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**STUDY OF THE EFFECTS OF THE REACTOR HYDRAULICS ON STRUVITE
PRECIPITATION AT MUNICIPAL SEWAGE WORKS**

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1. Introduction.

Struvite (MAP) controlled precipitation is today to some extent a well-established technology. However, the technology has found so far limited full scale practical application. There are many reasons for that situation. One reason could be the economy, the other uncertainty in getting continuously good results of crystallisation and crystals agglomeration.

Reviewing the extensive list of publications about both, operational difficulties caused by MAP precipitation in the sewage sludge stream, and investigations on controlled precipitation it was found that different structures of crystals were reported.

The different crystallisation forms should have an explanation. At least two different reasons or parameters affecting the structure could be considered. On one hand the structure could be affected by physical conditions, mainly the technique and rate of mixing. On the other hand some chemical impurities, like e.g. heavy metals could interfere and influence the structure of the formed crystals.

Mineralogists define struvite crystals as of orthorhombic structure, giving respective characteristic parameters. Others like e.g. Parsons (2001) are also describing the crystals as having a distinctive orthorhombic structure. Many authors also previously confirmed the orthorhombic structure of struvite.

Some authors however, have presented needle like crystals of different thickness and length. Needle like crystals have been shown by Schultze-Rettmer et al. (2001) Stratful (2001), Abbona (1984) and Hirasawa (1996). If both of the very different structures are struvite, what Hirasawa(1996) is claiming, then it must be a clear reason for. No convincing explanation was found in the literature. Only Hirasawa (1996) claims that the crystals structure vary with the Mg/P rate, having for $Mg/P = 1$ a orthorhombic structure and with Mg/P rate equal to 4, a needle like structure. Such explanation is difficult to be accepted.

The aim of this work was therefore to make a more profound insight into the problem and bring to a better understanding.

2. Methodology

2.1. Models and operational parameters.

Small semi-technical models have been constructed. Two different models in terms of the shape and volume were used. The reason for the use of two different models was at least twofold. One reason was the intention to carry out simultaneously investigations at two different sewage treatment plants. The other reason was to test slightly different hydraulic conditions. Both models have had the provisions for internal and external mixing. External mixing was assured through a recirculation pump. In addition, pressured air could be supplied by a manhole of a perforated pipe or ceramic porous stone (diffuser).

The smaller model shown in fig. 1 had a total volume of 10 litres.

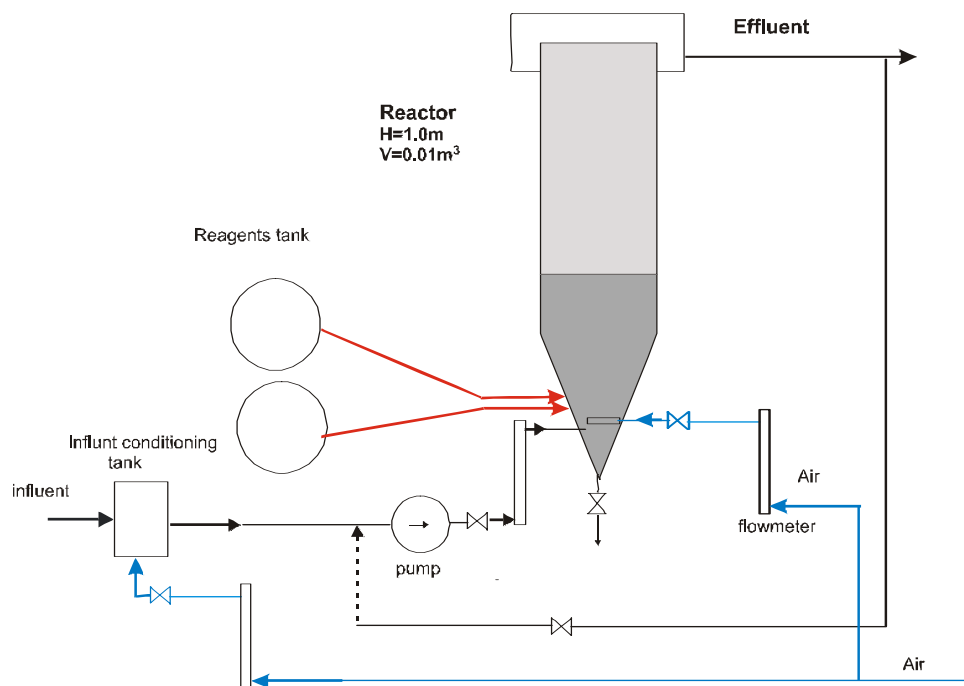


Fig. 1. Small continuous flow fluidised bed crystallisation reactor ($V = 0,01 \text{ m}^3$).

The conical lower part of the reactor had an obtuse angle of 20°. The sewage filtrate from the digested sludge dewatering press and required chemicals were supplied from the bottom. Also the recirculated reactors content entered at the bottom. The streams have been tangentially oriented in order to activate a spiral upward flow. The principle of that type of a 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. Slow mixing in the upper sections follows intensive mixing at the bottom. In the upper sections is therefore the formation and growth of crystals is allowed. An important feature was recirculation of the reactors content from a point above the suspended sludge blanket. Precaution was therefore taken to avoid disintegration of clusters of crystals (aggregates) in the recirculation pump.

The suspended (fluidised) sludge blanket at a constant flow of supplied filtrate of 44 l/h had a different high depending on the recirculation rate. The recirculation rate R was defined as;

$$R = Q_{\text{rec}}/Q_{\text{F}}$$

Where:

Q_{rec} – recirculation flow l/h

Q_{F} – supplied filtrate – l/h

The correlation of the solids blanket high and the recirculation rate or recirculation flow was presented respectively in Fig. 2 and 3.

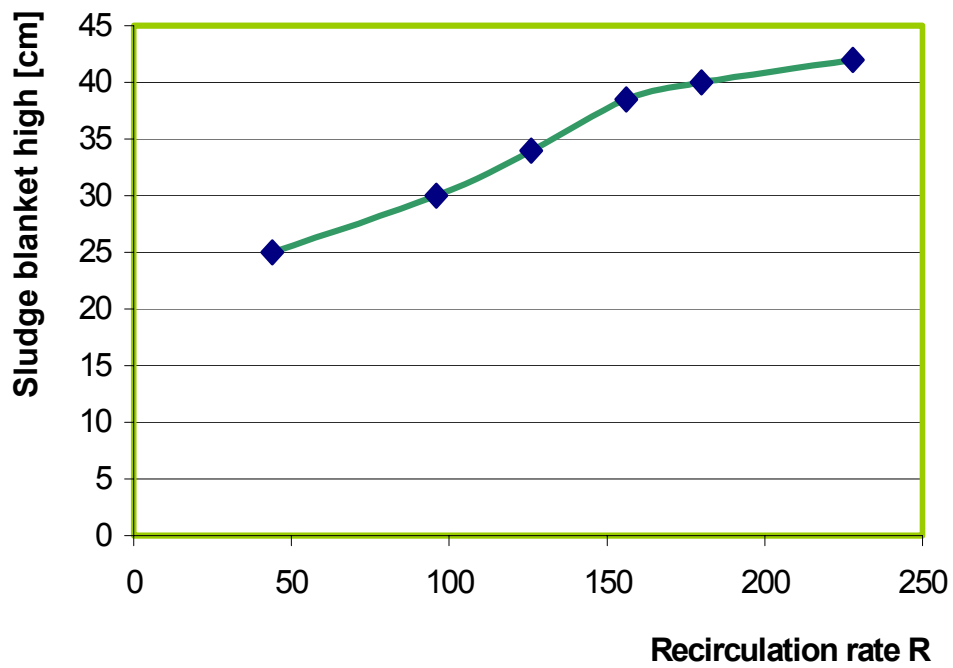


Fig. 2. Correlation between recirculation rate and sludge blanket high

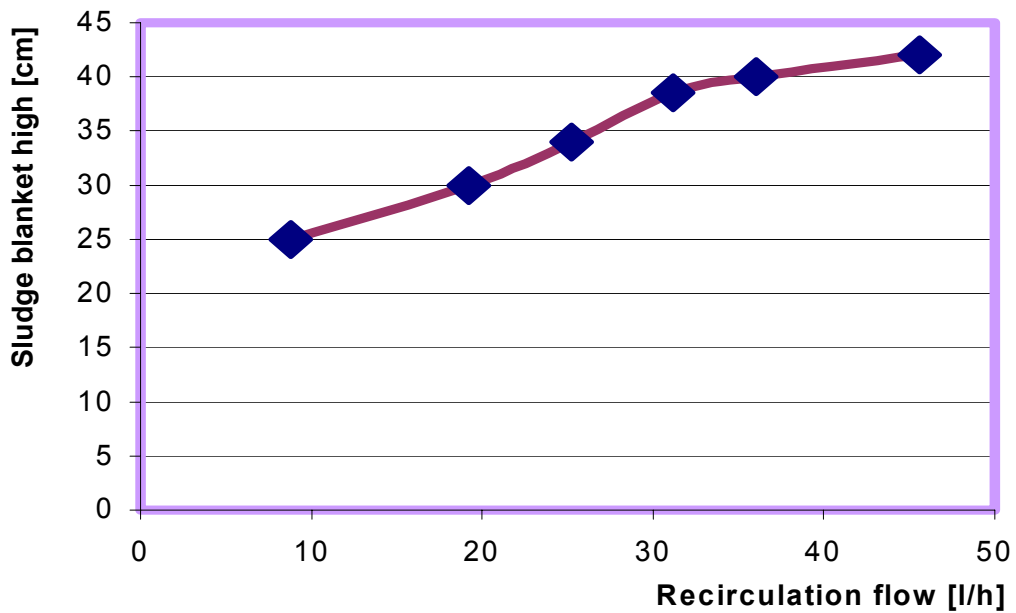


Fig. 3 Correlation between recirculation flow and sludge blanket high.

For the highest tested recirculation flow of 45,6 l/h the finest fraction of particulates have emerged from the blanket and where transported to the pump intake.

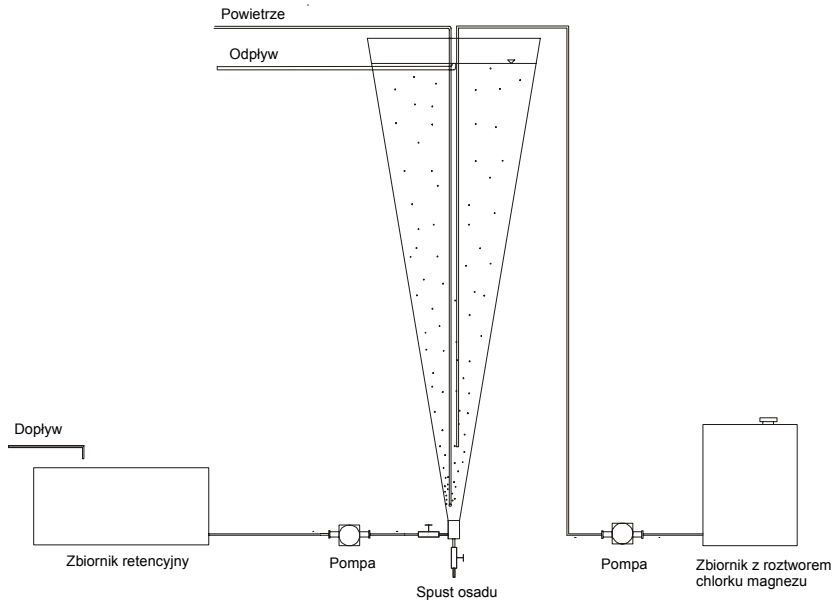


Fig. 4. Conical 0.1 m³ continuous flow reactor.

2.2. Preliminary experiments methodology and determinations.

In addition to continuous flow experiments at above described models, batch laboratory scale experiments have been performed. Beakers of a volume of 3 liters continuously stirred have been used.. All experiments have been executed at a constant temperature of 22 °C. and pH was recorded continuously

Phosphates have been determined colorimetrically using a spectrophotometer DR 4000 UV/VIS (HACH). The concentration of ammonia nitrogen was determined colorimetrically and by ion meter pMx 3000 (WTW) The concentration of magnesium atomic absorption spectrophotometer Aanalyst 100 – Perkin Elmer was applied for magnesium determinations.

In order to ascertain the precipitate is really struvite, X-ray diffraction analysis have been done. A wide angle X-ray (WAXS) apparatus, with a diffraction meter HZG-4 was used.

Also to observe the form of precipitated out crystals microscopic pictures have been made. The microscope used – NIKON ALPHAPHOT- 2 YS2 coupled with a camera PANASONIC GP-KR222 allowed also for size measurements used a programme LUCIA ScMeas Version 4.51.

The struvite precipitated particles size distribution was determined on a laser apparatus ANALYSETTE 22 - Fritsch (Germany). Results are printed out on tables and are presented graphically.

2.3. Materials

To cover the magnesium deficit different salts have been tested. Apart from $MgCl_2$ and $MgSO_4$, magnesium oxide was used. Commercially magnesium oxide was available as fertiliser, (98 % of MgO) fodder (96 % of MgO) and magnesite (78 % of MgO).

Due to the low solubility of magnesium oxide a 5 % mixture of the technical chemicals were used.

2.4. Substrate

2.4.1. Filtrate – Zabrze sewage treatment plant.

The Zabrze municipal sewage treatment plant has a maximum capacity of 63 000 m^3/d and was designed according to the advanced technology of organic substrate and nutrients removal. The present flow is 30 000 m^3/d . The applied process is according to the “Bardenpho” scheme. Sewage enters directly the biological reactors. There are two reactors, of which each consisted of one anaerobic chamber, two anoxic-denitrification chambers and three nitrification (aerobic) chambers.. In order to achieve the required total phosphorous concentration of 1,5 mg P/l in the effluent chemical precipitation with iron salts is used.

Excess sludge after thickening is anaerobically digested at a temperature of about 32 °C.

As a result of iron salts addition for phosphates removal to the required level of 1,5 mg P/l an increase of produced sludge volume of about 10 % was observed.

According to expectations the highest concentration of phosphates were measured in the sewage digested sludge filtrate. Anaerobically digested sludge is dewatered at belt filter presses, and the resulting filtrate had in average the following characteristic.

Table 1. Filtrate characteristic.

Parameters	Units	Concentration
pH		7,00 -7,60
P-PO ₄	mg/l	130 - 170
Ca	mg/l	15 - 20
Mg	mg/l	2,0 - 20,0
K	mg/l	350 - 350
Total suspended solids	mg/l	70
N-NH ₄	mg/l	800 - 1450

2.4.2. Centrate – Komorowice sewage treatment plant.

The Komorowice municipal sewage treatment plant of a total capacity of 90 000m³/d dry weather flow, is in fact divided into two parts, (1) about 40 years classical biological – activated sludge treatment plant, and (2) a new built in year 2000 biological –activated sludge – nutrient removal plant.

Phosphates are removed are only partially removed biologically, and the requirements are achieved by precipitation with iron salts. Excellent effects of organic carbon, nitrification and denitrification are achieved. What is relevant to this work, is anaerobic digestion of excess sludge at a temperature of 33 °C. Digested sludge is centrifuged for dewatering. The centrate from two installed centrifuges with a relatively high contend of phosphates was used in performed investigations.

The characteristic parameters of obtained centrate is presented below in Table. 2.

Table 2. Centrate characteristic.

Parameters	Units	Concentration
pH	-	7,19 -7,86
P-PO ₄	mg/l	65 - 106
Ca	mg/l	52 –69
Mg	mg/l	13 – 17
Total suspended solids	mg/l	70
N-NH ₄	mg/l	990 - 160

There was a relatively high variation in the centrate quality in connection to the digested sludge quality, which depended on origin of the sludge from one of the four digesters. In the period of investigations carried out, the digesters have not yet been equilibrated. (working in equal conditions).

3. Results and discussion

3.1. Preliminary investigations

In order to determine the operational parameters of the continuous flow models, several laboratory batch experiments have been performed. The main aim was to determine the required reaction time and optimal pH for the specific tested liquors. It was assumed that the effects of phosphates removal are a good indication of crystallisation of struvite, giving that magnesium and ammonia are present in sufficient amounts.

It has to be repeated, what already is known from many publications, that struvite precipitates out by itself, if the pH of the anaerobically digested sludge supernatant (liquor) is raised. This can occur “naturally”, allowing excess carbon dioxide to be released if brought to the atmosphere from the anaerobic digester chamber.

Enhancing of this process is possible by aeration, aiming at CO₂ stripping out – stripping the excess of CO₂ under atmospheric conditions as well as replacing a part of dissolved carbon dioxide by oxygen and nitrogen, present in the introduced air, dissolution. The typical aeration rate of approximately 10 normal cubic meters of air per cubic meter of the liquid, per hour, or more, was used in our investigations. In practical terms at laboratory conditions the aeration process can be described as intensive. (precise measurements, in laboratory batch tests, of air flow rates are useless. At least a container of 1 m depths is required to give indications of practical use).

Examples of pH increase are presented in figure 5. Although the kinetic of pH increase varies in a rather wide range, the most distinct pH increase takes place already within the first 15 minutes. Stabilisation of pH increase, where the increments are less pronounced can be seen to happen after about 60 minutes of aeration.

The effects of aeration are a pH increase in the order of one unit. The effects and rate of pH increase depends on many factors, which are continuously changing with operational anaerobic digester parameters, performance and exploitation.

The effects of pH increase changes however, if magnesium salts are added to complete the required, or add surplus amounts to fulfil the struvite formula. The most pronounced effect has magnesium chloride, and therefore on fig 6 and 7 the influence was shown.

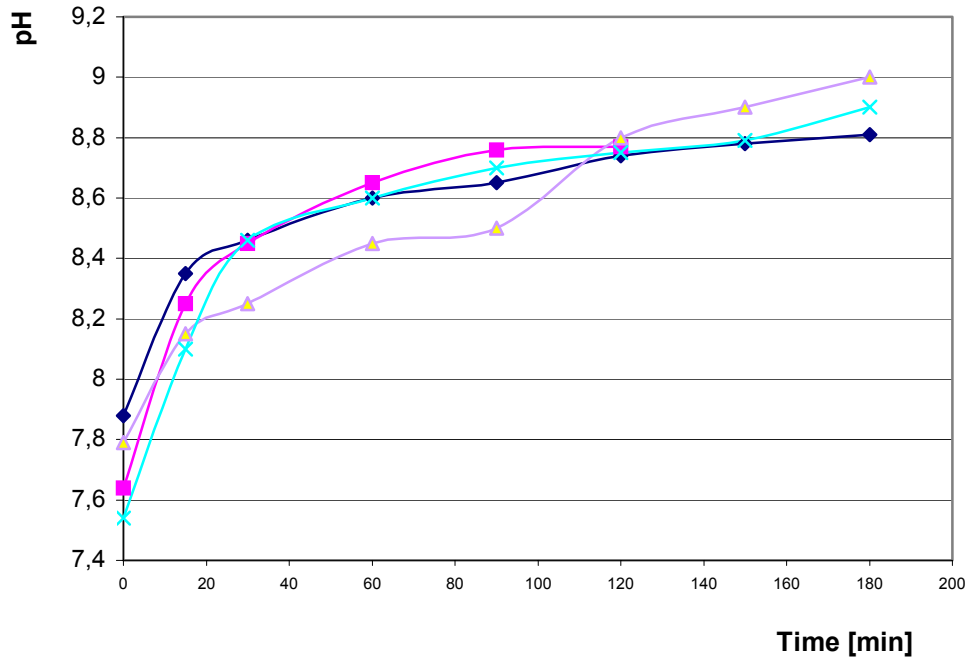


Fig. 5 Raise of pH by aeration

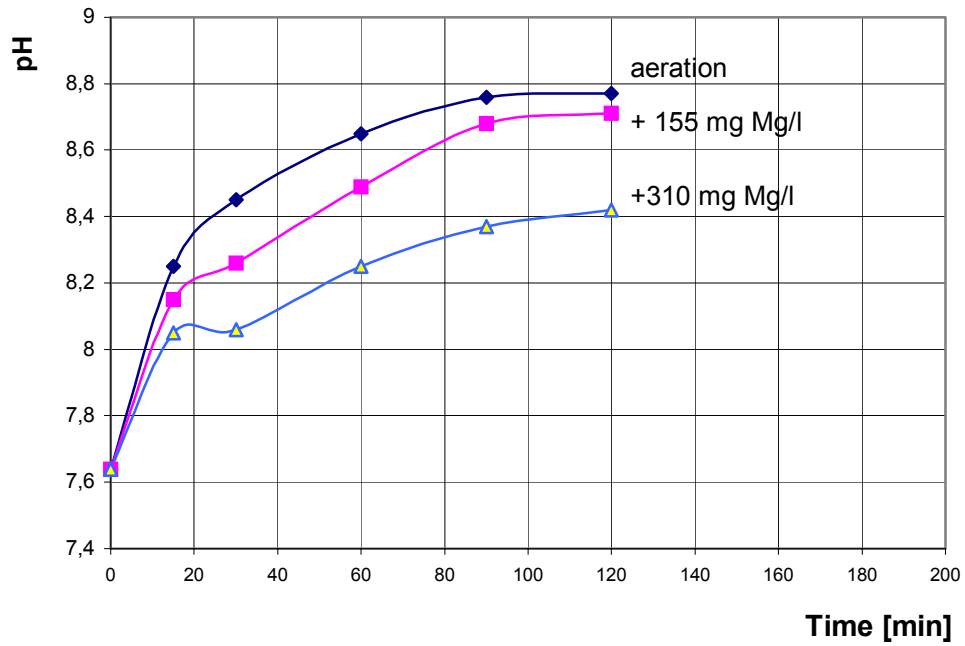


Fig. 6 The effects of magnesium chloride addition on pH raise

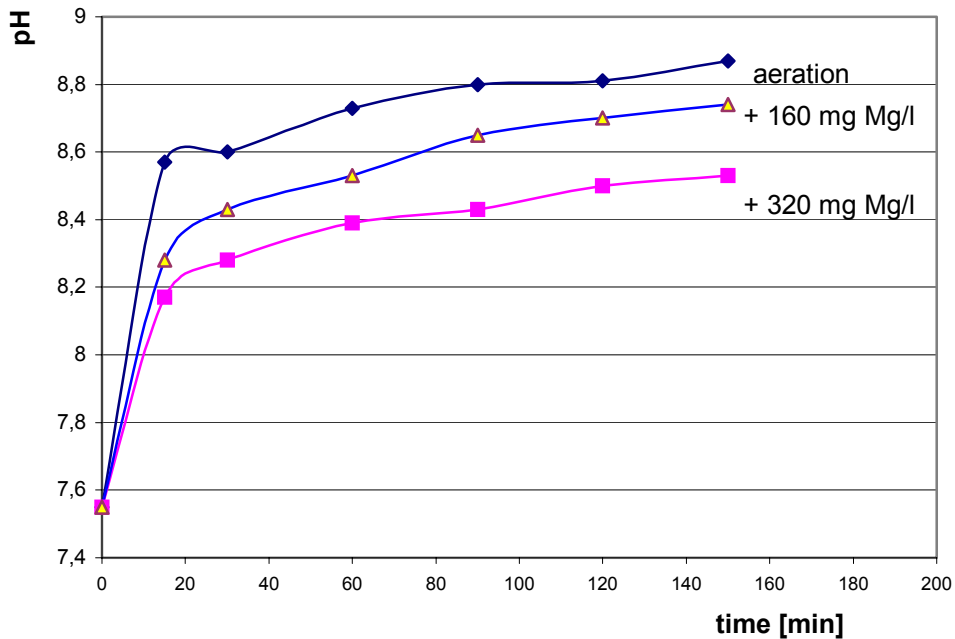


Fig. 7 The effects of magnesium chloride addition on pH raise.

As it can be seen from the above figures with the increase in the amount added the effect of pH decrease becomes more pronounced.

Adding magnesium in the form of magnesium oxide an increase in pH can be observed. The obtained results are however not unanimous, at least in our experiments and therefore are not shown here.

The effects of phosphates removal are strongly related to the Mg/P ratio below 1. If the struvite formula is not assured by the amount of magnesium present, only a partial phosphates removal can be expected. For “raw” sludge dewatering liquid the amount of magnesium present allows for a removal in the range of 19 to 55 %. Most often the phosphates removal rate encountered in our experiments was in the order of 40 %.

Higher rates of Mg/P allow for phosphates removal close or somewhat above 90 %.

On fig. 7 two examples are shown of the rate of phosphates removal in relation to the Mg/P rate. The removal rate of 39 and 52 % were obtained for liquor without magnesium addition. The high effects were obtained for rounded up amounts of magnesium chloride added, based on Mg/P ratio of 1 : 1, an 1 : 2, not counting the amount of magnesium originally present in the “raw” liquid.

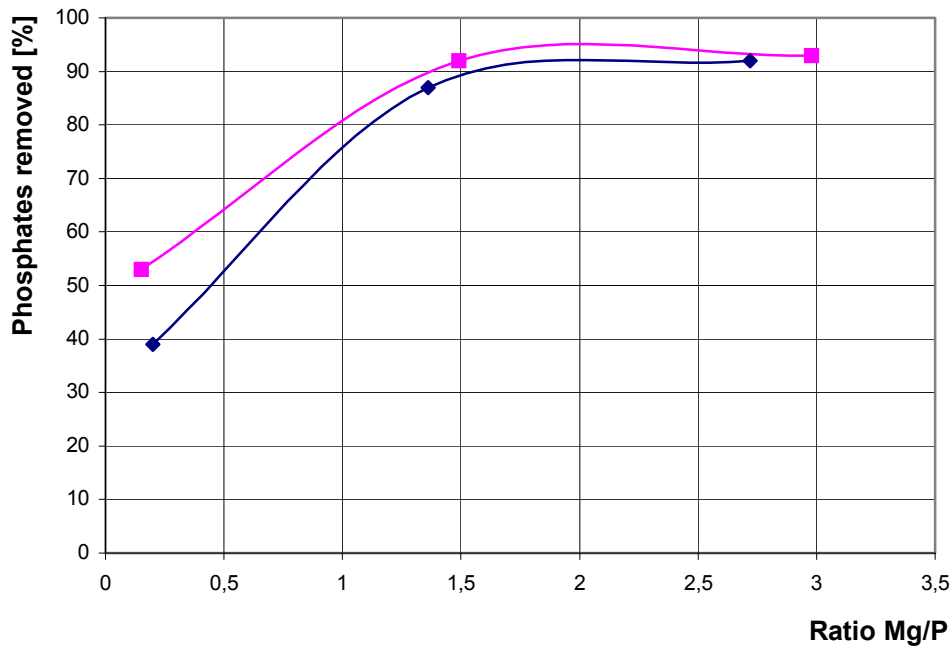


Fig. 7. Phosphates removed in correlation to the rate of Mg/P

It has to be stressed that the effects of phosphates removal depends strongly from the amount of ammonia present. In all of our experiments the filtrate or centrate used have always contained relatively large concentrations of ammonia. The concentrations in the order of roughly 1000 mg NH_4/l compared to the amount (concentration) of phosphates present, lets say around 300 mg PO_4/l , were more than ten times higher as required for the struvite formula. There were always superfluous amounts of ammonia present. In order to show the importance of ammonia to be present in higher than required amounts experiments have been carried out with ammonia to phosphates rates (NH_4/P) of 1 : 1, 1 : 5, and 1 : 20.

The obtained results are presented below in fig 8, and also in tables 1 – 6

On fig 8, the obtained values of phosphates (expressed as Phosphorous P- PO_4) remaining after mixing or aeration for a period of 4 hours, with different amounts of ammonia chloride added. For the rate $\text{NH}_4/\text{P} = 1$, only about 70 % of phosphates were removed. Increasing the NH_4/P rate to 5, phosphates could be removed in about 96 %. Almost 99 % of phosphates could be removed at the tested NH_4/P rate of 20. The experiments were carried out for clean water with chemical reagents added.

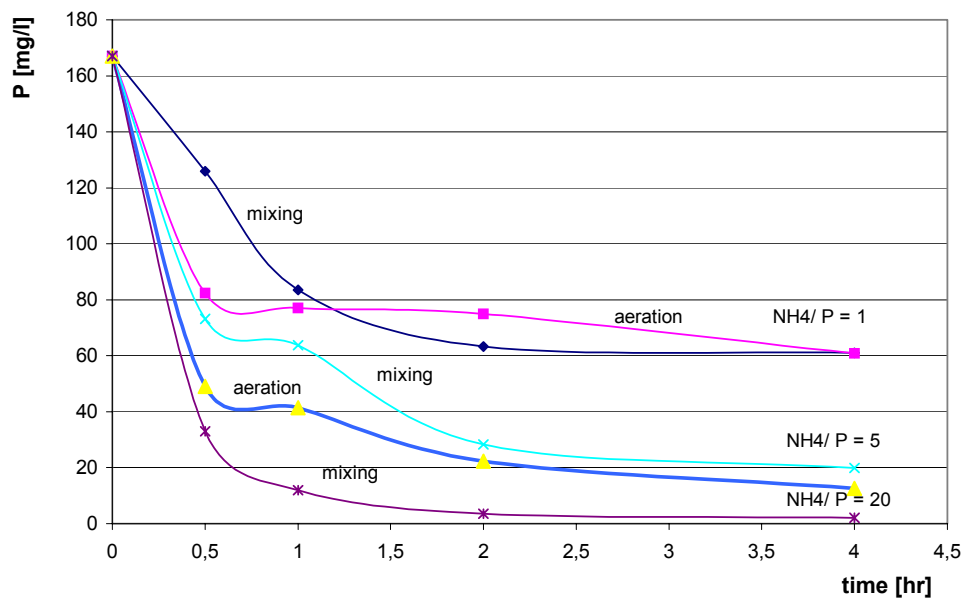


Fig. 8. The effects of the NH₄/P ratio on phosphates removal

In the above described experiments magnesium was added in the form of MgO. Magnesium oxide has a relatively low solubility and the determined concentrations are usually very low, mainly because the soluble form is immediately used for struvite crystallisation. The changes of magnesium concentration present in the soluble form do not follow a uniform pattern, Fig. 9. This can be clearly demonstrated based on the described experiments.

A rapid increase and final concentration in the order of 90 mg Mg/l could only be explained by entering into another salt, most probable was present as magnesium chloride.

The low solubility does however not hinder the rate of phosphates removal. On fig 10 a comparison of the effects of phosphates removal for magnesium added in the form of MgO and MgCl₂ was given.

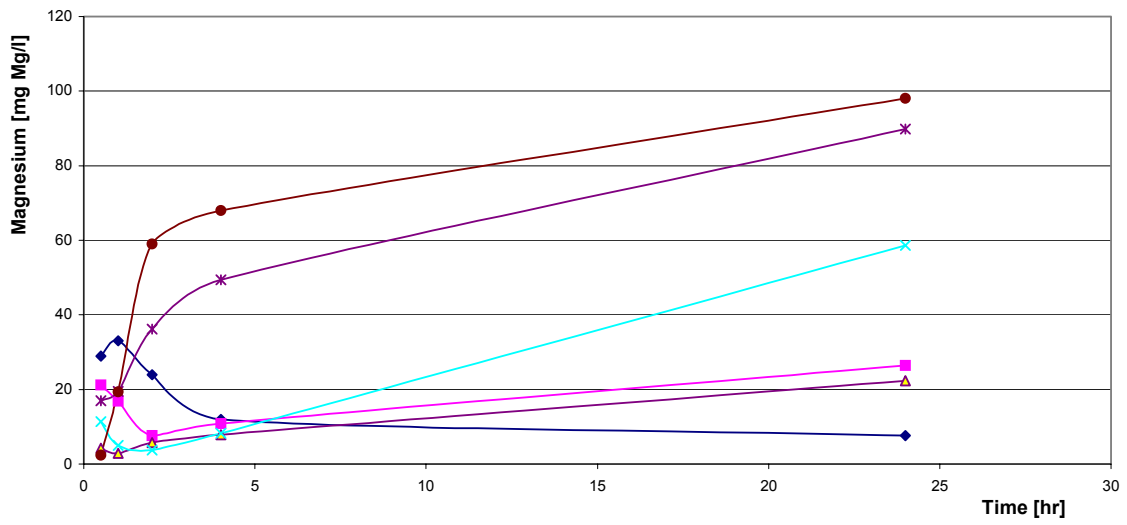


Fig. 9 Changes of magnesium concentration in the course of reaction (struvite precipitation)

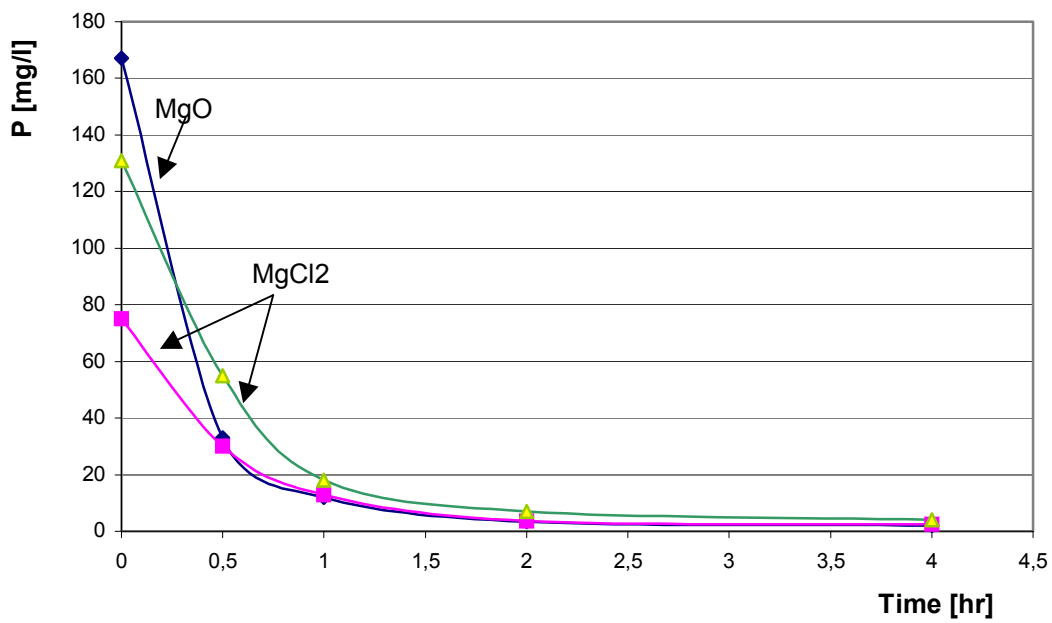


Fig. 10. Comparison of the effects of phosphates removal for magnesium added in different forms

**Table 3 Struvite precipitation with magnesium chloride and addition of 100 mg NH₄/l
Mechanical mixing**

Parameter	Units	Time [hr]					
		0	0,5	1	2	4	24
pH	-		9,56	9,83	10	10,43	10,54
Temperature	°C	22,9	24,6	24,9	25,3	25,1	24,3
Phosphates	mg PO ₄ /l	500	377,6	250,6	190	183,3	130,1
Ammonia	mg NH ₄ /l	100	69,32	49,84	38,72	22,6	12,32
Magnesium	mg Mg/l	120	29	33	24	12	7,6

**Table 4 Struvite precipitation with magnesium chloride and addition of 100 mg NH₄/l
Aeration**

Parameter	Units	Time [hr]					
		0	0,5	1	2	4	24
pH	-		9,55	9,58	9,24	9,13	9,07
Temperature	°C	22,9	22,7	22,3	19	19,8	19
Phosphates	mg PO ₄ /l	500	247,3	230,9	224,6	182,6	154,9
Ammonia	mg NH ₄ /l	100	41,88	36,24	28,8	21,2	10,4
Magnesium	mg Mg/l	120	21,2	16,8	7,6	10,8	26,4

**Table 5 Struvite precipitation with magnesium chloride and addition of 500 mg NH₄/l
Mechanical mixing**

Parameter	Units	Time [hr]					
		0	0,5	1	2	4	24
pH	-		9,03	9,08	9,12	9,11	8,78
Temperature	°C	22,9	24,1	24,3	24,6	24,1	32,6
Phosphates	mg PO ₄ /l	500	147,5	124,5	67,2	38,2	23,7
Ammonia	mg NH ₄ /l	500	321,7	305,8	283,3	291,2	273,1
Magnesium	mg Mg/l	120	4,3	2,9	5,7	7,9	22,3

**Table 6 Struvite precipitation with magnesium chloride and addition of 500 mg NH₄/l
Aeration**

Parameter	Units	Time [hr]					
		0	0,5	1	2	4	24
pH	-		8,95	8,95	8,98	8,88	8,79
Temperature	°C	22,9	23,1	22,6	20,1	19,1	19,9
Phosphates	mg PO ₄ /l	500	219,2	191,4	85,1	59,7	10
Ammonia	mg NH ₄ /l	500	322,8	315	305,1	275,5	234,2
Magnesium	mg Mg/l	120	11,3	5	3,8	8,2	58,6

**Table 7 Struvite precipitation with magnesium chloride and addition of 2000 mg NH₄/l
Mechanical mixing**

Parameter	Units	Time [hr]					
		0	0,5	1	2	4	24
pH	-		8,62	8,69	8,81	8,82	8,5
Temperature	°C	22,9	22,9	23,1	23	22,8	22,2
Phosphates	mg PO ₄ /l	500	97,3	35	10,5	6,3	7,2
Ammonia	mg NH ₄ /l	2000	1776	1595	1517	1520	1595
Magnesium	mg Mg/l	120	17	19,5	36,2	49,4	89,8

3.2. The effect of magnesium salts used and mode of mixing

Crystallisation of struvite takes place most easily when magnesium chloride is used to fulfil the stoichiometric requirements of the formula. The precipitated crystals have a regular orthorhombic structure (Fig. 11) independently of the substrate used – the source of filtrate or centrate. Similar regular structure was found when the deficit of magnesium was completed through the addition of magnesium sulphate. (Fig. 12) The regularity of formed crystals was however depended on the quality of filtrate or centrate. At many occasions performing the investigations exactly according to the adopted procedure the formed crystals resembled broken pieces.

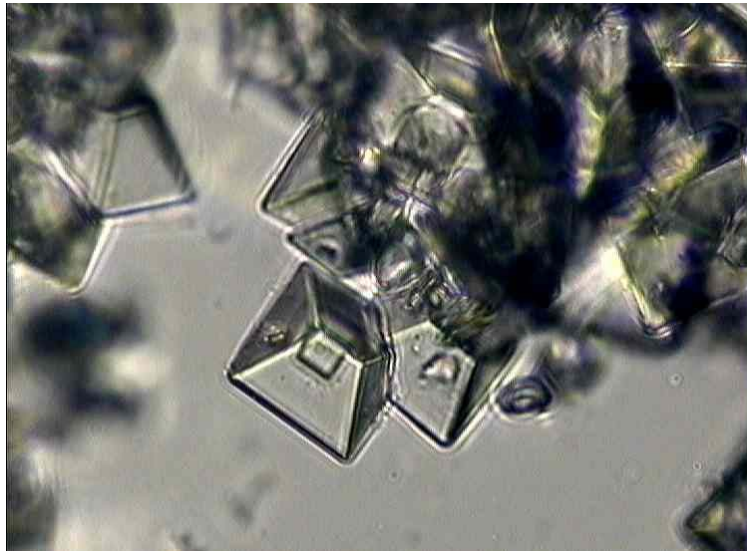


Fig. 11. Struvite crystals with magnesium chloride used as the source of magnesium



Fig. 12. Regular orthorhombic crystals structure of precipitated struvit using magnesium sulphate

Under certain conditions when magnesium oxide or magnesium chloride was added, apart from few regular orthorhombic crystals structures, the majority had a needle like

appearance. The supposition of Hirasawa [4] of the effect of the Mg/P rate could not be proved. We found no difference in the crystals structure in relation to Mg/P rate in between 1 and 4. Although Hirasawa [4] says that X-ray diffraction analysis have proved that for all the three different rates of Mg/P equal 1, 2 and 4 the different crystals structures are struvite, attention should be given to the results of crystals analyses. For the Mg/P rate equal to 1,0 the molar ratio of Mg : NH₄ : PO₄ was 1 : 1 : 1,03 what exactly corresponds to the formula of struvite - MgNH₄PO₄ . For the rate Mg/P = 4 the respective molar ratio was 1 : 1.27 : 1.06. That was therefore a 27 % excess of ammonia present.

Adding different amounts of magnesium in relation to the content of phosphates, Mg/P = 1, 2 or 4 we obtained crystals in the form shown in figures 13.,14 and 15

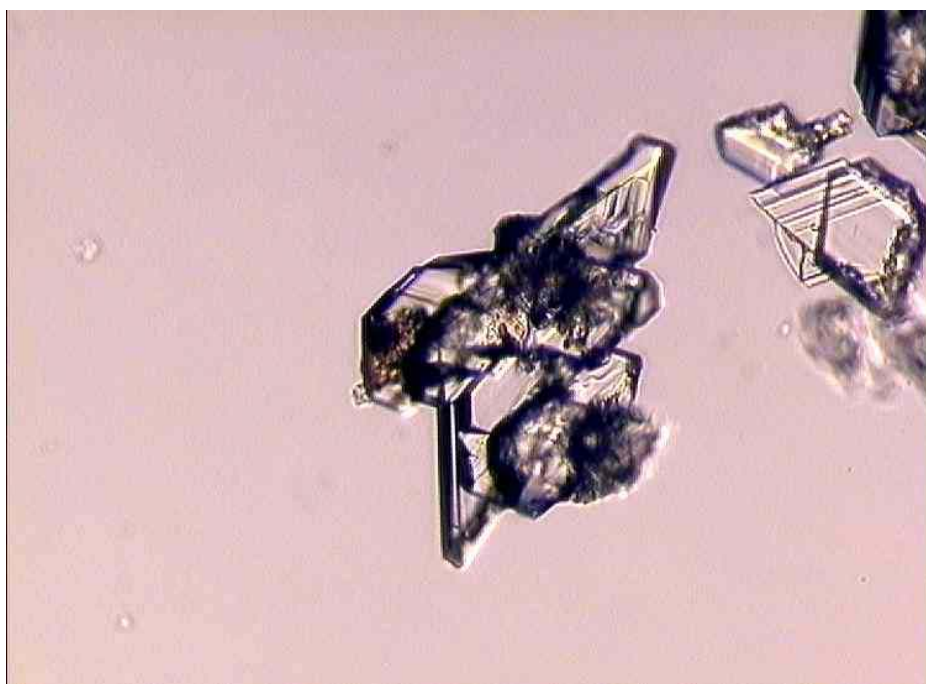


Fig. 13. Crystals formed for a Mg/P rate equal 1



Fig. 14. Crystals formed for a Mg/P rate equal 2

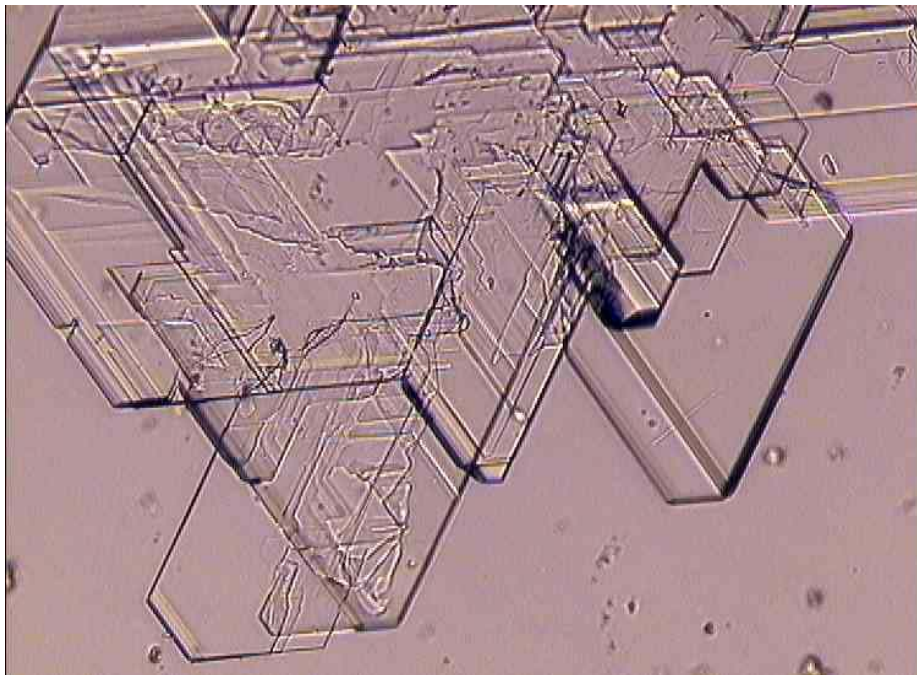


Fig. 15. Crystals formed for a Mg/P rate equal 4

It has to be mentioned also that Hirasawa [1996] has used in his experiments a very high excess of ammonia nitrogen which he added in the form of ammonia chloride. Also Schulze-Rettmer [2001] obtaining crystals in the form of needles has made his experiments for real waste water of very high content of ammonia.

The importance of ammonia presence in excessive to required amounts simultaneously to surplus of magnesium was confirmed in our experiments. It was found that addition magnesium oxide or magnesium chloride in surplus in relation to the content of phosphates and high ammonia concentration at the order of 1500 mg/l has resulted in precipitation of needle like crystals (Fig. 16). The needles had a length of up to 100 μm and a thickness of 5 to 10 μm (Fig. 17).

Occasionally few orthorhombic crystals could also be found. (Fig. 18).



Fig. 16. Needle like struvite crystals formed in the presence of excess amounts of ammonia

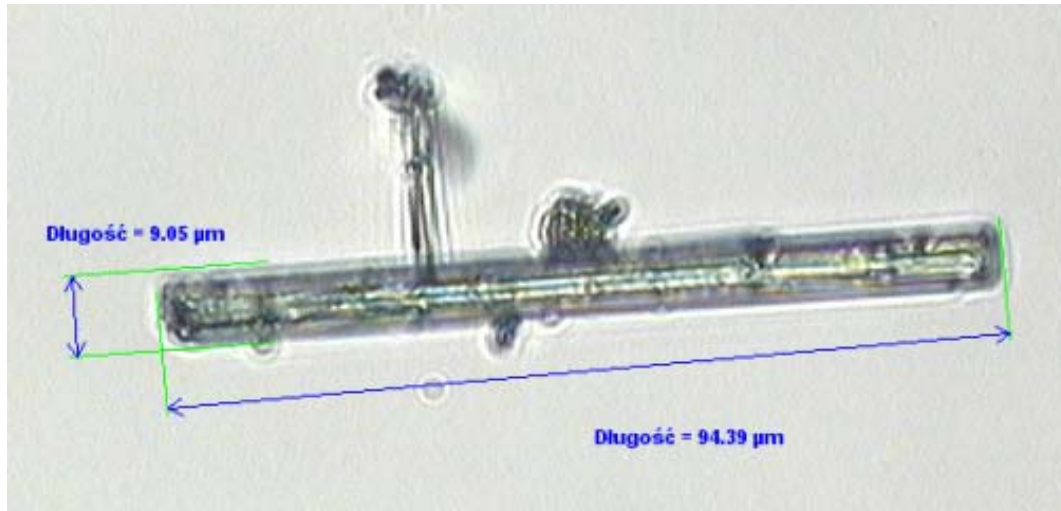


Fig.17. Enlargement of a needle crystal and dimensions



Fig.18. Needle like crystals with occasionally found orthorhombic structured crystals.

Magnesium oxide added to the small pilot scale reactor in excess, under continuous mechanical (hydraulic) mixing led to pH increase with a simultaneous liberation of free ammonia to the atmosphere. A strong smell of ammonia was always associated in the mode of the reactor operation when mixing was caused by filtrate and reactors content recirculation from the conical bottom. This mode of mixing is referred later as hydraulic mixing.

If in addition to hydraulic mixing pressured air was supplied from the bottom, mainly to enhance pH increase different crystals structure were produced. It has to be stressed that the only change in the reactors operation was addition of pressured air. The substrate – filtrate – 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, what could be the effect of dilution by the added air.

Obtained results are leading to a conclusion that the presence of high concentrations of free ammonia has a decisive impact on the precipitated crystals structure. The mentioned implication is to some extent supported by the results obtained by Stratful [2001]. Although Stratful [2001] in his experiments did not had large amounts of ammonia nitrogen (ammonia chloride was added) he increased pH to 10, what resulted in free ammonia liberation. Stripping of a substantial part of ammonia could be the effect of getting a phosphates removal rate of only about 85 %. The results of Stratful [2001] and our own results does not support the conclusion of Durrant at al. [1999] that the change of crystals structure is caused by supersaturation with magnesium and ammonia nitrogen ions. The results of Stratful [2001] and our own experiments had shown the importance of high pH, i.e. conditions for free ammonia forming.

The crystals structure is important for their aggregation in clusters large enough to be easily separated from the liquor. From the literature revision it could be concluded that the orthorhombic crystals structure have a higher affinity and form large enough agglomerates. Such a supposition is however not unanimous and no firm statement could be found in this respect.

Based on the carried out experiments it is possible to orient the process toward wanted crystals structure. The ability of aggregation of needle like or orthorhombic crystals structure is still an open question. Obviously 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.

3.3. Crystals aggregation.

The aim of the carried out experiments was to evaluate the dynamic of crystals aggregation in continuous flow (small) semi-technical reactors. Checking the aggregates growth from the very beginning (start) of the reactor it was found that the regular structure of crystals had become less regular but of larger dimensions.

Only after two weeks of continuous operation the process of particles aggregation became evident. Also a different aggregates size could be distinguished with the distance from the point of filtrate inflow i.e. the bottom of the reactor. Measurements of particles fractional distribution have been done at three different distances from the bottom. With the varying high of the particles “cloud” (blanket) it is easier to determine the sampling points as (1) bottom, (2) middle of the cloud high, and (3) surface of the particles in suspension.

The results of particles size measurements using the FRITSCH apparatus have unfortunately no significance.

Although from the particles distribution curve it could be concluded that most of the particles are larger in the bottom and middle sections, the real agglomerates size was not measured. This was because the friction forces in the measuring cuvette were too high, and disaggregation takes place.

Only based on visual observations it can be said that agglomeration took place and granules of approximately 1 mm are formed.

CONCLUSIONS

The struvite crystals structure was found to be depended on the presence of free ammonia. In practical cases free ammonia will occur when digested sludge liquor have a high ammonia concentrations and magnesium oxide or magnesium chloride is added under mechanical or hydraulic mixing conditions. In such conditions needle like structure of struvite crystals prevail.

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

At low concentration of ammonia, close to the stoichiometric requirements, struvite crystals are predominately have a orthorhombic structure. Also under such conditions the effects of phosphates removal are much lower in comparison to the those possible to obtain at high NH_4 concentrations.

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Additional data and illustrations

- A** Trying to prove our hypothesis that the rate of Mg/PO₄ has no effect on the formed crystal structure, we obtained also crystals of not clearly defined structure. The presented on Fig A-1, A-2, and A-3 structures were obtained for the respective rates of Mg to PO₄ of (1 : 1), (1 : 4) and (1 : 6), could be interpreted as being of a very similar structure. The structure however was neither typical for needle nor for orthorhombic shape.
- B.** Very high concentrations of NH₄ (2000 mg N-NH₄/l and above) does affect the orthorhombic crystals shape in the case of slow pH increase achieved by aeration . The crystals are more prolonged and many “broken” crystals can be found (B- 1)
Rapid pH increase to 9,0 (or above) due to addition of NaOH can result in a hybrid shape between needle and orthorhombic structure (B – 2)
- C.** The mode of mixing, however important, has not the detrimental effect on crystals form if a rapid pH change up to 9.0 by addition of NaOH is executed. Fig. C- 1 shows the results for mixing with air, and Fig C – 1b that obtained for mechanical mixing.

D. Kinetic of struvite precipitation

Adding magnesium to centrate or filtrate from the dewatering process of anaerobically digested sludge a relatively rapid decrease of phosphates can be observed. Within only 20 minutes an effect of 90 % removal of phosphates could be achieved. However, removal to a level of about 1.5 mg PO₄/l required a reaction time of 1 hour. The effects of phosphates removal are directly related to the increase of pH as a result of MgO hydration (Fig D - 1)

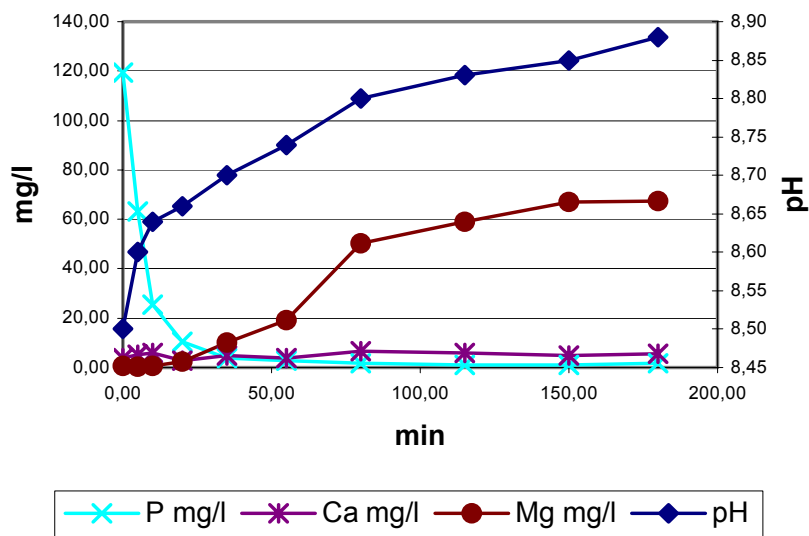


Fig D - 1. Selected cations and pH changes during phosphates precipitation with the addition of magnesium oxide

The rate of phosphates precipitation can be described by the general kinetic equation :

$$r = -\frac{dc}{dt} = kc^n$$

where:

$r = -dc/dt$ - the rate of phosphates precipitation [mg/l.min]

k - constant

n - reaction order

c - phosphates concentration [mg/l]

The logarithmic form would be

$$\ln r = \ln k + n \ln c$$

Based on obtained results the reaction rates for various phosphates concentrations could be calculated (Fig. D - 2)

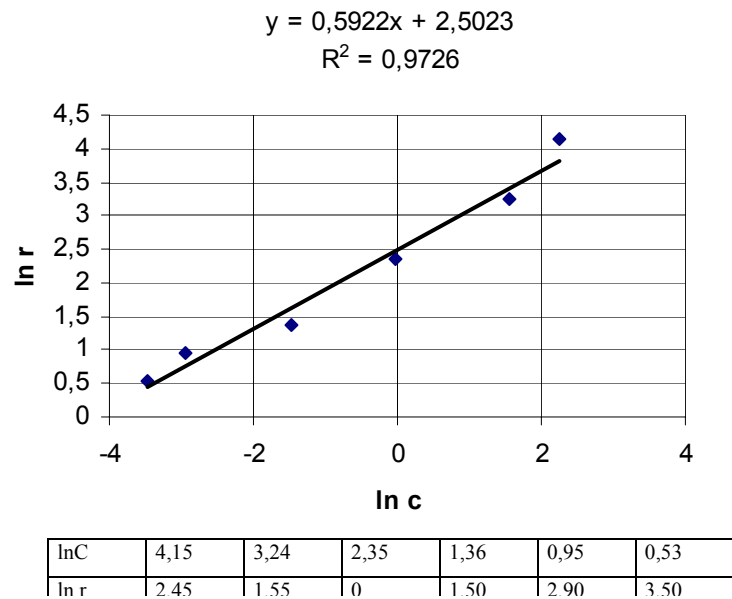


Fig. D - 3 The correlation between the reaction rate and phosphates concentration.

The reaction order was estimated from fig D - 2 was close to 2.5. It seems however that an order rate of 2.0 would better describe the process.

Integrating the aforementioned equation for $n = 2$ and within the limits $c_0 \rightarrow c$, and $0 \rightarrow t$ a linear form can be obtained

$$\frac{1}{c} - \frac{1}{c_0} = kt$$

The obtained straight line was shown in Fig. D - 3.

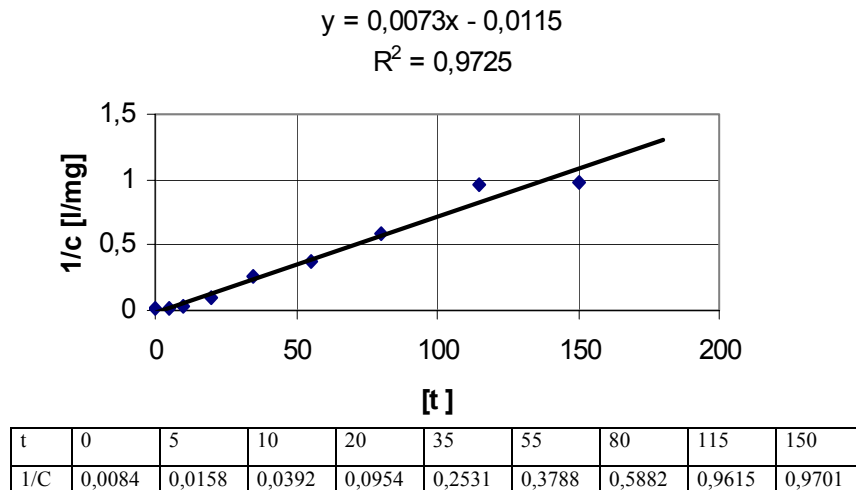


Fig. D - 3. Estimation of the phosphates precipitation constant rate

Applying the least square method the constant rate k was estimated to be equal to $1,15 \cdot 10^{-2}$ [l /mg min]

The struvite precipitation reaction could therefore to be described as:

$$r = 1,15 \cdot 10^{-2} \cdot c^2$$

If the reaction is of second order, as assumed, the effects of precipitation depends strongly of the phosphates concentration. Precipitation of struvite would be practical for high phosphates solutions.

E. Crystals dimensions

See below exemplary dimensions for a “needle” and orthorhombic crystal respectively E – 1a and E – 1b , and E – 2.

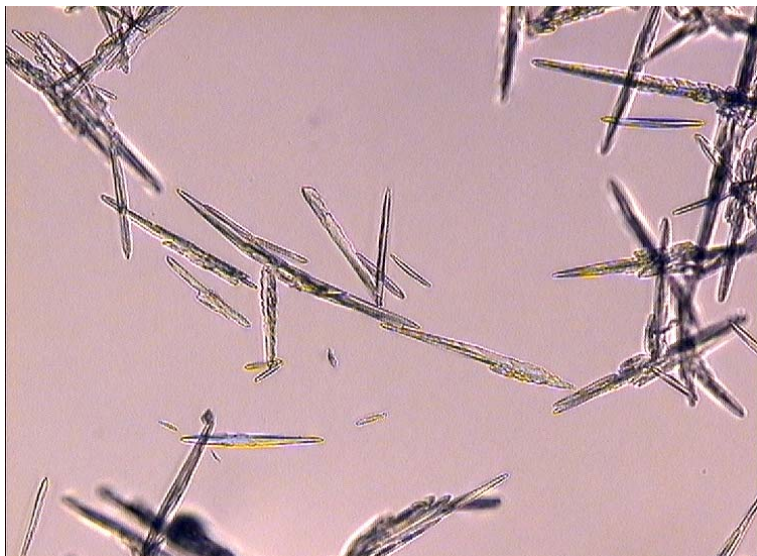
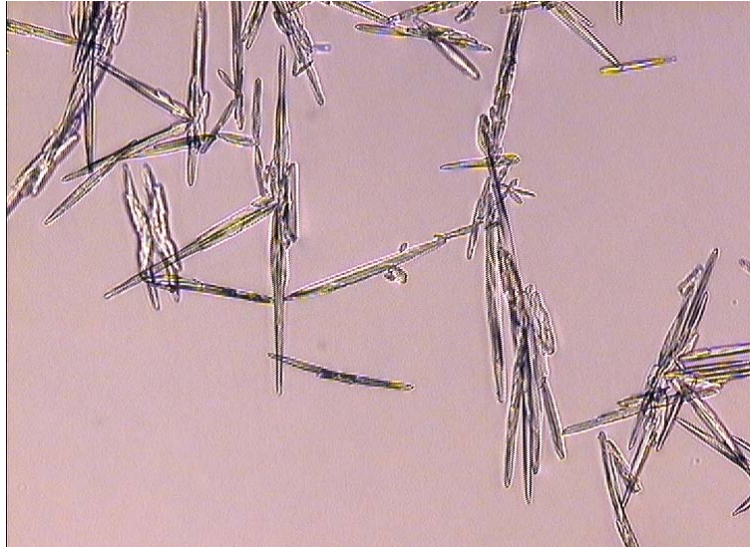


Fig A-1

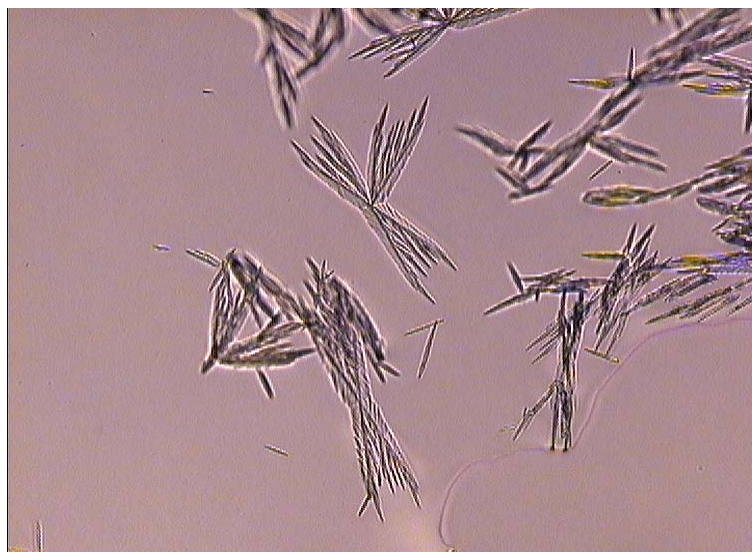
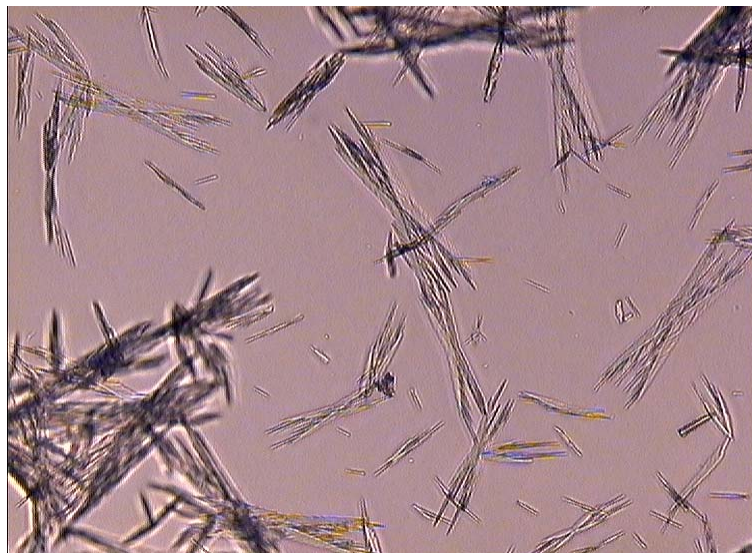


Fig A-2.

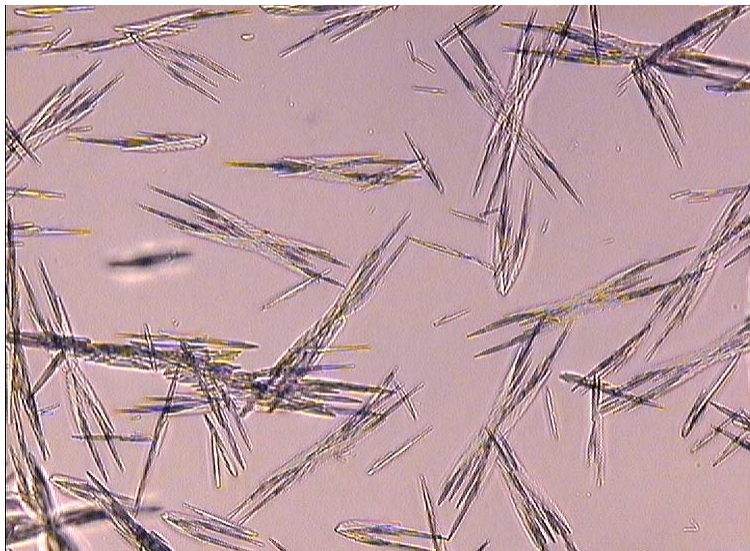
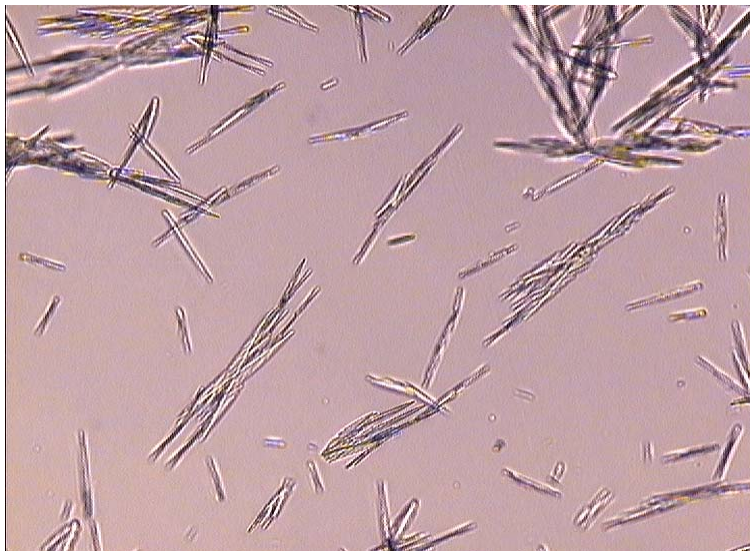


Fig A-3.

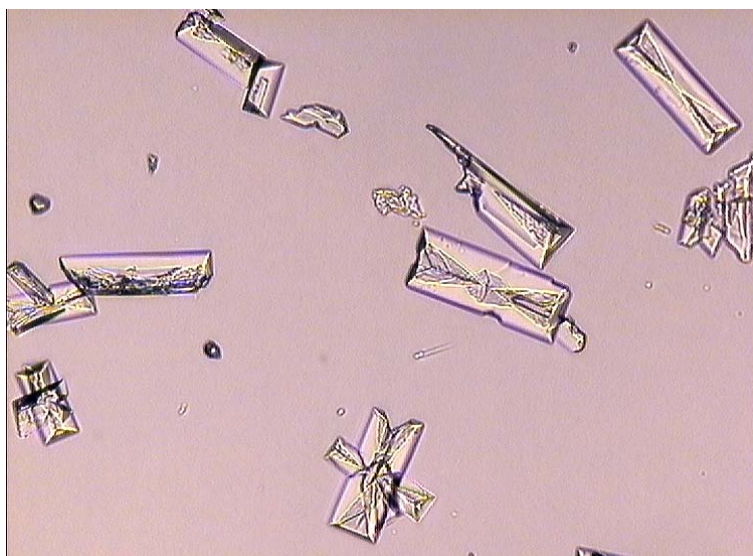
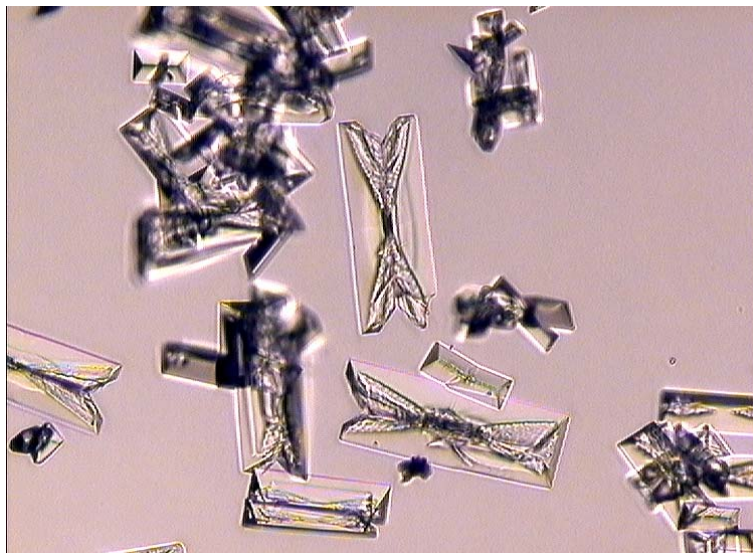
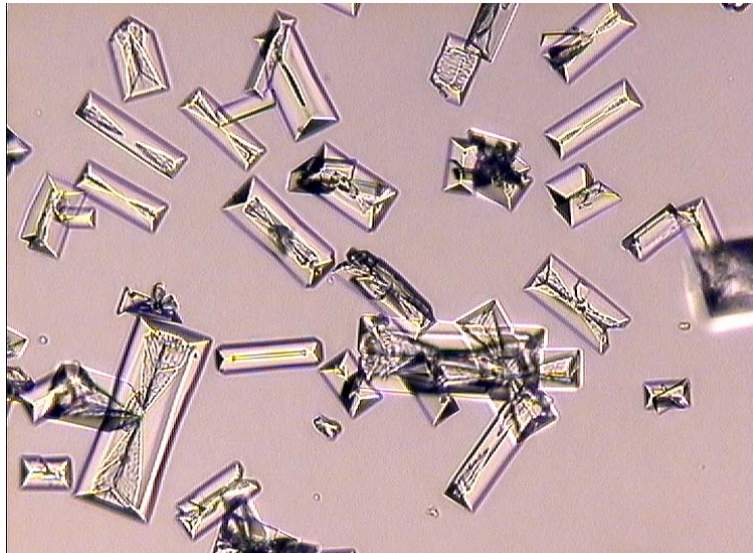


Fig. B-1

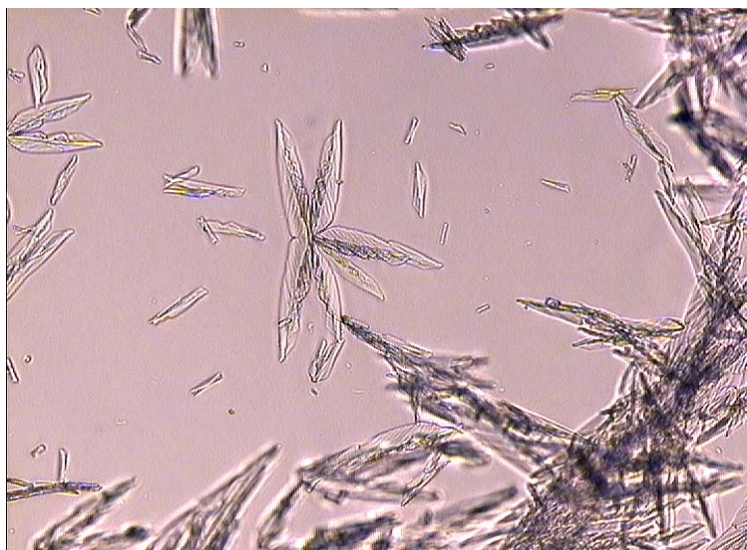
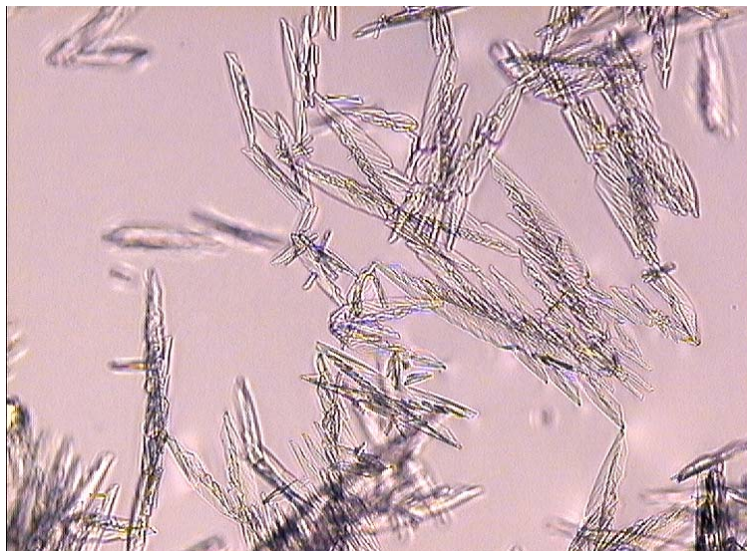


Fig. B-2

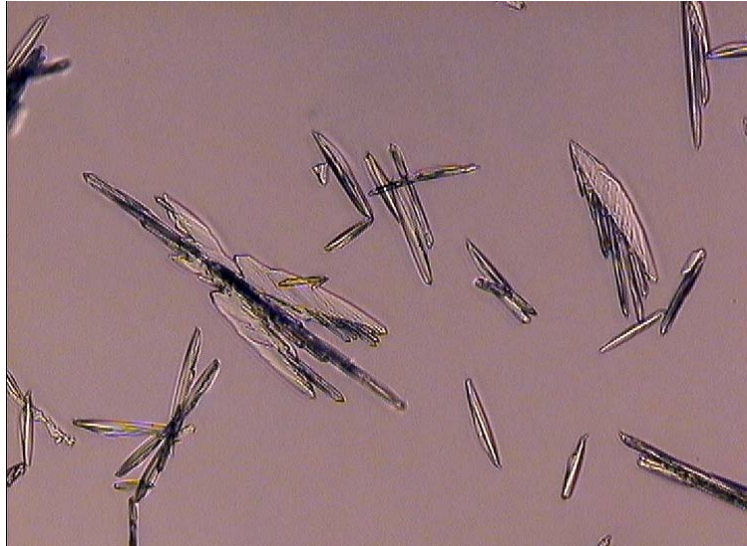


Fig. C-1a mixing by air (+NaOH) (pH = 9)

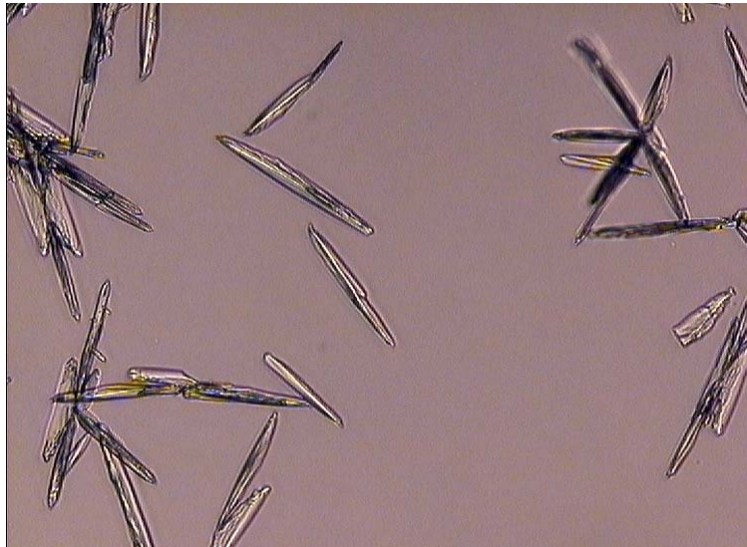


Fig. C-1b mechanical mixing (+NaOH) (pH = 9)

Annex

Additional explanations

Reactor tests

Tests have been carried out for two different reactors, different in volume and shape. They have been installed directly at the site in the rooms where the sludge dewatering filter press or centrifuge were located. Filtrate or centrate was collected into a chamber allowing continuous supply to the reactors by pumps. Another pump was installed for liquor recirculation from the reactor, from a point few centimetres above the sludge blanket (that point varied according to the level of the sludge blanket, adjusted manually) to the conical reactor's bottom. The reactors have been in continuous operation, the smaller for 85 days the larger for 67 days.

The aim of our reactor experiments were not oriented toward effectiveness of phosphates removal, but toward achieving struvite crystals and ultimately larger granules. Efforts were made to achieve a blanket of suspended solids, clearly visible and a sharp surface. Nevertheless, above the distinct sludge blanket level the liquid above was not necessarily clean without small particles. We tried to find hydraulic and chemical conditions in which a growth of crystals (granules) could be achieved. Indeed we found different agglomerates size in the conical part, increasing toward the bottom.

Only a limited number of chemical determinations have been made. Mainly the outflow quality has been evaluated. It has to be stressed that under continuous flow conditions based on real sludge dewatering liquor it is impossible to await a constant liquor quality. The sludge dewatering press and centrifuges were washed occasionally as a part of daily operational work, and the resulting liquor was more or less diluted. Only just to give an example in the case of the centrifuge centrate on one occasion the phosphates concentration measured was as low as 15,4 mg PO₄/l.

For both reactors mixing was achieved by introduction of the liquor to be treated and the recirculate to the bottom. In the case of the smaller reactor additional pressed air supply was

tested for only two weeks. In contrary the larger reactor was operated mainly with additional air supply, only for 12 days the reactor was solely mixed by recirculated liquid. The main reason for, were difficulties to keep the sludge blanket in suspension in the larger reactor without compressed air supply.

To the smaller reactor magnesium was added in the form of MgO. For practical reasons MgO was supplied as powder or as suspension in water once a day. The amount was calculated to have a rate of PO₄ / Mg of about 1 : 4, - assuming an average phosphates content of 350 mg/l. Some results of the effluent quality was given below, both for the period solely hydraulically mixed and with the supply of air.

Parameter	Units	Hydraulic mixing						+ aeration	
		1	2	3	4	5	6	7	8
Q	L/hr	10				12			
R	%	120				100			
pH	-	7,78	9,73	9,75	9,26	10,22*	8,95	9,02	8,82
Phosphates	mgPO ₄ /l	22,1	19,8	20,5	18,4	5,5*	18,8	16,8	15,2
Ammonia	mg NH ₄ /l	1280	1440	997	1220	1060	1350	879	954
Magnesium	mg Mg/l	4,2	15,8	21,7	17,6	22,8	22,2	22,5	18,6

* somewhat strange results

Experiments described above were based on filter press liquor (Zabrze WWTP). For the entire period with the addition of MgO and hydraulic mixing crystals have had always a needle like form. Occasionally in small number orthorombic crystals have been found. Adding compressed air a change in the crystals form was observed. An increase in the number of orthorombic crystals was found.

At the Zabrze WWTP a distinct increase of pH, often to the level of 9,7 was measured. (I do not have a good explanation for the relatively high values achieved)

The larger reactor was operated with addition of magnesium as MgO, MgCl₂ or MgSO₄. The experiments have been carried out at the Komorwice WWTP. The duration and mode of each experiment was given in table below.

Parameters	Units	+ MgO + aeration				+ MgCl ₂ + aeration			+ MgSO ₄ mixing and mixing + aeration		
Q	L/hr	35 days				12 days			20 days		
		44	20			20			20		
R	%	50	100			100			100		
pH	-	8,58	8,33	8,45	8,55	8,26	8,11	8,32	8,38	8,49	8,46
Phosphates	mgPO ₄ /l	77,9	87,5	54,8	113	43,3	56,6	64,2	19,4	54,6	115,2
Ammonia	mg NH ₄ /l	1410	1310	1250	1420	1540	1210	1280	1209	1580	1580
Magnesium	mg Mg/l	12,8	16,6	25,9	17,8	14,8	14,4	22,2	31,1	22,7	17,4
Calcium	mg Ca/l	56,2	61,6	61,1	79,2	57,5	-	-	29,3	61,4	29,1

Although magnesium was also added (like in the case of the Zabrze WWTP) in the form of MgO never higher than 8,82 values of pH haven been achieved. In all of the experiments Mg was added in surplus, in the order of Mg/PO₄ = 4.

Tables on batch experiments

Experiments in which needle shape crystals were obtained

Mg added as MgCl₂ to water

(Batch tests - mixing)

distinct smell of ammonia

Conditions	Units	Run No											
		1	2	3	4	5	6	7	8	9	10	11	12
pH		9,60	9,02	9,01	9,52	9,50	9,45	9,75	9,60	9,50	9,13	9,17	9,0
PO ₄	mg/l	500	500	500	500	500	500	500	500	500	500	500	500
NH ₄	mg/l	500	1000	2000	500	1000	2000	500	500	500	500	500	500
Mg	mg/l	128	128	128	128	128	128	128	517	767	128	516	128
PH - end		9,58	9,00	8,98	9,31	9,38	9,38	9,59	9,60	9,90	9,25	9,32	8,6

Experiments in which orthorombic crystals were obtained

Mg added as MgCl₂ to water

(Batch tests - aeration)

Conditions	Units	Run No					
		1	2	3	4	5	6
pH		7,20	7,02	7,70	7,32	7,65	7,54
PO ₄	mg/l	500	500	500	500	500	500
NH ₄	mg/l	100	200	500	2000	2000	2000
Mg	mg/l	128	128	128	128	512	767
PH - end		6,99	6,87	6,89	6,75	7,80	8,12

* KCl added – results of K determinations missed

Experiments in which orthorombic crystals were obtained

Mg added as MgO to water

(Batch tests – Mixing or aeration)

Conditions	Units	Run No						
		mixing						
		1	2	3	4	5	5	6
pH		8,99	9,02	8,78	8,88	9,12	8,52	7,90
PO ₄	mg/l	500	500	500	500	500	500	500
NH ₄	mg/l	2000	2000	2000	2000	2000	2000	2000
Mg	mg/l	1507	767	128	512	767	767	767
PH - end		8,90	8,95	8,02	8,78	9,01	8,32	6,65

Comment; MgO added as powder

Experiments in which orthorombic crystals were obtained
Mg added as MgO , MgCl₂ or MgSO₄ to anaerobically digested sludge filtrate
(Batch tests –aeration)

Conditions	Units	Run No									
		MgO					MgCl ₂				
		1	2	3	4	5	5	6	7	8	9
pH		8,33	8,63	9,28	7,94	7,94	7,94	8,11	8,56	7,79	8,00
PO ₄	mg/l	125	77,9	424,3	444,6	444,6	444,6	125	43,3	445	125
NH ₄	mg/l	928	1410	856	756	756	756	928	1580	756	928
Mg - added	mg/l	217	200	10000	112	224	450	220	220	112	220
Mg - end		12,8	56,2	-	-	-	-	14,8	-	-	22,7
PH - end		8,7	9,22	9,65	8,09	8,25	8,64	8,57	8,65	9,00*	8,50

Comment; PO₄ after 4 hours of aeration was not measured

* NaOH added to adjust pH

Experiments in which orthorombic crystals were obtained

Mg added as MgO , MgCl₂ or MgSO₄ to anaerobically digested sludge filtrate

(Batch tests –mixing)

Conditions	Units	Run No									
		MgO					MgCl ₂		MgSO ₄		
		1	2	3	4	5	5	6	7	8	9
pH		9,76	9,75	8,10	8,10	8,10	8,63	7,79	7,79	9,76	8,
PO ₄	mg/l	424,3	24,1	444,6	444,6	444,6	77,9	445	445	424,3	77
NH ₄	mg/l	1640	437	756	756	756	1410	756	756	1640	14
Mg - added	mg/l	10000	10000	112	220	450	200	112-	2450	450	20
PH - end		10,12	10,22	8,61	8,73	8,82	8,92	8,88	8,87	9,02	8,

Comment; PO₄ after 4 hours of aeration was not measured

Experiments in which orthorombic crystals were obtained
Mg added as MgO , MgCl₂ or MgSO₄ to anaerobically digested sludge centrate
(Batch tests –aeration)

Conditions	Units	Run No						
		No Mg added				MgO		
		1	2	3	4	5	5	6
pH		7,44	7,97	7,56	7,64	7,64	7,42	8,24
PO ₄ before	mg/l	230,2	238,4	249,1	303	303	303	326,2
PO ₄ end	mg/l	82	78,6	24,3	142,2	21,9	25,5	1,46
NH ₄ –before	mg/l	343	389	674	890	890	303	1870
NH ₄ - end	mg/l	318	359	450	-	-	-	557
Mg - added	mg/l	12,7*	24,6*	14,98*	13,22*	153	306	1000
Mg – end	mg/l	11,62	17,4	11,18	10,25	-	-	264
Ca – before	mg/l	39,8	46,3	68,6	-	-	-	69,8
Ca - end	mg/l	1,91	1,78	27,7	-	-	-	38,0
PH - end		8,75	8,82	8,43	8,77	8,86	8,80	10,00

* Mg was not added

Experiments in which orthorombic crystals were obtained

Mg added as MgO , to anaerobically digested sludge centrate

(Batch tests –mixing)

Conditions	Units	Run No	
		MgO	
		1	2
pH		7,77	7,79
PO ₄ before	mg/l	147,2	256,2
PO ₄ end	mg/l	62,0	75,2
NH ₄ –before	mg/l	1460	1550
NH ₄ - end	mg/l	1332	933
Mg - added	mg/l	220	220
Mg – end	mg/l	34,8	74,4
Ca – before	mg/l	159,7	183,9
Ca - end	mg/l	72,2	61,3
PH - end		8,80	9,97*

* pH adjusted – NaOH added