resemblance to the pattern found with unsupplemented Daspoort effluent (see Figure 6 and Table 6).

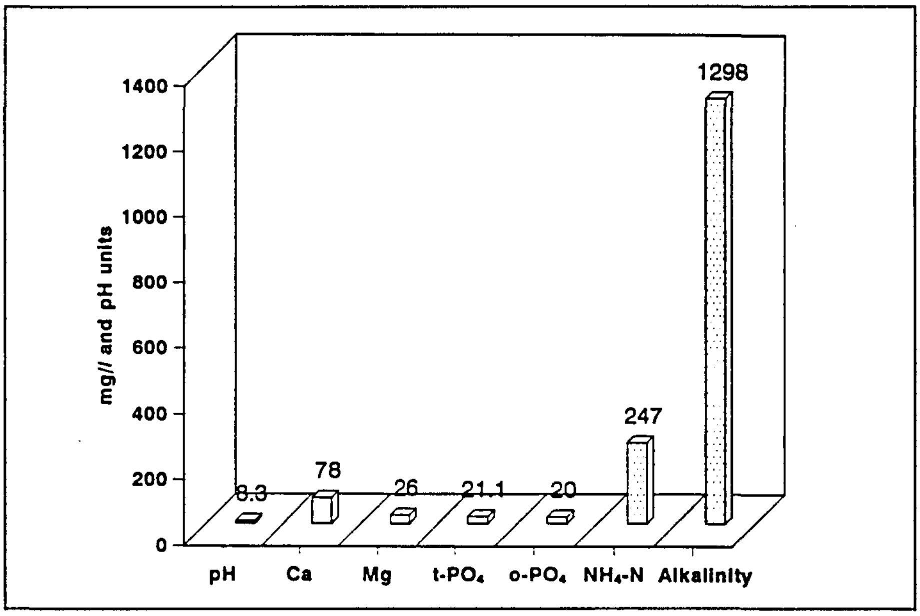

Figure 12. Concentration of relevant components in Rooiwal anaerobic digester supernatant.

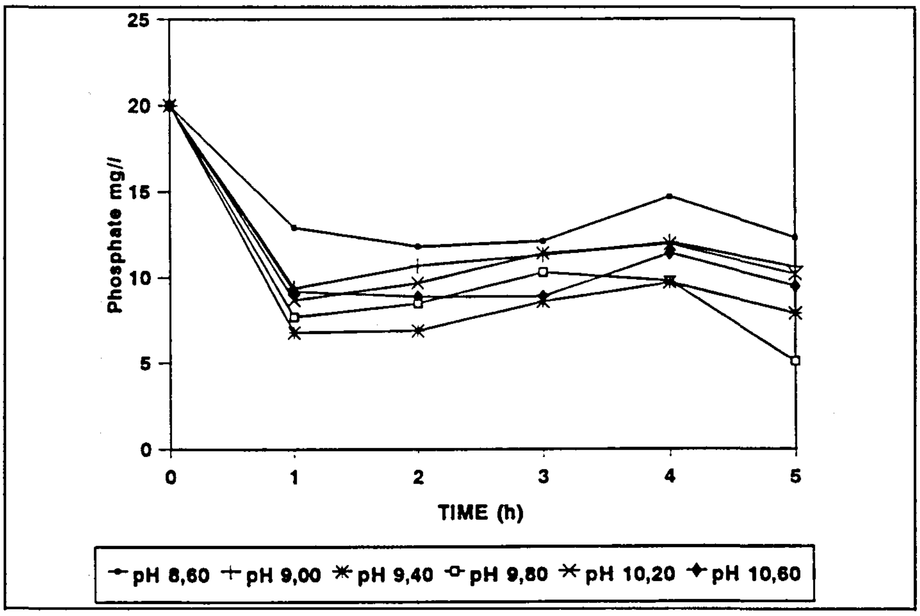

Figure 13: Phosphate removal as a function of time at various pH levels in an anaerobic digester supernatant from Rooiwal.

Table 10. **Summary of the experiments using unsupplemented Rooiwal anaerobic digester supernatant. For initial concentrations see Figure 12**

	pH					
	8,6	**9,0**	**9,4**	**9,8**	**10,2**	**10,6**
Av. P after treatment (mg/ℓ)	12,8	10,8	8,0	8,3	10,4	9,6
Av. P removed (mg/ℓ)	7,2	9,2	12,0	11,7	9,6	10,4
Av. P removed (%)	36	46	60	59	48	52
Av. Ca after treatment (mg/ℓ)	68,2	59,2	12,8	11,4	11,2	16,2
Av. Ca utilized (mg/ℓ)	9,8	18,8	65,2	66,6	66,8	671,8
Av. Ca utilized (%)	13	24	84	85	86	80
Av. Mg after treatment (mg/ℓ)	25,6	24,0	19,4	19,0	18,6	14,0
Av. Mg utilized (mg/ℓ)	0,4	2	6,6	7	7,4	12
Av. Mg utilized (%)	2	8	25	27	29	46
Av. NH_4 after treatment (mg/ℓ)	231,8	220,7	187,2	158,1	136,4	121,1
Av. NH_4 utilized (mg/ℓ)	15,1	26,2	59,7	88,9	110,5	125,8
Av. NH_4 utilized (%)	6	11	24	36	45	51

As in the case of Daspoort effluent the data in Table 10 suggest both hydroxyapatite and struvite formation. The Rooiwal effluent was then supplemented with magnesium and phosphate and acidified with hydrochloric acid in a similar fashion to the Daspoort effluent described above.

4.4.2 *Effluent supplemented with magnesium and phosphate*

Supplementation and acidification of the Rooiwal effluent resulted in a pH reduction from 8,2 to 6,8 and increased Mg^{2+} and PO_4^{3-} from 28 and 20 mg/ℓ to 49 and 96,6 mg/ℓ, respectively (Figure 14). Phosphate removal after supplementation and acidification at different pH values are given in Figure 15 and utilization data are summarized in Table 11. Overall percentage phosphate removal increased up to 88% after supplementation but actual residual phosphate levels remaining after treatment did not change significantly from the levels observed in the unsupplemented treatment (Table 10). The higher alkalinity (1094 mg $CaCO_3$/ℓ) in the supplemented Rooiwal effluent (Figure 14) could have played a role. In the supplemented Daspoort effluent experiments described earlier alkalinity was reduced to a low level (3 mg $CaCO_3$/ℓ) after acidification (see Figure 8). It is possible that calcite formation in Rooiwal effluent prevented phosphate reduction to the low levels observed in the Daspoort effluent.

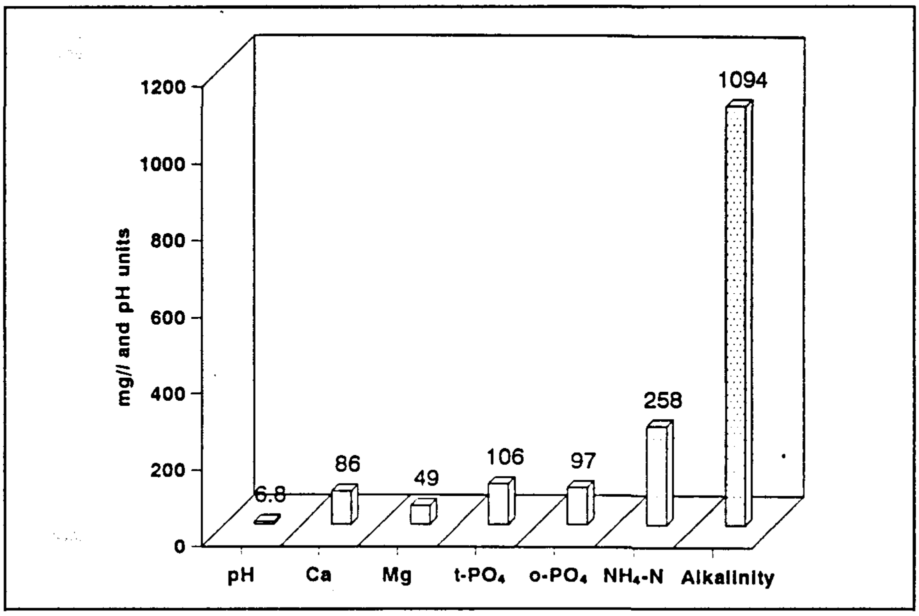

Figure 14. Concentration of relevant components in Rooiwal anaerobic digester supernatant after supplementation and acidification.

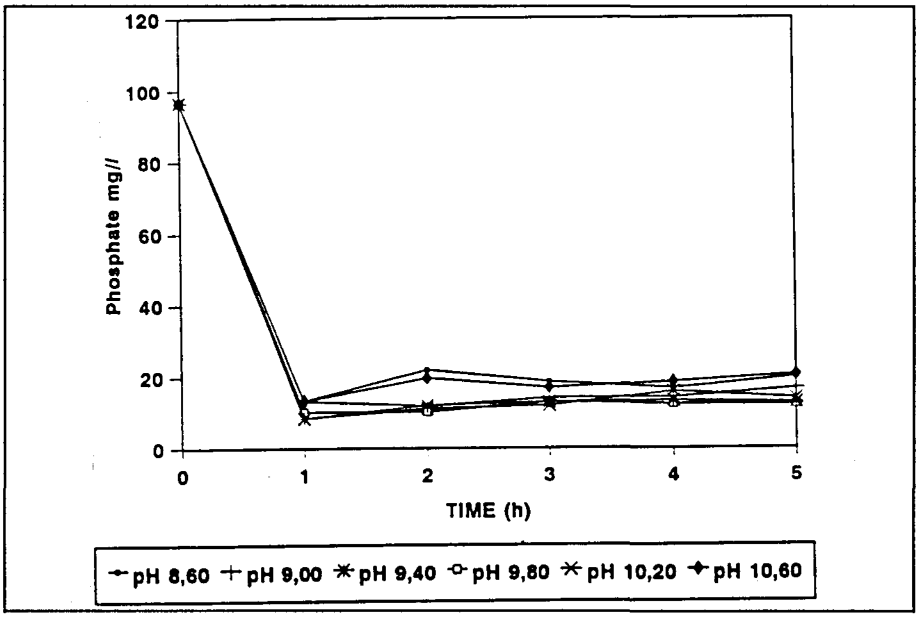

Figure 15. Phosphate removal from Rooiwal anaerobic digester supernatant after supplementation and acidification.

Table 11. **Summarizing experiments after supplementation and acidification of Rooiwal anaerobic digester supernatant. For initial concentrations see Figure 14.**

	pH					
	8,6	**9,0**	**9,4**	**9,8**	**10,2**	**10,6**
Av. P after treatment (mg/ℓ)	8,6	9,0	12,0	11,7	12,4	17,9
Av. P removed (mg/ℓ)	78,4	82,5	84,6	84,9	84,2	78,7
Av. P removed (%)	81	85	88	88	87	82
Av. Ca after treatment (mg/ℓ)	55,4	37,6	21,4	14,0	10,6	9,8
Av. Ca utilized (mg/ℓ)	30,6	48,4	64,6	72,0	75,4	76,28
Av. Ca utilized (%)	36	56	75	84	88	89
Av. Mg after treatment (mg/ℓ)	16,6	11,8	7,2	6,6	5,4	4,2
Av. Mg utilized (mg/ℓ)	32,4	37,2	41,8	42,4	43,6	44,8
Av. Mg utilized (%)	66	76	85	87	89	91
Av. NH_4 after treatment (mg/ℓ)	212,3	210,6	168,5	136,4	104,3	96,3
Av. NH_4 utilized (mg/ℓ)	45,8	47,5	89,6	121,7	153,8	161,8
Av. NH_4 utilized (%)	17	18	35	47	60	63

5. CHEMICAL MODELLING OF STRUVITE FORMATION

Data from the experiments with Daspoort anaerobic digester supernatant without and with supplementation were compared with theoretical equilibrium calculations using a Joint Expert Speciation System (JESS) currently under development at the Water Quality Information Systems Programme of the Division of Water Technology.

From the results in section 4.2 and 4.3 there was evidence of struvite formation, but it was not established what proportion of the phosphate removal represented struvite formation and what proportion was due to hydroxyapatite formation and softening.

Figures 16 and 17 represent calculated and observed phosphate removal data. Please note that MAP in Figure 16 refers to a Magnesium apatite precipitate which is distinct from magnesium-ammonium-phosphate (struvite) as shown in Figure 17, Magnesium ammonium phosphate - has also been abbreviated as MAP in earlier sections of this report.

From the model it appears that over the limited pH range of 8,9 to 9,8, Magnesium apatite may have been the major precipitate in the unsupplemented treatment (Figure 16 but that struvite was the major precipitate in the supplemented treatment.

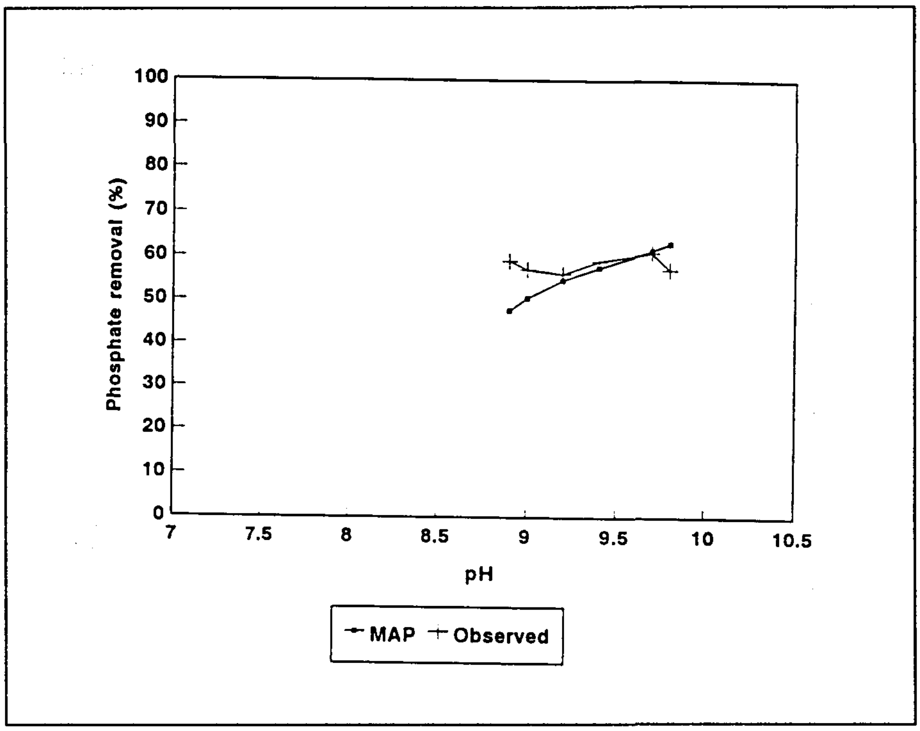

Figure 16. Calculated and observed phosphate removal from Daspoort anaerobic digester supernatant without supplementation (observed data from Table 6)

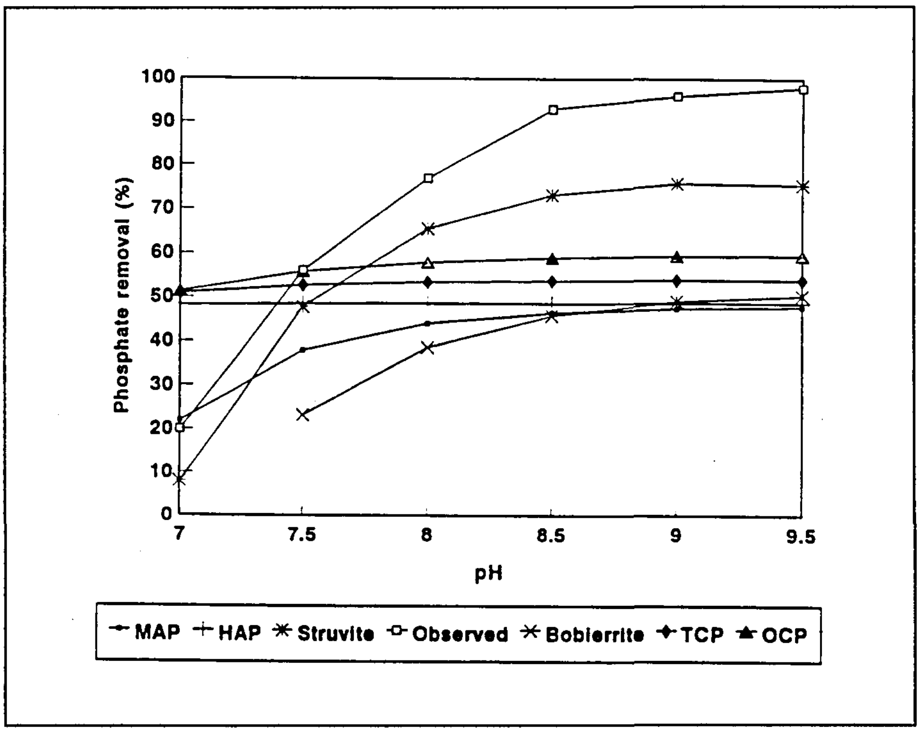

Figure 17. Calculated and observed phosphate removal from Daspoort anaerobic digester supernatant with supplementation (observed data from Table 8)

6. CONCLUSIONS

Anaerobic digester liquors readily form phosphate precipitates under favourable conditions as a result of the presence of calcium, magnesium and ammonia. Precipitation is encouraged by a rise in pH as a result of carbon dioxide evolution which usually occurs when effluent leaves the digester. The addition of alkali will further increase the potential for precipitation. Sewage works operators would not like struvite formation in pipelines, hence controlled precipitation of struvite could be advantageous.

Effective struvite formation can contribute significantly to phosphate removal and will depend on four major parameters:

- the presence of sufficient magnesium and ammonia
- the presence of sufficient phosphate
- an alkaline environment
- suitable seed material.

The required mass ratio (complying with the 1 : 1 : 1 molar ratio) for effective and efficient struvite formation is 1,71 Mg : 1 N : 2,21 P. While most sewage effluents contain large amounts of ammonia, there is usually a deficiency in magnesium and phosphate. Supplementation with these components was necessary to establish conditions in the effluent which were conducive to struvite formation.

Bench scale experimentation showed a phosphate fixation of 90% or more was attained at a dosage of about 1 mol Mg/mol. Magnesium ammonium phosphate was formed efficiently by adding magnesium to the supernatant, and by increasing the system pH to at least 8 with the addition of NaOH or by aeration. The phosphate removal ratio during pilot scale experiments was 70% and granulated struvite was produced.

Laboratory scale and pilot scale tests have indicated struvite formation in anaerobic digester effluents after dosing with $MgCl_2$ and adjusting the pH to above 8, phosphate fixation of up to 90% was attained.

Struvite crystallization in fluidized bed reactors showed that supplementation of anaerobic digester effluents with both $MgSO_4$ and K_2HPO_4 enhanced struvite formation. With pH adjustment to 9,5 , a phosphate removal of 99% could be attained in a continuous flow reactor as a result of both struvite and HAP formation.

The Daspoort and Rooiwal anaerobic digester effluents were very similar and both displayed the need for supplementation to enhance struvite formation. The complexity of these effluents complicates the task of supplementation to obtain a suitable ratio of magnesium, ammonia and phosphate for the most efficient controlled struvite formation. It was also found that on initial supplementation of the required components the effluent the required mass ratio was not realized and the effluent had to be acidified. This was attributed to precipitation as well as the high alkalinity found in both effluents. This presented a problem as the effluent required large amounts of NaOH obtain the desired pH level. This would affect the economical viability of the process.

Precipitation patterns can be complex in liquors or effluents with many components, but it is still possible to predict the types of precipitates that may be expected by chemical modelling. In this study the chemical modelling was used to confirm rather than to predict. It was shown that struvite formation did in fact occur, indicating that near optimal conditions were established and attained.

It was also found that the presence of high concentrations of calcium would result in phosphate removal by the simultaneous formation of HAP with the struvite formation at a pH level of 9,5, although HAP is more effectively formed at pH levels in the order of 10,5.

The use of quartz sand as a seed material proved to be suitable, as it did not interfere with the struvite formation and provided an inert surface on which the crystallization could take place.

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