

STRUVITE PRECIPITATION AND SIMULTANEOUS AMMONIA REMOVAL

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WYTRĄCANIE STRUWITU Z RÓWNOCZESNYM USUWANIEM AZOTU AMONOWEGO

Ciecz nadosadowa prefermentowanych osadów ściekowych zawiera znaczne ilości fosforanów i azotu amonowego. Fosforany można praktycznie całkowicie usunąć w procesie strącania struwitu. Jednocześnie, jeżeli dodaje się tylko sole magnezu także niewielka część azotu amonowego ulega usunięciu. Podniesienie odczynu cieczy do wartości powyżej 8,5 prowadzi do występowania wolnego amoniaku wpływającego na kształt wytrączanych kryształów struwitu. Istotne usunięcie azotu amonowego możliwe jest przez dodatek nawozu – superfosfatu. W zależności od ilości dodanego superfosfatu otrzymany produkt stanowić może “bio-glebę” lub “bio-nawóz”.

Summary

Anaerobic digested sludge supernatant is rich in phosphates and ammonia nitrogen. Phosphates can be almost completely removed in the process of struvite precipitation. Simultaneously, if only magnesium is supplied, usually only a minor part of ammonia equivalent to phosphates will be removed. Increase in pH to about 8.5 or above leads to the presence of free ammonia which affects the struvite crystals form. The possibility of additional ammonia removal with an external or internal source of phosphates was also accounted for. The final product (precipitate) could be considered as a “biofertilizer” or “biosoil” in connection to the technology applied.

INTRODUCTION

Liquors appearing in the process of anaerobically digested sludge dewatering contain high concentrations of phosphates and ammonia. A significant load of phosphorous and nitrogen could therefore be returned to the sewage treatment process. Precipitation of struvite from the liquors, with an efficiency of above 95% of phosphates removal, can contribute effectively to phosphorous removal from the main sewage stream. Also a part of ammonia in the process of struvite precipitation is removed to fulfil the respective formula. The amount of ammonia is however, relatively low in comparison to the concentration

present in dewatering liquors. The concentration of ammonia can reach 2000 mg N/dm³. Most often the concentration of ammonia is lower, in the order of 700 to 1000 mg N/dm³. Nevertheless, the amount of ammonia directly removed in the process of struvite precipitation is only about 5%. Obviously higher rates of ammonia removal could alleviate the overall effect of nitrogen removal from the main sewage stream.

Very little attention is given to ammonia in the process of struvite precipitation. Only occasionally the exact data on ammonia concentration in the supernatant after struvite precipitation are given. Ammonia nitrogen is distributed between NH₄⁺ and NH₃, as a function of pH according to the following reaction:



Where the equilibrium constant, K_a , is defined as:

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = 5.7 * 10^{-10} \quad (2)$$

With an increase of pH to that required for effective struvite precipitation above 8, a part of ammonia nitrogen will be present as free ammonia (NH₃), and according to Henry's law can be stripped off to the atmosphere. If for example as given by Celen and Turker [2] the process lasts for 10 days, and is performed at pH of 8.8, where 25% of NH₄ could be in the form of free ammonia, most probably a part of ammonia close to 25% is stripped off. Even at a much lower pH of 7.76 as given by Kumashiro *et al.* [5] twice as much ammonia as required by the formula of struvite was removed, most probable stripped off to the atmosphere.

Precipitation of struvite with the aim of phosphate removal requires addition of magnesium. Magnesium can be added as magnesium sulphate, magnesium chloride or magnesium oxide. In the case of MgSO₄ or MgCl₂ addition, pH has to be raised to the level above 8.5 by addition of e.g. NaOH. Magnesium oxide has a low solubility, but in the process of hydrolysis there occurs a simultaneous increase of pH, up to the required for struvite precipitation level.

MATERIALS AND METHODS

Experiments were carried out in the laboratory using beakers (2 dm³ in volume). The anaerobically digested sludge centrate produced in the process of dewatering at a municipal sewage treatment plant was the main substrate used. Magnesium required to fulfil the formula of struvite was added in the form of magnesium oxide, technical grade. All determinations were performed according to Standard Methods [8].

RESULTS

FREE AMMONIA AND STRUVITE CRYSTALS

As a result of low solubility of magnesium oxide also the process of hydrolysis is relatively slow and a reaction time of several hours is required. If compressed air is used for

mixing, or there is a prolonged mechanical mixing applied, a relatively high final pH level of 9.5 can be reached (Fig. 1). As a result, a partial stripping of ammonia takes place.

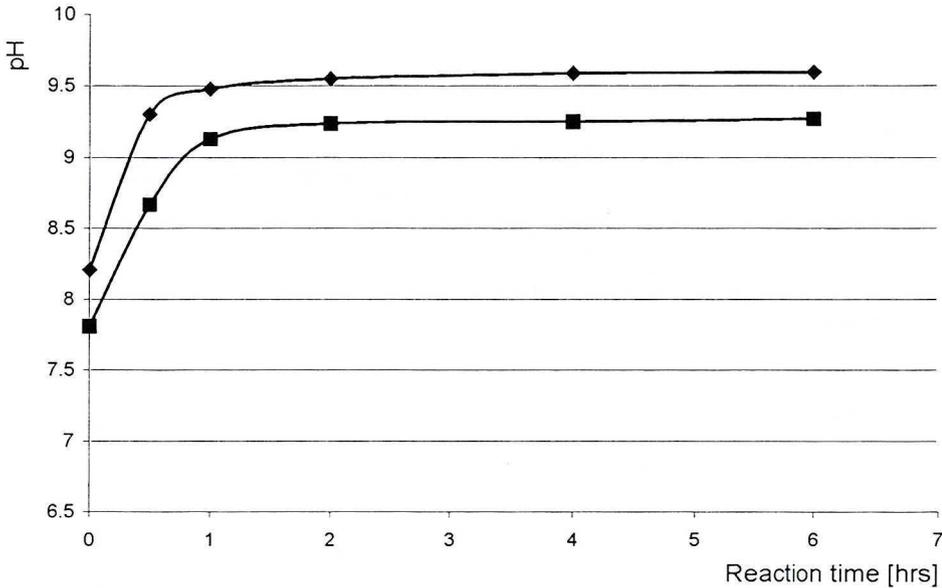


Fig. 1. Two examples of pH increase due to addition of MgO and mixing with compressed air

Although there is only a slight increase of pH after the first hour of reaction, a distinct decrease of ammonia continues for many more hours. The rate of ammonia decrease depends very much on the initial concentration (Fig. 2).

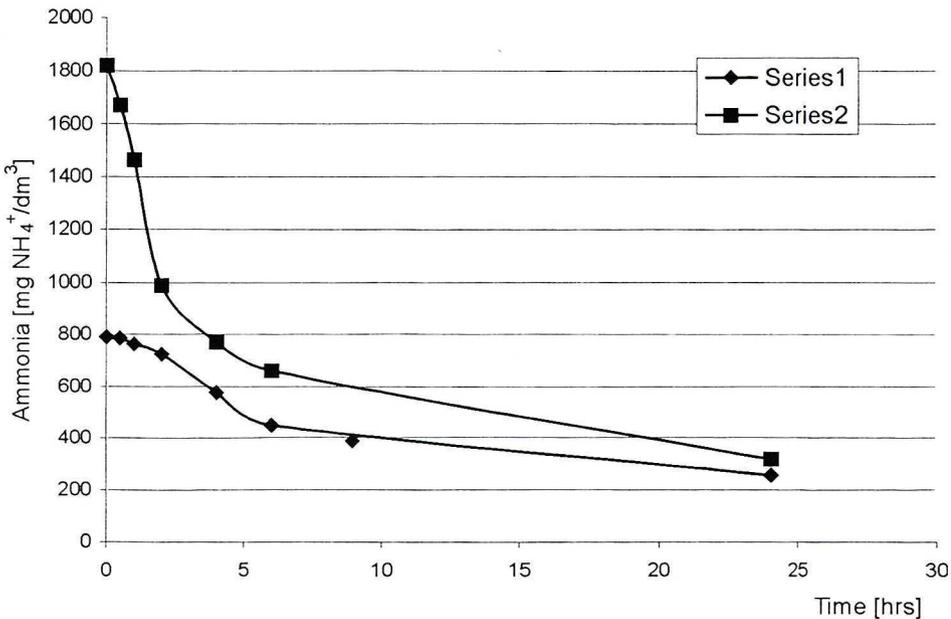


Fig. 2. Changes of ammonia concentration with time for two different concentration of ammonia

Obviously the reached final level of pH depends on the amount of magnesium oxide added (Fig. 3). In order to satisfy the struvite formula for concentration of e.g. $200 \text{ mg PO}_4/\text{dm}^3$

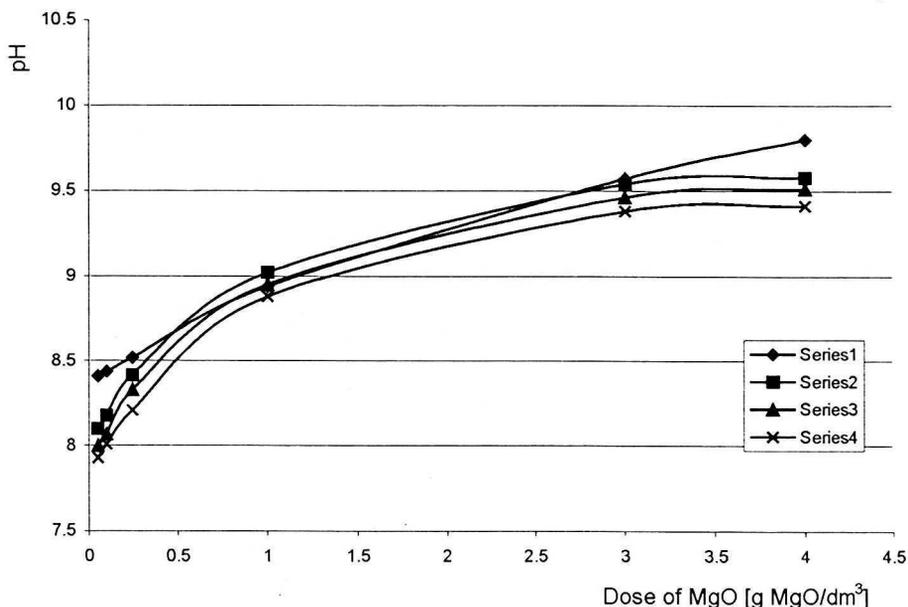


Fig. 3. The effect of magnesium oxide dose on pH increase for four different series of experiments

the required amount of magnesium oxide would be about 100 mg/dm^3 (for technical grade magnesium oxide used in the experiments). That amount however, would not be enough to raise the pH to a level of about 8.5. Although the reaction time is very important, the dominant effect of pH rise is achieved by the amount of added magnesium oxide. The effect of MgO dose is clearly demonstrated in Figure 4.

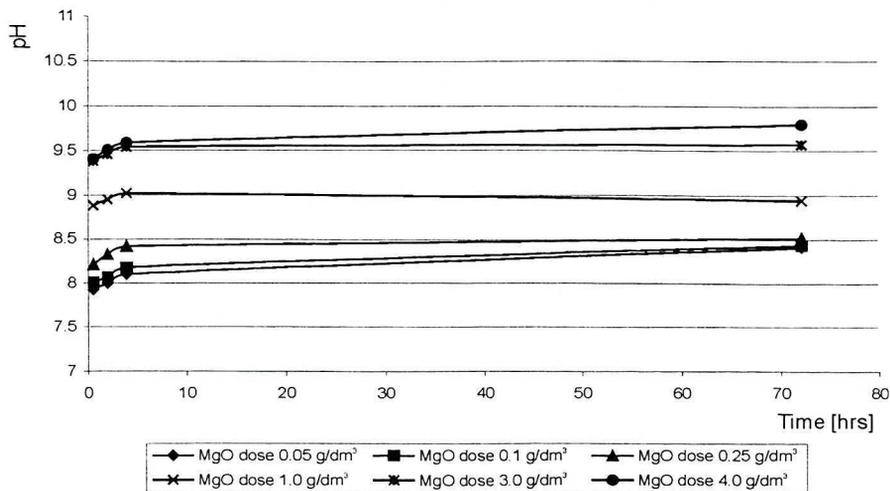


Fig. 4. The correlation between time of hydrolysis and pH for different magnesium oxide dose

Magnesium ammonia phosphate hexahydrate – struvite, may crystallise in many different forms. However, when precipitated at sewage or industrial waste water treatment plants mainly two different crystals forms are found. Parsons [6] 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 mineralogical correct but is widely used). Needle shapes of crystals have been shown by Abbona [1], Hirasawa [3], Schultze-Rettmer *et al.* [7] and Stratful [9]. Hirasawa [3] claimed that both of these very different forms are struvite. Accepting that statement then there must be a clear reason for the difference in crystal form, but no good explanation has been given so far. The only hypothesis offered is that of Hirasawa [3] who suggests that the crystal structure varies with the Mg/P molar ratio, having for Mg/P = 1 an orthorhombic structure and for Mg/P rate equal to 4, a needle like structure.

The claim of Hirasawa [3] about the effect of the Mg/P ratio 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. However, when magnesium oxide was added in surplus in relation to the content of phosphates and as aforementioned ammonia was present in high concentrations, struvite was precipitated out as needle like crystals (Fig. 5). It was concluded that due to the relatively fast increase of pH as a result of magnesium oxide hydrolysis a substantial part of ammonia nitrogen was present as free ammonia and affected the struvite crystals form.

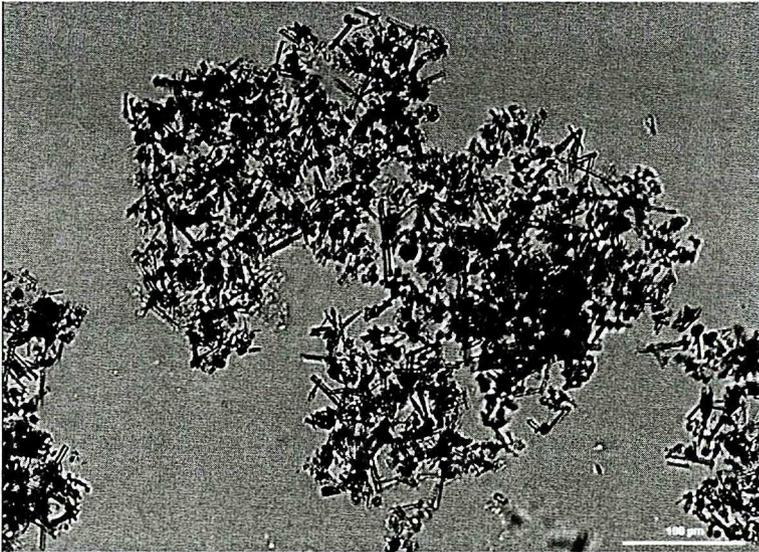


Fig. 5. Example of needle like struvite crystals

AMMONIA STRIPPING

In order to show the influence of reaction time on the effect of ammonia removal some results are presented in Figure 6.

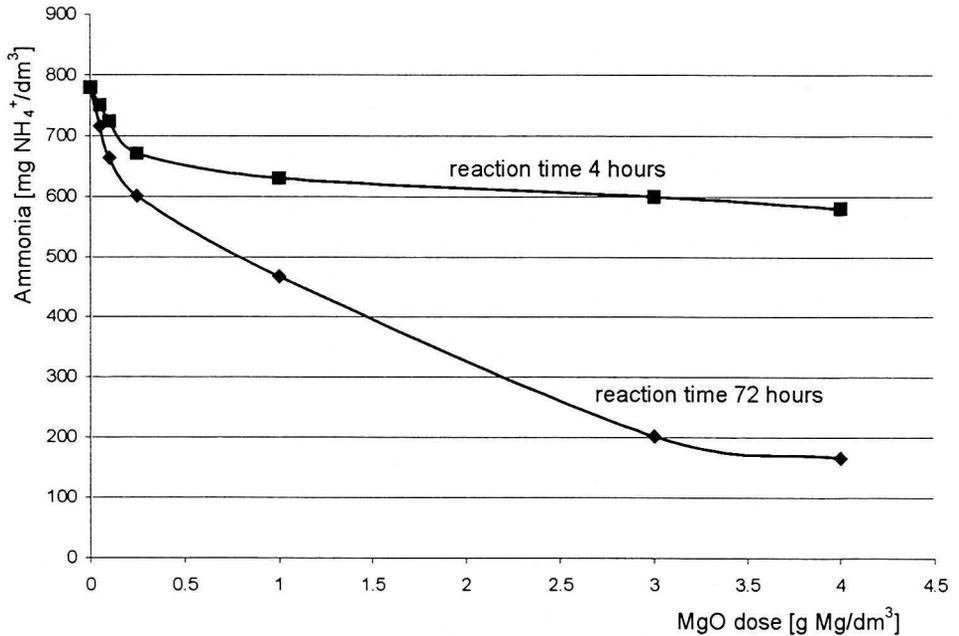


Fig. 6. The effect of reaction time on lowering the ammonia concentration

From the above results of ammonia removal it becomes obvious that an almost arbitrary level of remaining ammonia concentration is feasible. It is therefore possible to choose the desired load of returned ammonia to the main stream of treated sewage.

Although the release of ammonia is relatively slow it could be, however, too fast in terms of ammonia emission rate to the atmosphere. Considering e.g. the case with a medium amount of ammonia in the sludge dewatering centrate of about 800 mg N/dm³, the release during 6 hrs was about 400 mg N/dm³.

What does it mean in terms of emission rates to the atmosphere? From a tank of 1 m depth, the emission rate would be 400 g NH₃ in six hours what would equal about 66 g NH₃/m²·h. Such an emission rate is very high and might not be permitted in most of the EU countries. Even if for mixing pressured air was used at an extreme rate, applied e.g. in INKA aeration systems of 100 Nm³ air/m³ sewage · h, the concentration in the discharge air would be 0.66 g NH₃/m³. Often the permitted ammonia concentration at working sites is about 35 mg NH₃/m³, what is about 20 times lower than the aforementioned emission rate.

One approach to meet the permitted emission rates would be to slow down the pH increase and in consequence to slow down the ammonia emission rate. Such an approach is feasible; however, the reaction time should be extended as much as possible in each specific case. To show the impact of time prolongation an example is given below:

- (a) during 4 hours of reaction the ammonia release was 200 mg NH₃/dm³; what means an emission rate of $200/4 = 50$ mg NH₃/dm³ · h,

- (b) during 72 hours the release was $612 \text{ mg NH}_3/\text{dm}^3$; what means an emission rate of $612/72 = 8.5 \text{ mg NH}_3/\text{dm}^3 \cdot \text{h}$.

EXTERNAL SOURCES OF PHOSPHATES

By adding an external source of phosphate such as superphosphate or phosphoric acid to fulfil the formula of struvite, taking into consideration the concentration of ammonia in the supernatant of digested sewage sludge, ammonia can be almost completely removed. Kabdasi *et al.* [4], using phosphoric acid has achieved a 90% effect of ammonia removal from landfill leachate.

These experiments have proven that the effect of ammonia removal was independent on the chemicals used. An example of the decrease of ammonia concentration using superphosphate was presented in Figure 7. The residual ammonia concentration can vary, but values as low as $22 \text{ mg N}/\text{dm}^3$ can be obtained.

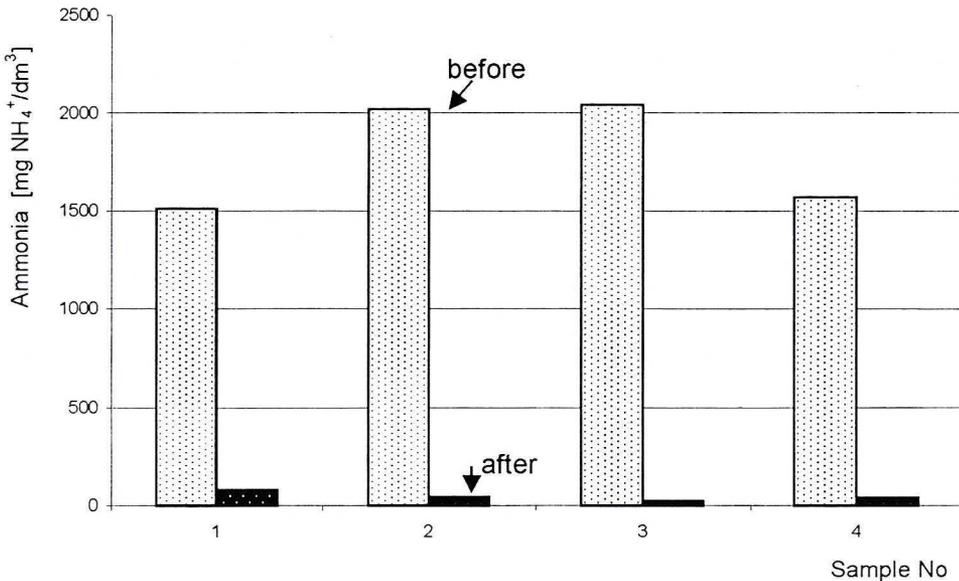


Fig. 7. The concentration of ammonia in the centrate before and after addition of superphosphate and magnesium oxide

As said before, precipitation of struvite requires a pH above 8.5, preferable in the order of 9.5. When phosphoric acid was used as a source of phosphates, pH of the sludge decreased to about 2.4. Consecutively the pH had to be raised in order to enable struvite precipitation. In the case of Na_3PO_4 , application no pH correction is needed. Next adding magnesium oxide a very high pH value of 11.8 can be reached, and the desired level of ammonia concentration achieved. As mentioned before the effects of ammonia removal do not depend on the source of external phosphates. There was however a distinct difference in potassium captures. A decrease from a level of about (on average) $160 \text{ mg K}/\text{dm}^3$ to about $16 \text{ mg K}/\text{dm}^3$ led to 90% removal if Na_3PO_4 was applied as the source of external phosphates. For other

sources of phosphates used in the experiments, at maximum only about 40% of potassium was retained.

The quality of digested sludge supernatant to which magnesium oxide and superphosphate was added was given in Table. 1.

Table 1. The quality of sludge liquor before and after superphosphate and magnesium oxide addition

Parameter	Units	Digested sludge	After addition of MgO + Ca(H ₂ PO ₄) ₂ *	After addition of Ca(H ₂ PO ₄) ₂ * + MgO
Temperature	°C	21.9	21.7	21.5
pH	–	7.10	8.93	8.69
COD	mg O ₂ /dm ³	825	747	363
Ammonia	mg NH ₄ /dm ³	1542	70	42
Phosphate	mg PO ₄ /dm ³	127	24	23
Magnesium	mg Mg/dm ³	13.6	30	30
Potassium	mg K/dm ³	121	117	97
Calcium	mg Ca/dm ³	71.1	58.3	43.8

* – 18.7% P₂O₅

The use of superphosphate instead of phosphoric acid or tribasic sodium phosphate for control of ammonia in anaerobic digested sludge in respect to possible agriculture application has many additional advantages. The most often used superphosphate 46 contains also 12% of sulphur, 30% of CaO, and some microelements.

In general, two different approaches can be considered. First, if superphosphate is added in an amount fulfilling, or below, the stoichiometric rate of the struvite formula, in respect to the ammonia concentration, the product could be used as “biosoil”.

Secondly, if superphosphate will be added in surplus, which could be understood as addition of sewage sludge to superphosphate, the product obtained could be used as “biofertilizer”.

The ratio of sewage sludge to superphosphate could vary and thus biofertilizers produced could have different quality.

INTERNAL SOURCES OF PHOSPHATES

Another approach could be the use of activated sludge or floating over biological reactors scum rich in polyphosphates as a source for struvite precipitation and enhanced removal of ammonia nitrogen. Before that the activated sludge or scum has to be disintegrated. In terms of the necessary volume of disintegrated sludge in comparison to the volume of dewatering liquids the proportion is about 3:1. The feasibility of internal (existing at the treatment plant) source of additional phosphates for enhanced ammonia removal was examined and positive results were obtained in terms of higher phosphates removal. Again, the product, depending on the conditions applied, could be considered as a biosoil or biofertilizer.

CONCLUSIONS

1. In order to achieve high nitrogen removal effects at medium and large sewage treatment plants removal of ammonia nitrogen from digested sludge supernatant is crucial.
2. Precipitation of struvite is so far the unique process allowing simultaneous removal of excess phosphates and ammonia from the liquor.
3. If substantial or almost complete removal of ammonia is required an addition of phosphates is necessary to fulfil the stoichiometric formula of struvite
4. The addition of an external source of phosphates in the form of superphosphate or an internal source of phosphates is feasible and has many advantages.
5. Depending on the ratio of sewage sludge to superphosphate added at least two different products can be obtained. If the amount of added superphosphate is limited only to the process of ammonia removal (fulfilling the formula of struvite) the product can be called "biosoil" if superphosphate would be added in much higher amounts, the product would be a "biofertilizer" of different quality.
6. An additional benefit of ammonium removal and binding in the form of struvite is the increase of nitrogen concentration in obtained "biosoil".
7. Drying and pelletization could result in obtaining a safe hygienic product.

REFERENCES

- [1] Abbona F., M. Calerri, G. Ivaldi: *Synthetic struvite, $MgNH_4PO_4 \cdot 6H_2O$; correct polarity and surface features of some complementary forms*, Acta Crystallographica, section B, Structural Science, **4**, 223–227 (1984).
- [2] Celen I., M. Türker: *Recovery of ammonia as struvite from anaerobic digester effluents*, Environ. Technol., **22**, 11, 163–178 (2001).
- [3] 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).
- [4] Kabdasli I., O. Tunay, I. Ozturk, S. Yilmaz, O. Arikan: *Ammonia removal from young landfill leachate by magnesium ammonium phosphate precipitation and air stripping*, Wat. Sci. and Technol., **41**, 1, 237–240 (2000).
- [5] Kumashiro K., H. Ishiwatari, Y. Nawamura: *A pilot plant study on using seawater as a magnesium source for struvite precipitation*, Second International Conference on Recovery of Phosphates from Sewage and Animal Wastes, 12–14 March, 2001, Noordwijkerhout, Holland.
- [6] 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).
- [7] 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.
- [8] *Standard Methods for Water and Wastewater Examination*, 17th ed. Amer. Public Health Association, Washington D.C. 1992.
- [9] Stratful I., M.D. Scrimshaw, J.N. Lester: *Conditions influencing the precipitation of magnesium ammonium phosphate*, Wat. Res., **35**, (17), 4191–4199 (2001).