

VARIOUS STRUCTURES OF STRUVITE CRYSTALS

JAN SUSCHKA¹, ELIGIUSZ KOWALSKI², SEBASTIAN POPLAWSKI¹¹ University of Bielsko-Biała, ul. Willowa 2, 43-309 Bielsko-Biała² Institute of Environmental Engineering of the Polish Academy of Science
ul. M. Skłodowskiej-Curie 34, 41-819 Zabrze

Keywords: struvite, magnesium ammonia phosphate, phosphorous recovery, crystal forms.

RÓŻNE STRUKTURY KRYSZTAŁÓW STRUVITU

Wytrącanie struwitu (fosforanu amonowo-magnezowego) ze ścieków cieszy się obecnie dużym zainteresowaniem, ponieważ stanowi może znaczną uciążliwość w wyniku wytrącania się w armaturze oraz ze względu na potencjalną możliwość odzysku fosforu wykorzystywanego jako cenny nawóz. Z doniesień literaturowych wynika, że struwit może ulec wytrąceniu w formie kryształów ortorombowych lub igłowych. Wyniki naszych badań sugerują, zarówno w odniesieniu do roztworów mianowanych jak i rzeczywistych ścieków, zależność formy krystalizacji od obecności w znacznych ilościach wolnego amoniaku w roztworze. Azot amonowy (jony NH_4^+) występuje zwykle w odciekach z odwadniania przefermentowanych osadów w bardzo dużych stężeniach (rzędu $1000 \text{ mg N-NH}_4/\text{dm}^3$). Wolny amoniak występuje jednak tylko w szczególnych warunkach procesu wytrącania struwitu. Te szczególnie warunki to szybka zmiana pH roztworu przez dodatek np. NaOH. W przypadku zastosowania sprężonego powietrza celem mieszania lub uwolnienia dwutlenku węgla z roztworu zmiany pH są powolne i wolny amoniak ulatnia się do atmosfery. Opublikowane prace w pewnym stopniu potwierdzają postawioną hipotezę zależności formy krystalizacji od obecności wolnego amoniaku. Potwierdzenie tej hipotezy posiada istotne znaczenie przy realizacji procesu wytrącania struwitu celem odzysku fosforu.

Summary

There is currently a considerable interest in the precipitation of struvite (magnesium ammonium phosphate) in waste waters, both because it can cause nuisance deposits in treatment works, and as a potential route to recover phosphates for recycling in the form of fertiliser. The literature shows that struvite crystals precipitated out from sewage can have either an orthorhombic or a needle-like shape. Our own experimental work on struvite precipitation, both in pure solutions and in waste water treatment plant liquors, suggested that the shape of the crystals formed was dependent on the presence or not in the reactor vessel of significant levels of free ammonia. Ammonium (NH_4^+ ion) concentrations are generally present in waste waters in relatively high concentrations (about $1.000 \text{ mg N-NH}_4/\text{dm}^3$ in sewage sludge liquors). Free ammonia, however, will only occur under certain reaction conditions: that is, if a rapid pH-increase occurs (e.g. if NaOH or other chemical addition is used to induce phosphate precipitation), but not if intensive aeration only is used for mixing or for CO_2 stripping (as this will drive off any free ammonia generated into the air). The published struvite crystallisation works on appear to confirm the hypothesis that the resulting crystal shape depends on free ammonia presence. This could have important implications for controlling and improving the processes for phosphorous recover for recycling by struvite precipitation.

INTRODUCTION

Theoretical bases and modelling of struvite formation are well described in the literature e.g. by Battistoni et. al. [2], Doyle and Parsons [4]. Precipitation of struvite from wastewater and sludge liquors requires conditions in which the solubility product K_{sp} is exceeded. This subject was examined extensively by Dole and Parsons [4]. In general, in municipal waste waters there is a deficit of magnesium in comparison to ammonia and phosphates, which has to be satisfied by addition of magnesium salt or seawater [3, 7, 12].

Magnesium ammonia phosphate – struvite, can crystallise in many different forms [6]. However, when precipitated at sewage or industrial waste water treatment plants mainly two different crystals forms are found. The basic literature, including chemical and mineralogical handbook, states that struvite crystals have an orthorhombic structure. Medical scientific papers show orthorhombic structured struvite crystals in urine describing them as having a “coffin” like structure.

Many authors reporting on the occurrence of struvite in the water industry have confirmed the orthorhombic structure of struvite crystals. Parsons *et al.* [9] has stressed that crystals of struvite have a distinctive orthorhombic structure.

Some authors, however, have reported crystals of a thin prolonged shape of different thickness and length and described them as having a “needle like” form (this term is not mineralogically correct but is widely used). Needle shape of crystals has been shown by [1, 6, 10, 12]. Hirasawa [6] confirmed on the basis of X-ray diffraction analysis, that both of these very different forms are struvite. If the above finding is to be accepted, then there must be a clear reason for the difference in crystal form, however no good explanation has been given so far. The only hypothesis offered is that of Hirasawa [6] who suggests that the crystal structure varies with the Mg/P ratio, having for Mg/P = 1 an orthorhombic structure and for Mg/P ratio equal to 4 a needle like structure.

The results of our experimental do not support the explanation given by Hirasawa [6]. The research results presented here suggest a different reason for the two forms of struvite crystals. The explanation of the reasons for the varying form of struvite crystal could be of interest for the water industry because the crystals structure may have a decisive effect on scaling of pipes and incrustation on different parts of sewage sludge handling equipment. Also process parameters of phosphorous recovery by struvite precipitation could be influenced.

METHODOLOGY

MODELS AND OPERATIONAL PARAMETERS

Two small sub-pilots models, different in shape and volume, were constructed. The reason for the use of two different models was twofold. This allowed us to carry out simultaneously investigations at two different sewage treatment plants, and to test somewhat different hydraulic conditions. Both models had provisions for internal and external mixing. External mixing was assured by a recirculation of the reactor content by a pump. In addition, the pressured air could be supplied by means of a perforated pipe or ceramic porous stone (diffuser).

The smaller model shown in Figure 1 had a total volume of 10 dm³. The total height of the reactor was 500 mm, and had a diameter of 125 mm. The conical part had a height of 220 mm.

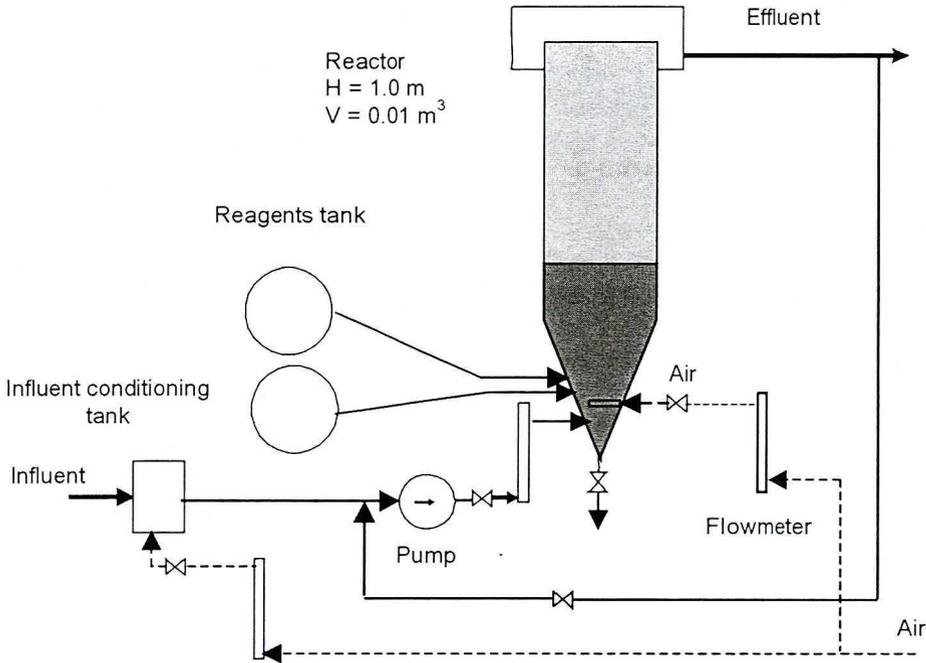


Fig. 1. Small continuous flow fluidised bed crystallisation reactor ($V = 0.01 \text{ m}^3$)

The larger model with an active volume of 100 dm³ is shown in Figure 2. The conical reactor had an obtuse angle of 20°. The total height was 1800 mm, and the upper diameter was 510 mm. The conical reactor was filled to the height of 1700 mm, at which the diameter was 480 mm. The sewage filtrate from the digested sludge dewatering press and required chemicals were supplied from the bottom. Also the recirculated reactor fluid re-entered at the bottom. The inflow streams were tangentially oriented in order to obtain a spiral upward flow. The principle of this type of reactor is based on varying flow velocity across the reactor. There is a decrease of velocity with the increase of the distance from the bottom in the conical part of the reactor. Slow mixing in the upper sections follows intensive mixing at the bottom. In the upper section therefore the formation and growth of crystals (agglomeration) can take place. An important feature was the recirculation of fluid (outflow) from a point above the suspended solids blanket in order to avoid disintegration of clusters of crystals in the recirculation pump.

Magnesium was added to the smaller reactor in the form of MgO. For practical reasons MgO was supplied as powder or as suspension into water once a day. The amount was calculated to have a ratio of PO₄/Mg of about 1:4, – assuming an average phosphates content of 350 mg/dm³. The overdose of MgO was intentional, because added MgO has low solubility and hydrolysis might not be complete under the variable quality (phosphates concentration) of continuously supplied (over 24 hours) with real sludge supernatant.

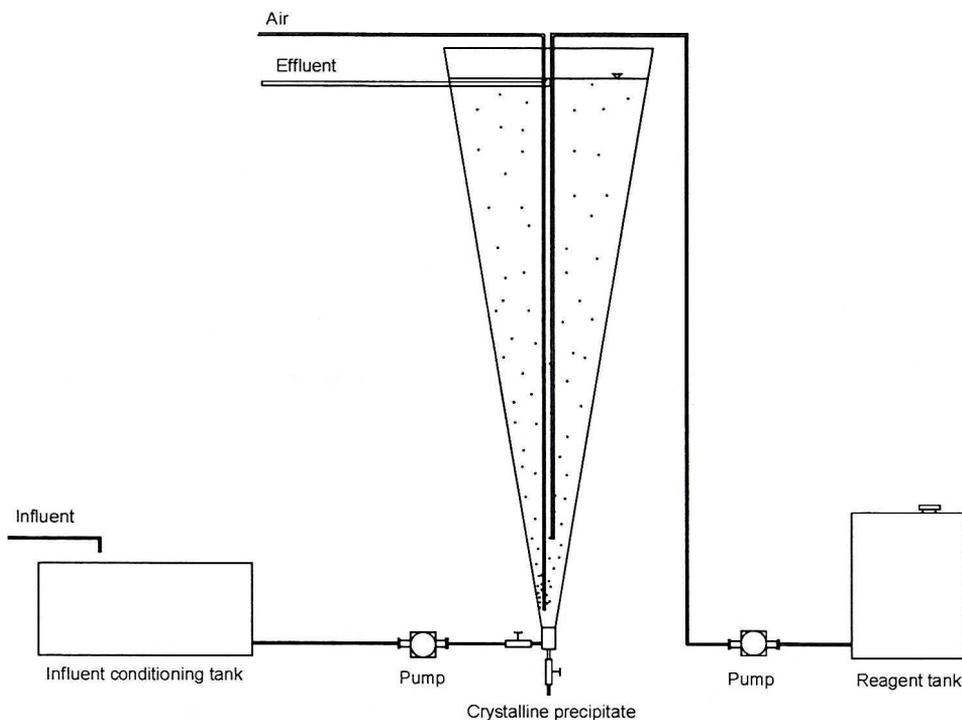


Fig. 2. Conical 0.1 m³ continuous flow reactor

The larger reactor was operated with addition of magnesium as MgO, MgCl₂ or MgSO₄. The smaller reactor was operated continuously for 85 days, and larger one for 67 days.

Also, beaker tests (beaker volume of 2 dm³) were carried out to test a wide range of parameters. Apart from tests of struvite precipitation in real filtrate or centrate just by raising the pH, the tests were made by addition of different amounts of magnesium. Magnesium was added in the form of MgO, MgCl₂ and MgSO₄. Also different concentrations of ammonia were investigated. Tests were also run for pure tap or distilled water to which the appropriate reagents were dosed in different rates. In total more than 80 beaker tests were performed. The samples were mixed with blade stirrers of low rpm, sufficient however, to maintain the particles in suspension.

ANALYTICAL PROCEDURE

Phosphates were determined colorimetrically according to Standard Methods 17th Ed. [11], using a spectrophotometer DR 400 UV/VIS (HACH co., USA). The concentration of ammonia nitrogen was determined by an Ion meter pMx 3000 (WTW). Periodically the accuracy was verified by using a Kjeltex system 1002 distilling unit in accordance with Standard Methods 17th Ed. [11]. For determination of magnesium concentration, an atomic absorption spectrometer AAnalyst 100 – Perkin Elmer was used.

In order to ascertain whether the precipitate was struvite, X-ray diffraction analyses were carried out. A wide angle X-ray (WAXS) apparatus, with a diffraction meter HZG-4 was used.

Also to observe the aspect of precipitated crystals, microscope pictures were taken. The microscope used – NIKON ALPHAPHOT-2 YS2 coupled with a camera PANASONIC GP-KR222 allowed also for size measurements and used LUCIA ScMeas Version 4.51 program.

MATERIALS AND SUBSTRATE USED

To cover the magnesium deficit different salts were tested. Apart from $MgCl_2$ and $MgSO_4$, magnesium oxide was also used. Commercial magnesium oxide was available as fertiliser, (98% of MgO) fodder (96% of MgO) and magnesite (78% of MgO). Because of the low solubility of magnesium oxide, a 5% mixture of the technical chemicals was used.

Digested sludge liquors from two municipal sewage treatment plants were used for the investigations reported here. One of the municipal sewage treatment plants had a maximum capacity of 63 000 m^3/d and was designed for both of organic and nutrient removal. The actual flow at the time of the experiments was 30 000 m^3/d . The applied process was done according to the “Bardenpho” flow sheet. Excess sludge after thickening was anaerobically digested at a temperature of about 32°C.

Anaerobically digested sludge was dewatered by belt filter presses, and the resulting filtrate had the most often found characteristics given in Table 1. According to expectations the highest concentrations of phosphates were measured in the digested sludge filtrate.

Table 1. Filtrate characteristics

| Parameters | Units | Concentration range* |
|------------------------|----------------------|----------------------|
| pH | – | 7.00–7.60 |
| P- PO_4 | mg P/dm ³ | 130–170 |
| Ca | mg/dm ³ | 15–20 |
| Mg | mg/dm ³ | 2–20 |
| K | mg/dm ³ | 150–350 |
| Total suspended solids | mg/dm ³ | 70–80 |
| N- NH_4 | mg N/dm ³ | 800–1450 |

* Data based on daily determinations over a period of three month

The other municipal sewage treatment plant had a total capacity of 90 000 m^3/d dry weather flow, and was divided into two parts, (1) approximately 40 year old classical biological – activated sludge treatment plant, (30 000 m^3/d), and (2) a newly built (2000) biological – activated sludge – nutrient removal plant (60 000 m^3/d).

Phosphates were only partially removed biologically, and the required discharge concentration was achieved by addition of iron salts. Excellent organic carbon removal, nitrification and denitrification were being achieved. Relevant to this work was the anaerobic digestion of excess sludge at a temperature of 33°C. Digested sludge was dewatered by centrifuges. The centrate from the two installed centrifuges, which had a relatively high phosphate concentration, was used in the performed investigations.

The characteristic parameters of this centrate are presented below in Table. 2.

Table 2. Centrate characteristics

| Parameters | Units | Concentration range* |
|------------------------|----------------------|----------------------|
| pH | – | 7.19–7.86 |
| P-PO ₄ | mg P/dm ³ | 65–106 |
| Ca | mg/dm ³ | 52–69 |
| Mg | mg/dm ³ | 13–17 |
| Total suspended solids | mg/dm ³ | 70–80 |
| N-NH ₄ | mg N/dm ³ | 990–1600 |

* Data based on daily determinations over a period of three month

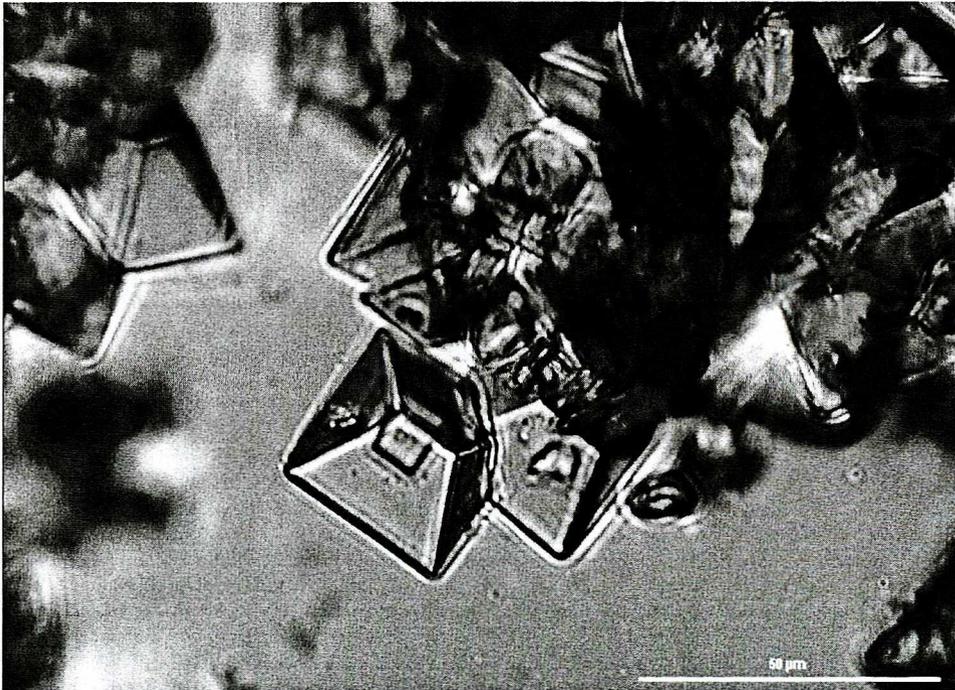
There was a relatively high variation in the centrate quality related to the digested sludge quality, depending on which of the four digesters the sludge came from. In the period relevant to this research, the digesters had not yet achieved stable operating conditions.

RESULTS AND DISCUSSION

In our experiments crystallisation of struvite took place most easily when magnesium chloride was used to fulfil the stoichiometric requirements of the formula – MgNH₄PO₄·6H₂O. The precipitated crystals had a regular orthorhombic structure (Fig. 3) independently of the substrate used – Plant 1 filtrate or Plant 2 centrate. Similar regular structure was found when the deficit of magnesium was completed through the addition of magnesium sulphate (Fig. 4). Not always as regularly as shown in Figures 3 or 4, orthorhombic structure was formed.

When magnesium oxide was added, apart from a few regular orthorhombic crystals, the majority had a needle like shape. The supposition [6] concerning the effect of the Mg/P rate on the crystals structure was not confirmed: we found no difference in the crystals structure in relation to the Mg/P ratios from 1 to 4 when magnesium was added as MgCl₂ or MgSO₄. Although it was stated [6] that X-ray diffraction analysis had proved that for the three different ratios of Mg/P (1, 2 and 4) the different crystals structures are struvite, attention should be given to molar ratio based on chemical analyses. For the Mg/P ratio of 1 the molar ratio of Mg:NH₄:PO₄ was 1:1:1.03 which almost exactly corresponds to the formula of struvite – MgNH₄PO₄. For the Mg/P ratio of 4 the respective molar ratio was 1:1.27:1.06, corresponding to a 27% excess of ammonia present in the precipitate.

It has to be mentioned also that Hirasawa [6] used in his experiments a very high excess of ammonia nitrogen which he added in the form of ammonia chloride. Also in other case [10], crystals in the form of needles have been obtained when real waste water of a very high ammonia content was used.



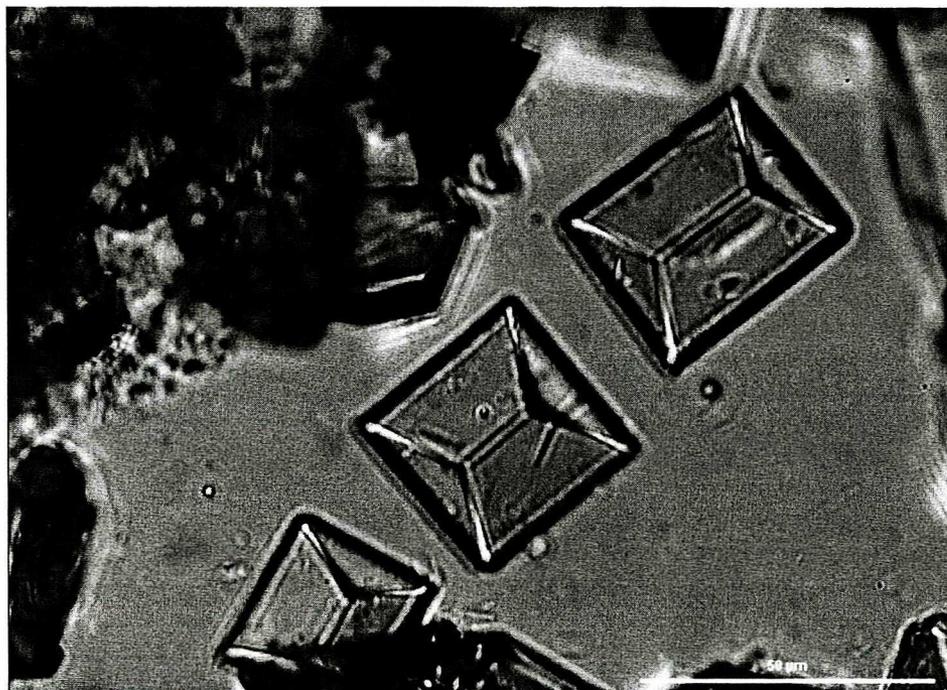
| Parameters | Units | Concentration before | Concentration after |
|-------------|---|----------------------|---------------------|
| pH | – | 8.08 | 8.57 |
| temperature | °C | 20.1 | 20.3 |
| phosphates | mg PO ₄ ³⁻ /dm ³ | 424.3 | 43.3 |
| ammonia | mg NH ₄ ⁺ /dm ³ | 1640 | 1540 |
| magnesium | mg Mg ²⁺ /dm ³ | 4.6 | 14.8 |

1 hr aeration, 102.6 mg Mg/dm³ added as MgCl₂

Fig. 3. Struvite crystals with magnesium chloride used as the source of magnesium

The importance of ammonia presence in excess to required amounts simultaneously to surplus of magnesium was confirmed in our experiments. It was found that the addition of magnesium oxide in surplus in relation to the content of phosphates and high ammonia concentration at the order of 1500 mg/dm³ resulted in precipitation of needle like crystals (Fig. 5). The needles had in average a length of up to 100 µm and a thickness of 3 to 10 µm. Occasionally a few orthorhombic crystals could also be found (Fig. 6).

Magnesium oxide added in excess under continuous mixing leads to a relatively rapid pH increase with a simultaneous liberation of free ammonia. A strong smell of ammonia was always associated with this mode of reactor operation when mixing was caused by filtrate supply and recirculated reactors content to the conical bottom. This mode of mixing is referred later as hydraulic mixing. Free ammonia was not analytically determined. The high



| Parameters | Units | Concentration before | Concentration after |
|-------------|---|----------------------|---------------------|
| pH | – | 8.08 | 8.58 |
| temperature | °C | 20.1 | 19.9 |
| phosphates | mg PO ₄ ³⁻ /dm ³ | 424.3 | 54.6 |
| ammonia | mg NH ₄ ⁺ /dm ³ | 1640 | 1580 |
| magnesium | mg Mg ²⁺ /dm ³ | 4.6 | 22.7 |

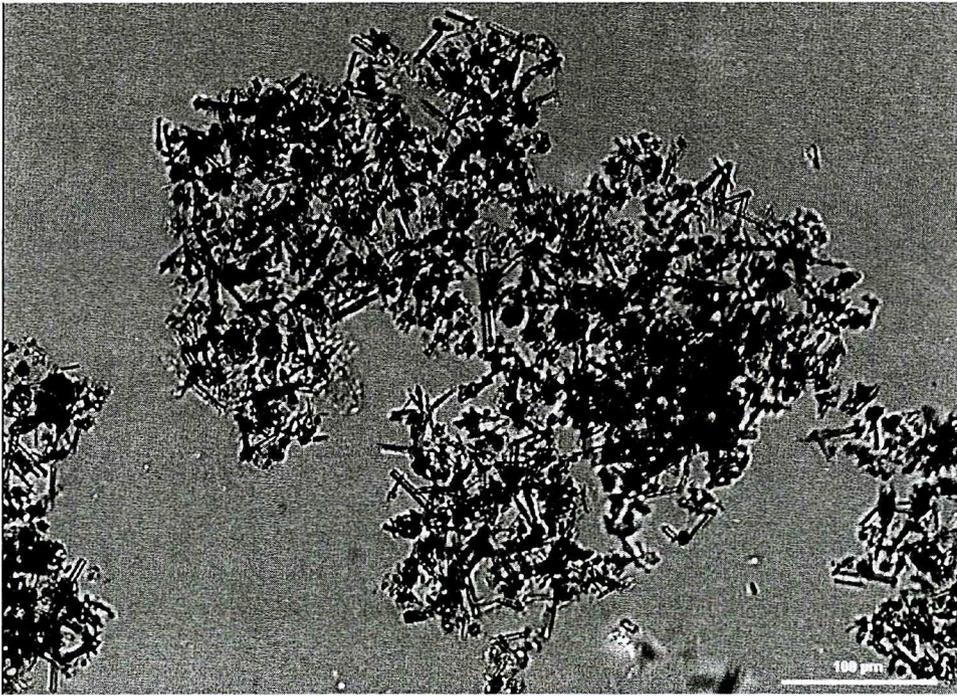
1 hr aeration, 102.6 mg Mg/dm³ added as MgSO₄

Fig. 4. Regular orthorhombic crystals structure of precipitated struvite using magnesium sulphate

pH and smell of ammonia over the sample surface is however, a sufficient prove of the presence of free ammonia.

If in addition to hydraulic mixing, pressured air was supplied from the bottom, mainly to enhance pH increase, a different crystal structure was produced. The only change in the reactors operation was the addition of pressured air. The substrate – filtrate or centrate experiments – as well as the amount of added magnesium remained unchanged. The addition of pressured air resulted simultaneously in superfluous carbon dioxide stripping and rapid removal (also stripping) of free ammonia. The smell of ammonia was much less pronounced, probably because of the dilution by the added air.

A very rapid increase of pH due to the addition of NaOH causes a shift in the equilibrium of ammonia ions and free ammonia in the solution. For example, at pH of 9.5 (Fig. 7) about 60% of ammonia in water would be present as free ammonia.



| Parameters | Units | Concentration before | Concentration after |
|-------------|---|----------------------|---------------------|
| pH | – | 7.85 | 9.88 |
| temperature | °C | 18.1 | 20.2 |
| phosphates | mg PO ₄ ³⁻ /dm ³ | 410.0 | 98.3 |
| ammonia | mg NH ₄ ⁺ /dm ³ | 1550.0 | 990.0 |
| magnesium | mg Mg ²⁺ /dm ³ | 5.8 | 17.8 |

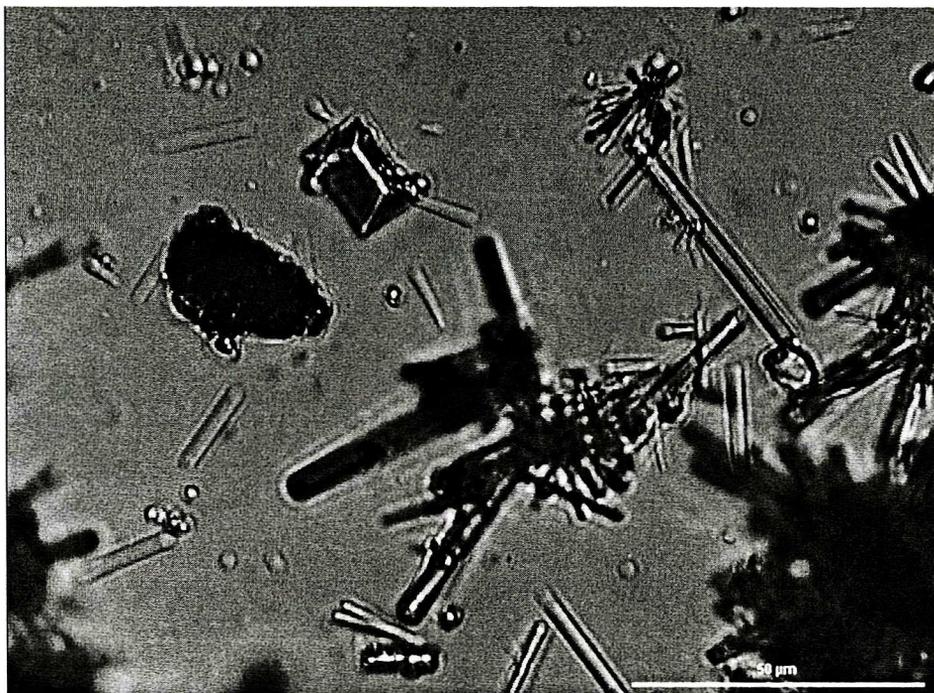
10 g MgO/dm³ added

Fig. 5. Needle-like struvite crystals formed in the presence of excess amounts of ammonia

In addition, when there was a surplus of ammonia in relation to PO₄ and or Mg, the needle shaped crystals prevailed. In Figure 8 another example shows crystals for an initial concentration of 500 mg/dm³ of ammonia (relative to magnesium, this was a 5 times surplus), with a change of pH up to 9.0 and hydraulic mixing.

However, when there was no rapid pH increase (i.e. without addition of sodium hydroxide) but a slow pH increase by aeration, allowing the formed free ammonia to be progressively stripped off, the orthorhombic structure of crystals predominated (Fig. 9).

The hypothesis of different crystal structures formed in the presence or absence of free ammonia was confirmed for various rates of Mg:NH₄:PO₄. It has to be mentioned however that the observed shapes of crystals were not always all in one form – needle shape or orthorhombic structure. In some cases intermediate forms were produced. To show this,



| Parameters | Units | Concentration before | Concentration after |
|-------------|---|----------------------|---------------------|
| pH | – | 7.94 | 10.12 |
| temperature | °C | 18.3 | 22.3 |
| phosphates | mg PO ₄ ³⁻ /dm ³ | 380.0 | 210.0 |
| ammonia | mg NH ₄ ⁺ /dm ³ | 1410.0 | 1015.0 |
| magnesium | mg Mg ²⁺ /dm ³ | 4.8 | 22.3 |

10 g MgO/dm³ added

Fig. 6. Needle-like crystals with occasional orthorhombic crystals

another example for the rates of Mg:NH₄:PO₄ equal to 767:2000:500 mg/dm³ is shown in Figures 10 and 11. In Figure 10, crystals were obtained with a rapid pH increase to 9.0 while in Fig 11 the crystals were produced at gentle change of pH.

Our results lead to the conclusion that the presence of high concentrations of free ammonia has a decisive impact on the form of the precipitated crystals. This is to some extent supported by the results obtained by Stratful *et al.* [12], who in their experiments did not add large amounts of ammonia nitrogen (ammonia chloride was added instead) they increased pH to 10, resulting in free ammonia to be present in the liquid. Stripping of a substantial part of this ammonia could explain why the phosphate removal rate was only about 85%. The results of Stratful *et al.* [12] and our own results do not support the conclusions of Durrant *et al.* [5] that the change of crystal form was caused by supersaturation with magnesium and ammonia nitrogen ions.

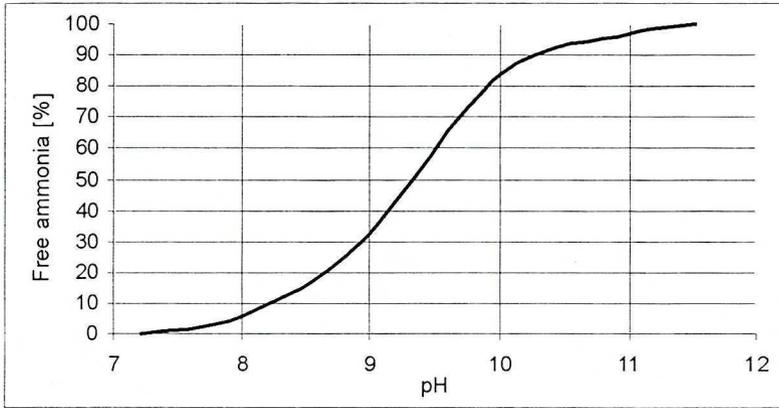
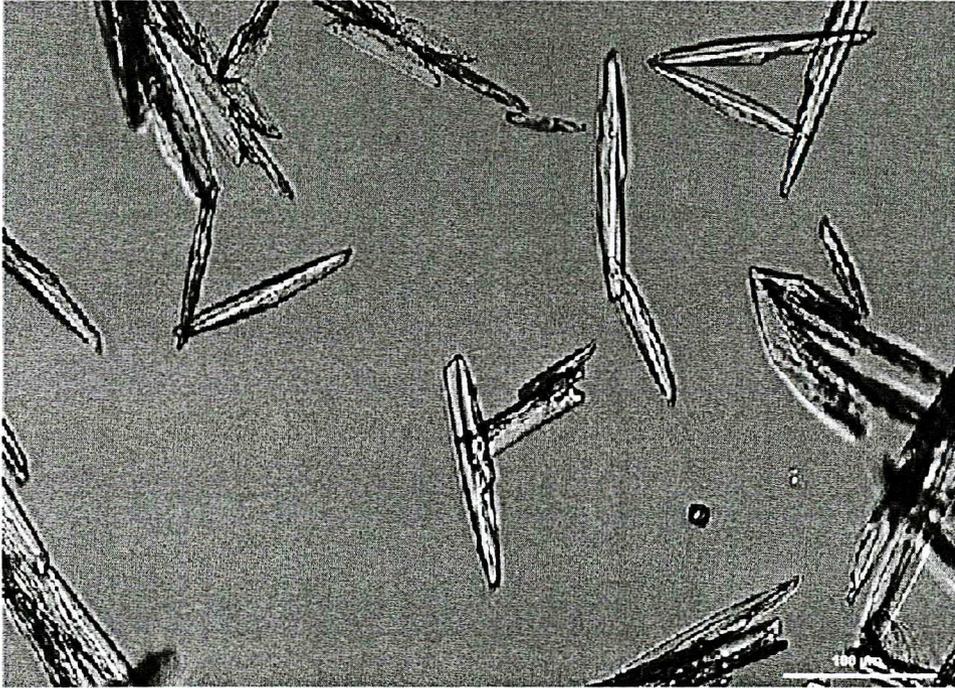


Fig 7. Changes of ammonia forms in relation to pH [8]



| Parameters | Units | Concentration before |
|-------------|---|----------------------|
| pH | - | 9.00 |
| temperature | °C | 20.1 |
| phosphates | mg PO ₄ ³⁻ /dm ³ | 500 |
| ammonia | mg NH ₄ ⁺ /dm ³ | 500 |
| magnesium | mg Mg ²⁺ /dm ³ | 128 |

Mixed sample, clean water, addition of NaOH

Fig. 8. Needle-like structure of crystals obtained due to rapid pH increase



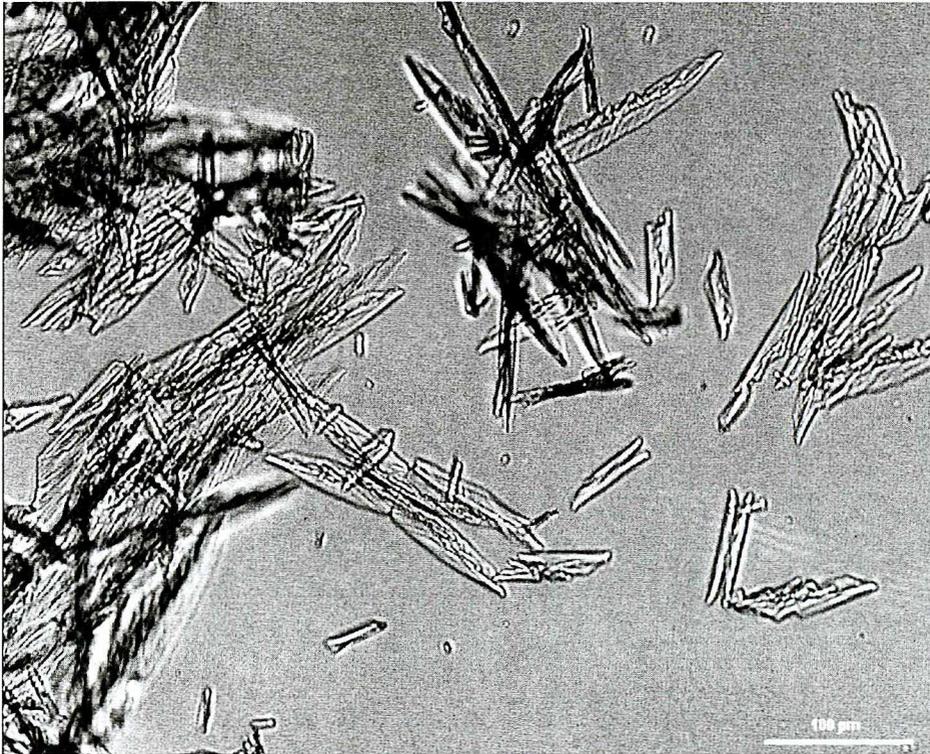
| Parameters | Units | Concentration before |
|-------------|---|----------------------|
| pH | – | 7.78 |
| temperature | °C | 21.3 |
| phosphates | mg PO ₄ ³⁻ /dm ³ | 500 |
| ammonia | mg NH ₄ ⁺ /dm ³ | 500 |
| magnesium | mg Mg ²⁺ /dm ³ | 128 |

Aerated sample, clean water

Fig. 9. Similar conditions of struvite precipitation as shown in Fig. 8, except for pH modification

The crystal shape seems to be of great importance for their aggregation ability in clusters (agglomerates) large enough to be easily separated from the liquor. From the literature it appears that the orthorhombic crystals structure may have a higher affinity and form larger agglomerates. This hypothesis is however not proven. Our experiments suggested that the needle shaped struvite crystals form clusters faster. This aspect requires further investigations.

Based on our experiments, it seems to be possible to control the struvite precipitation process towards one or other crystal form. The ability of aggregation of needle like or orthorhombic crystals is still an open question. Obviously the mixing rate and hydraulic conditions will have an impact on the aggregation phenomenon. At present however the results of aggregation are more an art than an engineering process.



| Parameters | Units | Concentration before |
|-------------|---|----------------------|
| pH | - | 8.98 |
| temperature | °C | 22.4 |
| phosphates | mg PO ₄ ³⁻ /dm ³ | 500 |
| ammonia | mg NH ₄ ⁺ /dm ³ | 2000 |
| magnesium | mg Mg ²⁺ /dm ³ | 767 |

Mixed sample, clean water, addition of NaOH

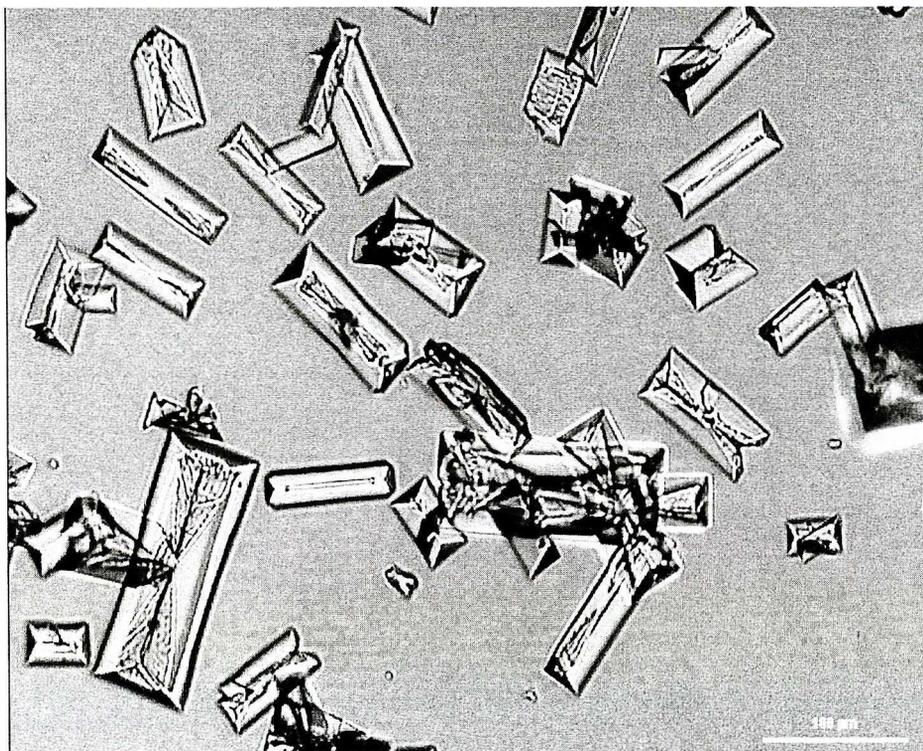
Fig. 10. Another example of needle-like crystals obtained as a result of rapid pH increase

CONCLUSIONS

Precipitated struvite crystal shape was found to depend on the presence of free ammonia. In practice free ammonia will occur when digested sludge liquor has high ammonia concentrations and magnesium oxide is added under mechanical or hydraulic mixing. Under such conditions the needle like forms of struvite crystals will prevail.

However, if mixing is executed with pressured air, even if high amounts of ammonia are present, most of the free ammonia (produced as the result of pH increase) is stripped off and the crystals formed have a regular orthorhombic structure.

At low concentrations of ammonia, close to the stoichiometric requirements, struvite crystals will predominately have an orthorhombic structure.



| Parameters | Units | Concentration before |
|-------------|---|----------------------|
| pH | – | 7.58 |
| temperature | °C | 21.2 |
| phosphates | mg PO ₄ ³⁻ /dm ³ | 500 |
| ammonia | mg NH ₄ ⁺ /dm ³ | 2000 |
| magnesium | mg Mg ²⁺ /dm ³ | 767 |

Aerated sample, clean water

Fig. 11. Orthorhombic forms obtained without pH modification

ACKNOWLEDGEMENTS

The authors would like to thank CEEP for partially sponsoring of this work and especial thanks are dedicated to Chris Thornton of CEEP for encouraging, patience and valuable advise given.

REFERENCES

- [1] Abbona F., M. Calerri, G. Ivaldi: *Synthetic struvite, MgNH₄PO₄·6H₂O, correct polarity and surface futures of some complementary forms*, Acta Crystallographica, section B, Structural Science, **40**, 223–227 (1984).

- [2] Battistoni A., De Angeles, M. Priscicandro, R. Boccadoro, D. Bolzonella: *P removal from anaerobic supernatants by struvite crystallization: long term validation and process modelling*, *Wat. Res.*, **36**, (8), 1927–1939 (2002).
- [3] Doyle J.D., K. Oldring, J. Churchley. S.A. Parsons: *Struvite formation and the fouling propensity of different materials*, *Wat. Res.*, **36**, (16), 3971–3978 (2002).
- [4] Doyle J.D., S.A. Parsons: *Struvite formation, control and recovery*, *Wat. Res.*, **36**, (16), 3925–3940 (2002).
- [5] Durranat A.E., M.D. Scrimshaw, I. Stratful, J.N. Lester: *Review of the feasibility of recovering phosphate from wastewater for use as a raw material by the phosphate industry*, *Env. Technol.*, **20**, (7), 749–758 (1999).
- [6] Hirasawa I.: *Study on the recovery of ions in wastewater by crystallization*, *Memories of the Scholl of Science and Engineering*, Waseda University, **60**, (97), 119 (1996).
- [7] Matsumiya Y., Y. Ueno, M. Fujii: *Phosphorous removal from side streams by crystallisation of magnesium ammonium phosphate using seawater*, *J. Chart. Inst. Water Environ. Manage*, **14**, 291–296 (2000).
- [8] Metcalf & Eddy Inc.: *Wastewater Engineering: Treatment and Reuse*, 4th ed., McGraw-Hill, New York 2003.
- [9] Parson S., F.Wall, J.D. Doyle, K. Oldring, J. Churchley: *Assessing the potential for recovery of struvite from digested sludge liquors*, *Environ. Technol.*, **22**, 1279–1286 (2001).
- [10] Schulze-Rettmer R., P. Metzen, P. Alfter, B. Diering, R. Fricks: *MAP precipitation – pilot plant investigation in Germany, manure as the most important phosphate resource*, [in:] Second International Conference on Recovery of Phosphates from Sewage and Animal Wastes, 12–14 March, Noordwijkerhout, Holland, 2001.
- [11] *Standard Methods for Water and Wastewater Examination*, 17th ed. American Public Health Association, Washington, D.C. 1995.
- [12] Stratful I., M.D. Scrimshaw, J.N. Lester, *Conditions influencing the precipitation of magnesium ammonium phosphate*, *Wat. Res.*, **35**, (17), 4191–4199 (2001).

Received: October 25, 2004, accepted: April 4, 2005.