

PHOSPHORUS RECOVERY

- LABORATORY SCALE EXPERIMENTS

Jan Suschka and S. Popławski

Technical University of Łódź, Filial Bielsko-Biała, Poland, ul. Willowa 2, 43-309 Bielsko-Biała.

ABSTARCT

Laboratory scale experiments have been conducted with the aim of phosphorus precipitation in a useful form. The intention was to recovery phosphorus as magnesium ammonium phosphate (MAP) from liquors after digested sludge dewatering. In order to have a better understanding of the potentiality of MAP crystallisation determinations of calcium and magnesium in sewage at different treatment plants have been carried out. Following the changes of magnesium concentration in the course of biological treatment some interesting observations have been made. It was demonstrated that in favourable stoichiometric condition MAP can be crystallised out by simple pH changes as a result of aeration.

KEYWORDS

Phosphorus recovery, struvite,

INTRODUCTION

Biological phosphorus removal from municipal sewage is already a well-established process. A high degree of removal is required principally at large sewage treatment plants, and the treated effluent should have a concentration of total phosphorus below 1.5 mg P/l at present, and probable 1.0 mgP/l in the near future. Biological phosphorus removal means a surplus uptake by activated sludge microorganisms, above the normal amount of about 2.0 % of dry matter. Ironically for large sewage treatment plants agriculture use of sludge is rather a wish than a real possibility, even assuming having a “good” sludge without metals, PCB’s and pathogenic organisms. The most often used procedure is sludge deposition on municipal solid waste land fills. In many cases phosphorus release from the deposited sludge happens and a large part is again discharged to the environment.

Phosphorus is a part of minerals and industrial use of phosphorus is depended on mineral resources, which according to some reports will last for the next 50 years, as a pessimistic view, or for 100 years in the opinion of optimists. Phosphorus is therefore valuable and should not be waste or even worse recycled to the environment.

The problem of phosphorus recovery from municipal sewage or excess sludge is not a new problem, and a long list of technical papers describing various alternatives can be provided. The simplest process is based on lime addition to different streams at a treatment plant. Lime addition was proven to be an effective phosphorus removal process, which unfortunately is not without negative side effects or technical problems. Primarily large amounts are required to raise pH to a level of about 10.5, and next neutralisation is required. Also the amorphous form of sludge with impurities is difficult to handle – dewater and transport. Separated sludge cannot be used directly as a fertiliser since the calcium phosphates are mainly in the form of hydroxide apatite (HAP), which is insoluble in water.

Advanced biological treatment processes including nutrients removal and using anaerobic sludge digestion are facing very frequently scaling problems in discharge pipes and in the dewatering process. The deposited hard material causes serious operational problems and is recognised as a hazard. The deposited substance is usually a mineral – magnesium ammonium phosphate (MAP) known as struvite. So far many attempts have been made to control the process of self-deposition and recover MAP as fertiliser, which can be used directly for agricultural purposes. While only slightly soluble in water and soil solutions, MAP was found to be a highly effective source of phosphorus, nitrogen and magnesium for plants through both foliar and soil application (Lunt et al., 1964) The main difficulties are connected with precipitation in a form suitable to be easily separated from the liquid.

This paper shows results of MAP crystallisation principally from liquids coming from the sludge dewatering stage.

MATERIALS AND METHODS

Investigations carried out have based on real sewage sampled at different municipal sewage treatment plants. At all of investigated treatment plants advanced processes have been applied abranging nitrogen and phosphorus removal. With relatively high biological phosphorus removal only occasionally chemicals have been added. Several series of determination of calcium and magnesium have been made with the application of different determinations techniques. Since our main interest was in the proper magnesium determination several methods of determination were evaluated. Presented in this paper results were obtained with the atomic absorption spectrometric and calculated method described Standard Methods, 1995.

From the three treatment plants under investigation only at one plant anaerobic sludge digestion was used. Sludge after digestion is dewatered at a filter press where occasionally small amounts of crystalline material are found. The out flowing water (liquor) from the filter press was used in laboratory investigations.

MAGNESIUM AT TREATMENT PLANTS

The two advanced treatment plants at which magnesium was measured had a capacity of approximately 6000 and 8000 m³/d. At both treatment plants the biological reactor consisted of an anaerobic zone (chamber), two anoxic denitrification zones and finally the aerobic nitrification zone. The biological reactors were followed by secondary settling tanks The magnesium concentration in the sewage inflow was in the range of about 5 to 7 mg Mg/l. The mentioned values have been determined in filtered sewage. Surprisingly the magnesium content in non-filtered, but only settled sewage was approximately twice as high between about 10 and 14 mg Mg/l.

In the course of treatment after an increase in the first anaerobic (dephosphatation) zone, which most probable was the result of the addition of magnesium with the externally recirculated activated sludge, a diminishing of the concentration was observed (Fig. 1 and 2)

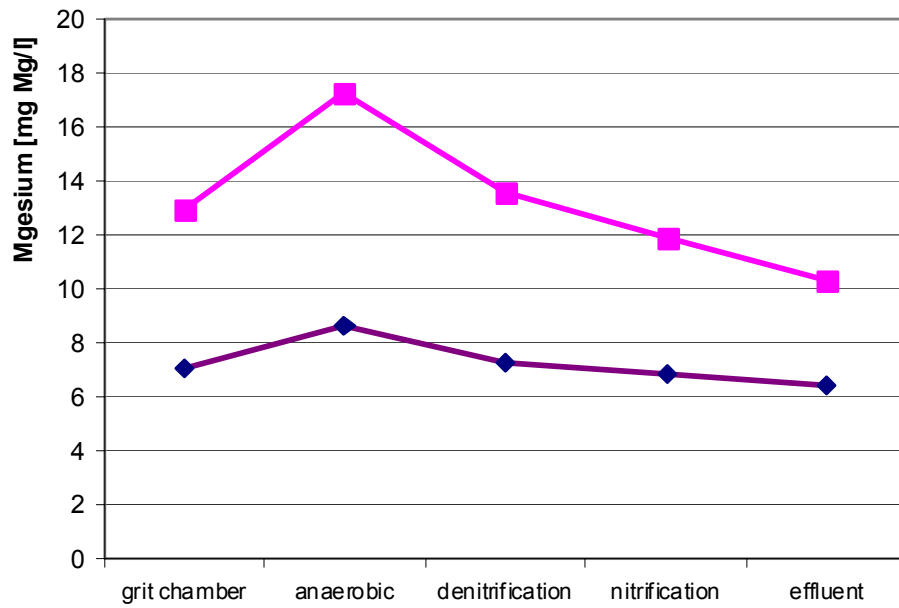


Figure 1. Changes of magnesium at treatment plant A.

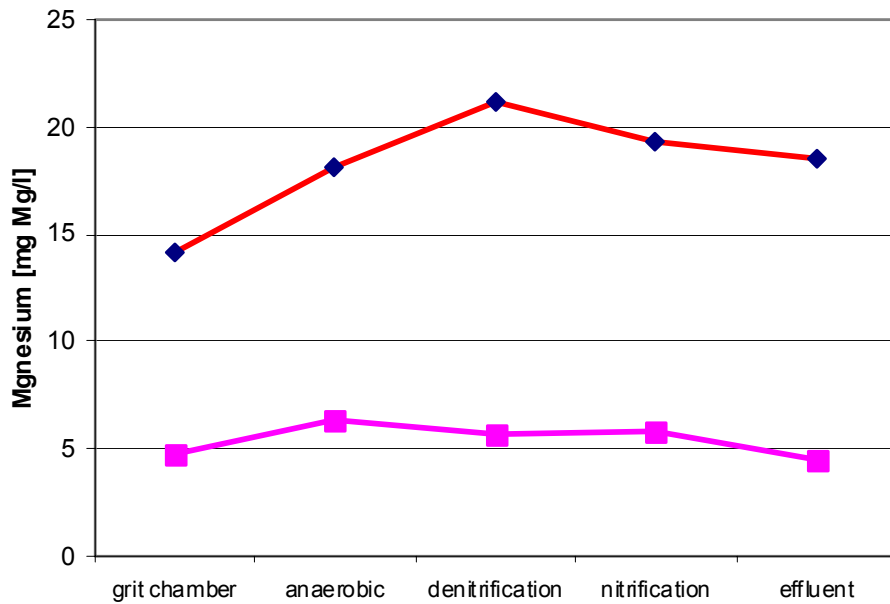


Figure 2. Changes of magnesium at treatment plant B.

From the various measurements shown in Fig 3 it can be concluded that between the inflow to the biological reactor (to the anaerobic zone) and the discharge of the secondary settling tank there is an approximate average difference of about 2.0 mg Mg/l.

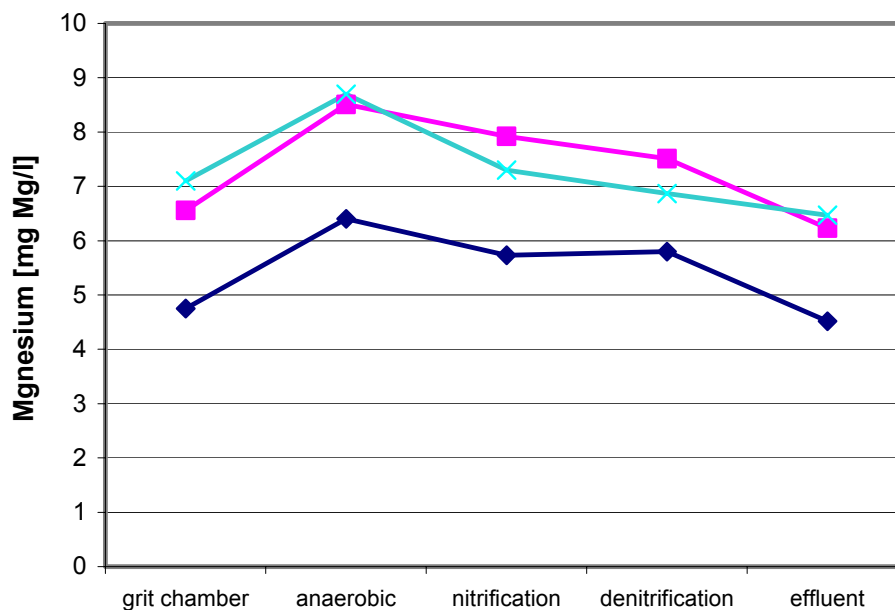


Figure 3. Changes of soluble magnesium.

One explanation can be the formation of struvite. Although the effective crystallisation requires a pH in the range between 8.6 to 10.6, crystallisation at lower pH seems also to be possible (Battistoni et al., 1997). The decrease of pH from 8.55 to 7.5 caused according to Battistoni et al., (1998) a reduction in the efficiency from 86.7 % to 58.2 %. It is therefore likely to have a partial formation of struvite at the investigated treatment plants where the pH of treated sewage was in the range of 7.2 to 7.8.

With the assumption of MAP formation along with biological phosphorus removal, a part of phosphorus is chemically removed. As a matter of fact it can be a quite substantial part for the molar rate of Mg : PO₄ as 1 : 1, the difference of 2.0 mg Mg/l can mean a removal of about 8.0 mg PO₄/l.

Magnesium in liquors from sludge dewatering can be present in much higher concentrations than in the treated sewage. In Fig. 4 examples from three different sewage treatment plants are presented. There is no reasonable explanation for the high concentration in the order of e.g. 100 mg Mg/l.

STRUVIT

Crystallisation of struvite, if there are magnesium, ammonia and phosphates present in sufficient amounts, preferable close to the stoichiometric rate of at least two components is feasible through increase of pH. There is however a distinct difference in the procedure of pH increase in dependence of the origin of waste water. As mentioned earlier liquids from sludge dewatering have usually the highest concentration of magnesium, ammonia and phosphates, providing that dewatered sludge originates from an enhanced nutrients removal process.

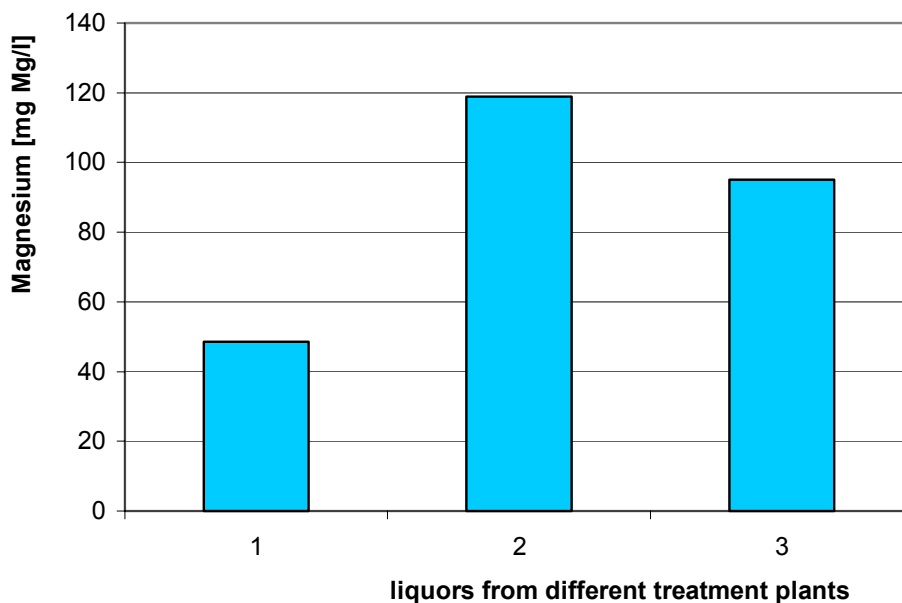


Figure 4. Possible concentration of magnesium in sludge liquors.

If the dewatered sludge to be wasted is coming from an aerobic sludge stabilisation process (or prolonged nitrification faze), even after partial anaerobic digestion in the course of sludge thickening the usually low pH cannot be raised sufficiently by simple aeration. If struvite has to be precipitated than addition of NaOH or $\text{Ca}(\text{OH})_2$ (Woods et al., 1999) is required. Addition of lime finally ends with calcium phosphate compounds, probable mainly HAP precipitation. Small changes in magnesium concentration means that a marginal struvite crystallisation takes place.

However, sludge taken from closed anaerobic digesters are prone to substantial pH increase by simple aeration. The process of decarbonisation – release of excess carbon dioxide dissolved under higher than atmospheric pressure in the anaerobic digester, is resulting as an effect indistinct pH increase.

During laboratory investigations an aeration period of several hours is required in dependence to the aeration intensity. In Fig. 5 the increase in pH of the liquid from the digested sludge dewatering in the course of aeration was presented.

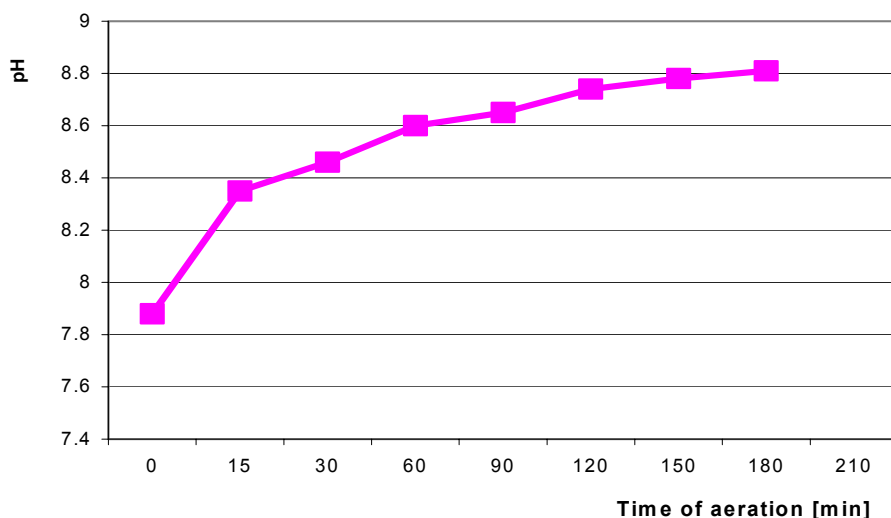


Figure 5. The effects of aeration on pH.

Parallel to the increase of pH, an increase of turbidity was measured (Fig. 6). In the range of pH between 8.2 and 8.6, an almost straight relation of turbidity and pH was demonstrated. (Fig. 7).

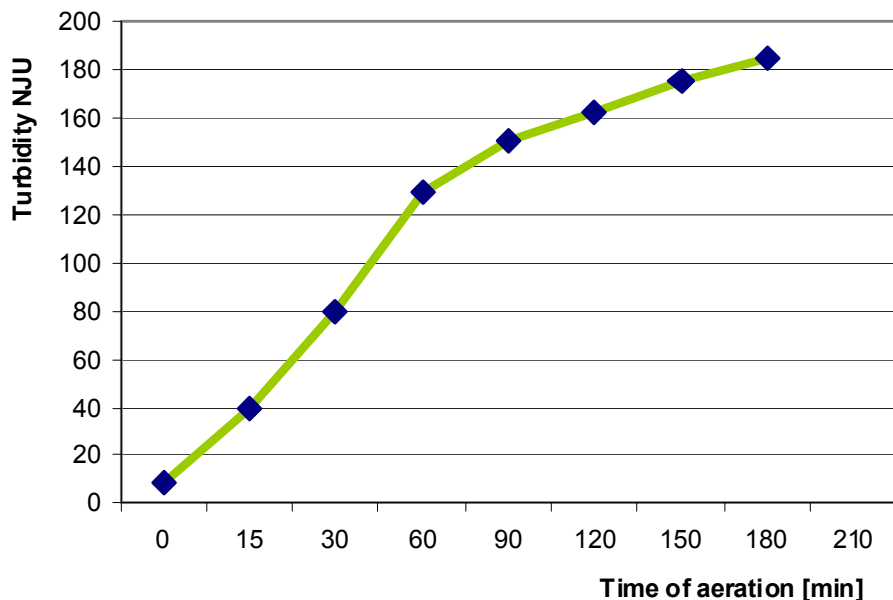


Figure 6. Increase of turbidity with time of aeration.

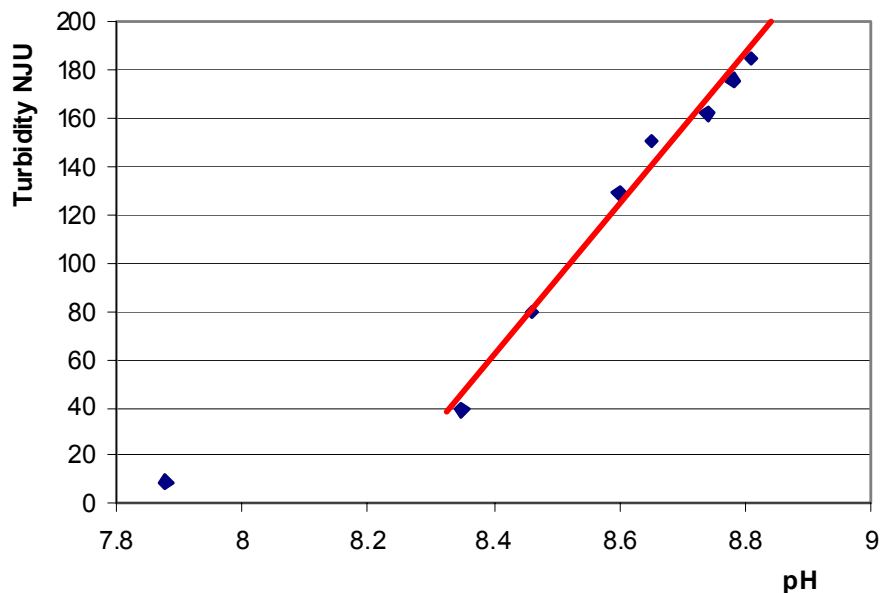


Figure 7. The correlation between turbidity and pH.

The increase of turbidity was attributed to crystallisation of struvite. The aforementioned supposition was proved by chemical analysis showing a decrease of phosphates from 125 mg PO₄/l to 55 mg PO₄/l and a decrease of magnesium from 21.7 to 8.5 mg Mg/l, which apparently is close to the stoichiometric rate of struvite. The removal of ammonia does not correspond to the molar ratio of struvite. The amount of ammonia removed was much higher, what can be the result of ammonia stripping with the increase of pH.

CONCLUSIONS

The carried out experiments are in accordance with observations made by other authors and have proven the feasibility of simultaneous removal of ammonia (nitrogen) and phosphorus from the sewage treatment system.

Recovery in the form of struvite is an attractive phosphorus recovery process, apart from nitrogen removal. The recovery of struvite as a fertiliser in the side stream (in the sludge processing stream) of sewage treatment can have a decisive effect on the overall biological phosphorus removal efficiency. Also removal of a substantial part of nitrogen through binding in the solid form of struvite and partial stripping to the atmosphere has a potential for diminishing of the required bioreactor volume for nitrification and denitrification.

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