Modelling of sediment precipitation containing struvite from aqueous solutions on the inner walls of steel pipelines

Justyna Czajkowska*, Maciej Malarski, Tadeusz Siwiec

Warsaw University of Life Sciences, Poland

*Corresponding author's e-mail: justyna_czajkowska@sggw.pl

Abstract: The complexity and uncontrolled formation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) and its deposition in the technological equipment of wastewater treatment plants (WWTPs) are still the subject of research aimed at understanding the causes and proposing a remedial action. In order to reduce the intensity of the precipitation of struvite in wastewater treatment plants, it is recommended, among others, to limit flow velocity to below 1.5 m·s^{-1}. Literature analysis showed that there are no studies on the precipitation of struvite deposits in pipelines. Most studies focus on the deliberate precipitation of struvite, for example phosphorus recovery, resulting in a molar ratio of 1:1:1 (NH_4^+:PO_4^{3-}:Mg^{2+}). In fact, in WWTPs, such concentrations do not occur, but there have been cases of the precipitation of this mineral (and its mixtures) in the sludge parts. In this paper, the study aimed at determining conditions for the precipitation of deposits with a significant participation of struvite on the inner walls of steel pipes. The study was conducted at a non-stoichiometric concentration of ingredients at different pH values, as well as under dynamic conditions with flow velocity below 1.5 m·s^{-1}. A mathematical formula (ANOVA) that can be used to determine the mass of deposits in relation to the concentration of ammonium, phosphate, pH and flow velocity was developed. Computational models were developed on to investigate struvite precipitation under different pH levels (8.0–9.5) and ionic concentrations. The studies were carried out on solutions containing ammonium (NH_4^+), phosphate (PO_4^{3-}), and magnesium (Mg^{2+}), at a flow velocities of 0.4, 0.9 and 1.4 m·s^{-1}. In order to determine the mathematical formula thanks to which the mass of precipitates can be determined, a special pilot study installation was constructed. The XPS surface analysis of sludge from sewage treatment plants showed a similar composition of compounds with sediments obtained in own research. The presence of struvite was suggested, but the share of atomic percentage of bonds to which struvite was classified is small and amounts to less than 4%. This means that sediments precipitated in the technological installations are a mixture of various compounds of which pure struvite may constitute only a small part.

Introduction

With the development of technology for biological nutrient removal (BNR), the problem of uncontrolled precipitation of magnesium ammonium phosphate, commonly called struvite, was observed in wastewater treatment (Xue and Huang 2007). Researchers established that the formation favors increased concentrations of phosphate and ammonium ions for the stabilization process of sludge, which is the result of biological processes. An important factor was the pH of the solution (Ohlinger et al. 1998). It was also observed that struvite deposits are formed faster in a zone of high turbulence resulting from the high flow velocity and direction changes for the various bends and curves of the inner surface than in zones with low turbulence and the flow taking place in relatively straight pipes (Ali and Schneider 2006, Konieczny 2002). Struvite crystals usually form on the surfaces of pipes, mixers, and submerged mechanical equipment in WWTPs, limiting their efficacy. This results in the lowering of flow abilities in pipes and leads to the necessity of increasing the level to which pumps are raised as well as increased hydraulic losses, generating higher operating costs. Fouling is often so extensive that processes are rendered inoperable and entire pipe systems have to be replaced (Ohlinger et al. 1998).

The theoretical molar ratio at which struvite precipitation occurs is 1:1:1 (NH_4^+:PO_4^{3-}:Mg^{2+}). However, in practice, the possibility of precipitation of struvite at various molar ratios (other than 1:1:1) has also been noticed by other scientists in their research (Kuglarz et al. 2014).

Mineral deposits released in WWTPs are heterogeneous. The composition of sludge depends on the presence of various minerals and organic compounds found in WWTPs. Minerals that may occur with along struvite include potassium magnesium phosphate ($KMgPO_4 \cdot 6H_2O$), hydroxyapatite ($Ca_5OH(PO_4)_2$),

magnesium hydrogen phosphate ($MgHPO_4 \cdot 3H_2O$), as well as calcium phosphates and carbonates and many others (Petruzzelli et al. 2004, Zou and Wang 2017).

Struvite is a very good fertilizer. Therefore, the recovery of struvite from various sources, e.g. wastewater, landfill leachate or livestock wastewater, is the subject of many studies. These sources must have high concentrations of COD, BOD, ammonium and phosphorus. Some of these parameters can be determined using modelling (Huang et al. 2016, Kim et al. 2014, Siwiec et al. 2018).

The aim of the paper was to determine the model by which it will be possible to determine the mass of precipitated deposits depending on such parameters as: liquid flow velocity, pH, and the concentration of magnesium, ammonium and orthophosphate ions.

Analyzing the available literature, no research was found to determine the effect of pH, flow velocity and struvite-building ions on the mass of precipitated deposits on steel pipelines, therefore an experimental installation was built.

Material and methods

Methodology for pilot plant research

The pilot plant installation shown in Fig. 1 was a closed system in which the main parts were: a tank [1] with a capacity of 210 dm³, a pump [3] and a circulation pipe [2] connected to the discharge port of the pump, and a return line [10] connected to the tank. On the discharge side of the pump there was also throttle [4], whose function was to control the flow of the test solution to the pump at the time of start-up (this prevents the destruction of the plant, which comprises a plurality of connections and knees). The most important part of the pilot plant was made up of three measurement sections which were connected with the circulation pipe [2] and pipe [10] via the respective clusters. At each measurement section there was a ball valve [5] (to control the flow over the section), a flow meter [6], and a 50-cm length of steel pipe with a diameter of 2" – which is the main measuring section [7], also shown in Fig. 1. Saddle branches [8] were installed at the beginning and end of each of the three sections for connecting a differential pressure meter [9]. Test solutions were injected into the pipe after passing through the measurement sections [10] and returned to the tank [1]. A vent [11] was located at the highest point of the system to remove air from the entire hydraulic system. Flow meters, differential pressure meters and a temperature sensor were connected to a recorder [12]. Seeing as how the elements related to measurements [5], [8] are the same in each of the three measurement sections, they are numbered for only a single pipeline in Fig. 1 for clarity. Moreover a temperature sensor [13] and a cooler [14], which was made from a rubber duct, were installed in the tank. Water from a deep well with a temperature of approx. 12°C was used for cooling.

Test solutions were prepared on the basis of distilled water and the reagents used in laboratory studies (Czajkowska and Siwiec 2011, Czajkowska 2012). These solutions were based on NH_4Cl, $MgSO_4 \cdot 7H_2O$ and KH_2PO_4. pH adjustment (to a specified value) was performed using a KOH solution.

The research methodology consisted of preparing an appropriate solution in the tank [1] (Fig. 1) and starting-up the pump [3]. As a result, the solution flowed through the pipeline [2], then all the measuring portions, and through the pipe [10] back into the tank. The system worked in 70-hour cycles. After this time, the pump was stopped, the measurement pipeline dismantled, and next measurements and inspection of the inner surface of the pipeline carried out, along with photographic documentation. Measurement consisted of weighing the
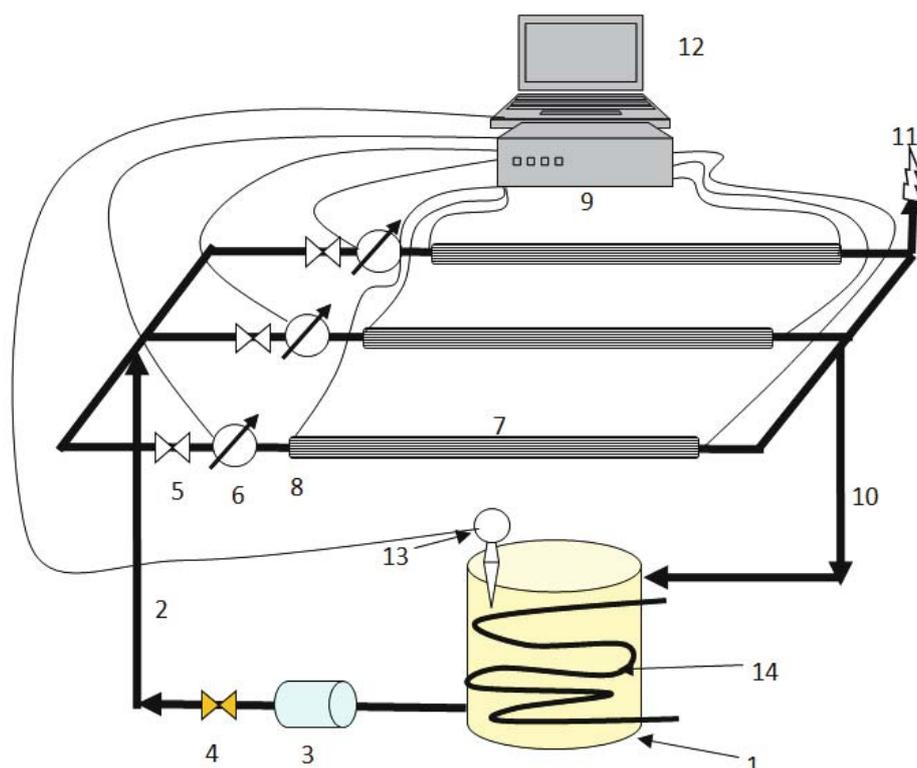

Fig. 1. Schematic diagram of the pilot plant (markings in the text)

relevant pipeline, with the increase in deposits on the inner surface of the measuring tube determined from the difference in weight at the end and at the beginning of a cycle. Measurements were done using a laboratory scale with an accuracy of 0.1 g. In the present study, three flow velocities were assumed, i.e. 0.40, 0.90 and 1.40 m·s^{-1}. Based on the results, four values of concentration of ammonium ions (100, 400, 700 and 1000 mg NH$_4^+$·dm^{-3}) and five concentrations of phosphate ions (50, 100, 150, 200 and 250 mg PO$_4^{3-}$·dm^{-3}) were selected for the studies. The concentration of magnesium (determined on the basis of laboratory tests) (Czajkowska and Siwiec 2011, Czajkowska 2012) was lowered by 10%. This results in a clear solution with no precipitation.

Methodology for testing the surface composition of sediments

The XPS method (X-ray photoelectron spectroscopy) or x-ray photoelectron spectroscopy was used for sediment tests. Photoelectron spectroscopy studies were carried out using an ESCALAB-210 photoelectron spectrometer from VG Scientific (England) at the Mazovian Center for Surface Analysis of the Polish Academy of Sciences.

Results

Pilot plant results

Tables 1 to 4 show selected results for the four pH values. The tables contain the results of research carried out in a pilot plant. The mass of deposits decreased with increasing concentrations of phosphate and with increasing flow velocities and pH. The ground deposits increased with an increasing concentration of ammonium ions.

Analyzing the above tables, it can be stated unequivocally that an increase in flow velocity results in a decrease in precipitating sediments, and vice versa. With increasing flow velocity from 0.4 to 1.4 m·s^{-1}, the mass of the precipitate is reduced for all pH values. This relationship is curvilinear. For example, at pH 8.5 (Tab. 3) ammonium ion concentration of 1000 mg·dm^{-3}, concentration of phosphate of 50 mg·dm^{-3} and a flow velocity of 0.40 m·s^{-1}, precipitated mass was 2.1 g, while for the same concentration of ammonium ions and a flow velocity of 1.4 m·s^{-1}, the mass was 0.9 g. This trend holds true for all phosphate concentrations and pH values. It is notable that a higher mass of sediment was observed for higher pH (9.5) and higher values of ammonium ions (1000 mg·dm^{-3}). For a flow velocity of 0.90 m·s^{-1}, pH of 8.5 (Tab. 3), phosphate ion concentration of 250 mg·dm^{-3}, and a concentration of ammonium ions of 100 and 1000 mg·dm^{-3}, sediment weights were 0.7 g and 1.1 g respectively.

In the case of pH = 8.0 (Tab. 4) at a concentration of phosphate at 250 mg·dm^{-3} and two flow velocities (0.9 and 1.4 m·s^{-1}), no deposits were observed.

It was also observed that, for a constant concentration of phosphate ions and pH, a change in the concentration of ammonium compounds does not significantly affect the precipitate mass in pipelines. For example, for ammonium compounds at 400 mg·dm^{-3} and 700 mg·dm^{-3}, a concentration of phosphate ions of 250 mg·dm^{-3} and a flow velocity of 0.4 m·s^{-1}, the precipitate mass has a similar size, i.e. 0.5 g.

It was observed that with a decrease in pH, the impact of flow velocity on the mass of precipitates has a decreasing tendency. For example, for 1000 mg·dm^{-3} ammonium ion concentration, 50 mg·dm^{-3} phosphate ion concentration and 0.4 m·s^{-1} flow velocity, the mass of precipitates for pH values

Table 1. Measurement of precipitate mass on steel pipes depending on the concentration of ammonium ions, the concentration of phosphate and pH = 9.5 (Czajkowska 2013)

Concentration PO$_4^{3-}$ [mg·dm^{-3}]	Flow velocity [m·s^{-1}]	Concentration NH$_4^+$ [mg·dm^{-3}]							
		100		400		700		1000	
		Mass [g]	Mg^{2+} [mg·dm^{-3}]	Mass [g]	Mg^{2+} [mg·dm^{-3}]	Mass [g]	Mg^{2+} [mg·dm^{-3}]	Mass [g]	Mg^{2+} [mg·dm^{-3}]
50	0.40	2.4	20.33	2.7	6.63	3.2	5.97	3.4	3.98
	0.90	0.7		2.0		2.2		2.3	
	1.40	0.6		1.9		2.1		2.1	
100	0.40	2.1	7.29	2.2	4.65	2.5	3.98	2.7	3.98
	0.90	0.7		1.6		1.8		1.9	
	1.40	0.6		1.5		1.8		1.9	
150	0.40	1.5	5.97	1.7	3.32	2.3	3.32	2.7	3.32
	0.90	0.6		1.1		1.8		1.8	
	1.40	0.5		1.0		1.6		1.7	
200	0.40	1.4	3.98	1.6	3.32	2.1	2.66	2.4	2.66
	0.90	0.5		0.9		1.2		1.3	
	1.40	0.4		0.8		1.1		1.2	
250	0.40	1.0	3.98	1.5	3.32	1.8	2.66	2.0	2.66
	0.90	0.2		0.7		0.7		1.0	
	1.40	0.3		0.6		0.5		0.7	

Table 2. Measurement of precipitate mass on steel pipes depending on the concentration of ammonium ions, the concentration of phosphate and pH = 9.0

Concentration PO_4^{3-} [mg·dm⁻³]	Flow velocity [m·s⁻¹]	Concentration NH_4^+ [mg·dm⁻³]							
		100		400		700		1000	
		Mass [g]	Mg^{2+} [mg·dm⁻³]	Mass [g]	Mg^{2+} [mg·dm⁻³]	Mass [g]	Mg^{2+} [mg·dm⁻³]	Mass [g]	Mg^{2+} [mg·dm⁻³]
50	0.40	2.2	35.65	2.3	14.49	2.3	12.54	2.5	11.23
	0.90	0.7		1.1		1.2		1.5	
	1.40	0.6		1.1		1.1		1.2	
100	0.40	1.9	22.91	2.0	8.60	2.1	7.29	2.2	7.29
	0.90	0.7		1.0		1.1		1.4	
	1.40	0.5		0.8		0.9		1.0	
150	0.40	1.4	15.14	1.5	5.97	1.8	5.31	2.0	3.98
	0.90	0.5		0.8		1.0		1.1	
	1.40	0.3		0.7		0.8		0.9	
200	0.40	1.3	10.57	1.3	4.65	1.4	3.98	1.6	3.32
	0.90	0.4		0.7		0.8		0.8	
	1.40	0.3		0.6		0.7		0.8	
250	0.40	0.9	10.57	1.1	4.65	1.2	3.98	1.3	3.98
	0.90	0.4		0.7		0.7		0.8	
	1.40	0.3		0.6		0.6		0.7	

Table 3. Measurement of precipitate mass on steel pipes depending on the concentration of ammonium ions, the concentration of phosphate and pH = 8.5

Concentration PO_4^{3-} [mg·dm⁻³]	Flow velocity [m·s⁻¹]	Concentration NH_4^+ [mg·dm⁻³]							
		100		400		700		1000	
		Mass [g]	Mg^{2+} [mg·dm⁻³]	Mass [g]	Mg^{2+} [mg·dm⁻³]	Mass [g]	Mg^{2+} [mg·dm⁻³]	Mass [g]	Mg^{2+} [mg·dm⁻³]
50	0.40	X	X	1.9	31.22	2.0	20.98	2.1	17.09
	0.90	X		1.0		1.0		1.1	
	1.40	X		0.7		0.9		0.9	
100	0.40	1.6	50.00	1.6	13.84	1.7	13.19	1.8	13.19
	0.90	0.6		0.8		0.9		1.0	
	1.40	0.3		0.6		0.7		0.8	
150	0.40	1.4	29.31	1.4	11.88	1.5	10.57	1.6	9.26
	0.90	0.4		0.6		0.8		0.8	
	1.40	0.2		0.4		0.6		0.7	
200	0.40	1.1	16.44	1.2	7.98	1.2	6.63	1.3	5.97
	0.90	0.3		0.4		0.6		0.6	
	1.40	0.2		0.3		0.4		0.6	
250	0.40	0.7	15.79	0.9	7.94	1.1	5.97	1.1	5.95
	0.90	0.2		0.3		0.4		0.5	
	1.40	0.2		0.2		0.3		0.4	

X – no data

Table 4. Measurement of precipitate mass on steel pipes depending on the concentration of ammonium ions, the concentration of phosphate and pH = 8.0

Concentration PO_4^{3-} [mg·dm⁻³]	Flow velocity [m·s⁻¹]	Concentration NH_4^+ [mg·dm⁻³]							
		100		400		700		1000	
		Mass [g]	Mg^{2+} [mg·dm⁻³]	Mass [g]	Mg^{2+} [mg·dm⁻³]	Mass [g]	Mg^{2+} [mg·dm⁻³]	Mass [g]	Mg^{2+} [mg·dm⁻³]
50	0.40	X	X	1.4	129.29	1.5	69.44	1.6	50.00
	0.90	X		0.8		0.9		1.0	
	1.40	X		0.8		0.8		0.8	
100	0.40	X	X	1.2	42.55	1.4	31.22	1.4	24.19
	0.90	X		0.6		0.6		0.7	
	1.40	X		0.4		0.5		0.6	
150	0.40	X	X	1.0	24.19	1.2	19.69	1.2	17.74
	0.90	X		0.4		0.5		0.5	
	1.40	X		0.3		0.4		0.4	
200	0.40	0.7	102.09	0.8	22.27	0.9	18.39	0.9	15.14
	0.90	0.3		0.3		0.4		0.4	
	1.40	0.2		0.3		0.3		0.3	
250	0.40	0.4	74.80	0.5	16.44	0.5	14.49	0.6	11.23
	0.90	X*		X *		X*		X*	
	1.40	X*		X*		X*		X*	

X – no data
X* – no precipitation

of 9.5, 9, 8.5 and 8 are 3.4 g, 2.5 g, 2.1 g, and 1.6 g respectively. From the pilot plant studies, the roughness of a clean pipeline and one containing precipitate was determined. The results have been summarized in Table 5.

Deposition of struvite affects changes in the pipe surface, resulting in increased hydraulic resistance. Under the technical conditions in the sewage treatment plant, an increase in resistance results in a decrease in the flow rate. Initially, this is barely noticeable; however, the longer the system operates, the more serious the effects become, seeing as how the accreting particles of the deposit, after lining the entire inner surface of the pipe, will not only change the roughness, but will also reduce the diameter of the pipeline. The reduction of the pipeline's diameter has a much faster effect on the hydraulics of the system. The roughness results (Table 5) confirmed the visual assessment of changes resulting from the interior view of the pipes shown in Fig. 2.

As shown in the photographs (Fig. 2), the precipitate in the tested steel pipeline does not cover its inner surface regularly, depositing itself on the uneven areas of the rough surface. These irregularities can stop (on their surface) earlier precipitated sediments carried along with the solution or facilitate the retaining of particles that can lead to the formation of struvite.

Modelling

Based on the results of research, ANOVA regression was performed using the Statgraphics Centurion XVI package (in order to determine the mass of deposits DEO function is used). The ANOVA linear regression model for indicating mass is as follows (1):

$$
\begin{aligned}
y = &-71.1258 + 11.783 \cdot pH + 0.428839 \cdot Mg^{2+} \\
&+0.174606 \cdot PO_4^{3-} - 0.0544725 \cdot NH_4^+ + 19.0113 \\
&\cdot v - 0.0566054 \cdot pH \cdot Mg^{2+} - 0.0291044 \\
&\cdot pH \cdot PO_4^{3-} + 0.00661503 \cdot pH \cdot NH_4^+ - 4.01544 \\
&\cdot pH \cdot v - 0.0000241514 \cdot Mg^{2+} \cdot PO_4^{3-} + 0.000113193 \\
&\cdot Mg^{2+} \cdot NH_4^+ + 0.00943789 \cdot Mg^{2+} \cdot v \\
&+0.00000745438 \cdot PO_4^{3-} \cdot NH_4^+ + 0.031522 \\
&\cdot PO_4^{3-} \cdot v - 0.000223013 \cdot NH_4^+ \cdot v
\end{aligned}
\tag{1}
$$

where:
y   – precipitate mass [g·m⁻²],
pH   – pH value [-],
Mg^{2+} – concentration of magnesium ions [mg·dm⁻³],
NH_4^+ – concentration of ammonium ions [mg·dm⁻³],
PO_4^{3-} – concentration of phosphate ions [mg·dm⁻³],
v   – flow velocity [m·s⁻¹].

The range of applicability is as follows: pH from 8.0 to 9.5, NH_4^+ from 100 to 1000 mg·dm⁻³, PO_4^{3-} from 50 to 250 mg·dm⁻³, Mg^{2+} from 2 to 130 mg·dm⁻³ and flow velocity from 0.4 to 1.4 m·s⁻¹.

In order to assess the impact of individual variables on the mass of the precipitate from aqueous solutions in Fig. 3, the main effects of each variable are presented. The positive or negative influence of a given factor on the precipitate mass can be determined by the direction of the straight lines. The pH and concentration of magnesium and ammonium ions have a positive effect on the mass of the precipitate, while the concentration of phosphoric ions and the flow velocity have a negative effect. This means that as pH value increases from

Table 5. Change in roughness of pipes during research

Flow velocity [m·s^{-1}]	Roughness of the clean pipe k [mm]	Roughness of the pipe with sediment k_{os} [mm]	Roughness increase [%]
0.40	0.74	1.92	161.0
0.90	0.87	1.49	70.5
1.40	0.89	1.36	53.4
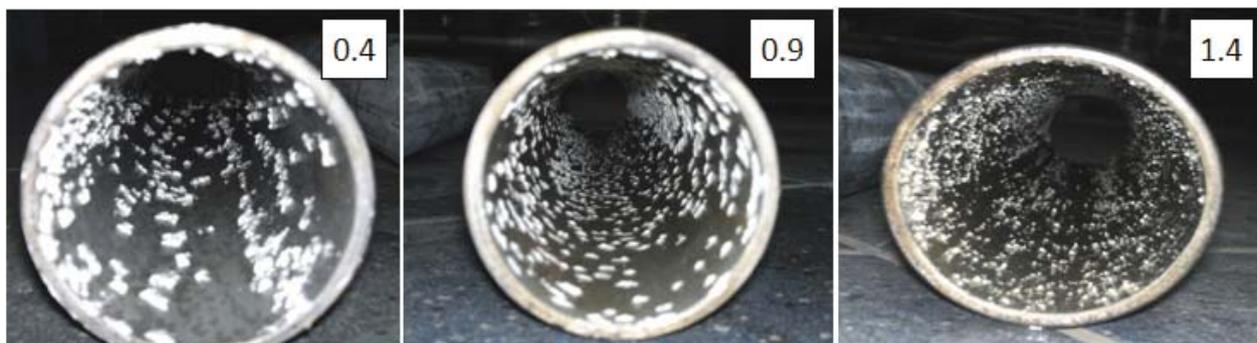
Fig. 2. Appearance of precipitated sediment at a flow velocity of 0.4, 0.9 and 1.4 m·s^{-1}, concentration of ammonium ions of ~1000 mg·dm^{-3}, concentration of phosphate ions of 50 mg·dm^{-3} and pH = 9.5 (Soares et al. 2017)
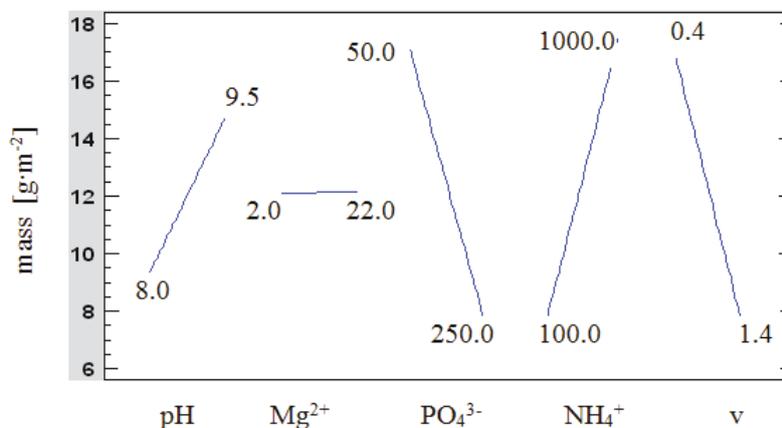
Fig. 3. Influence of pH, magnesium ions, phosphate ions, ammonium ions and flow velocity on the mass of the precipitate

8.0 to 9.5, together with an increase in the concentration of: magnesium ions (from 2 to 130 mg·dm^{-3}) and ammonium ions (from 100 to 1000 mg·dm^{-3}), the mass of the precipitate increases as well. The opposite situation occurs with the concentration of phosphorus ions and flow velocity. The increase of these factors makes the mass of the precipitate lower. The greater the slope of the straight line, the greater the influence of a given factor on the mass of the precipitate. Flow velocity and further, the concentration of phosphorus ions, ammonium ions, pH and the concentration of magnesium ions have the highest impact on the mass of the precipitate.

The results obtained by ANOVA analysis using the Statgraphics Centurion XVI package are shown in Table 6. The significance level "p" for the analysis was 0.05. A value of parameter "p" lower than 0.05 means that the tested factor significantly influences the mass of the precipitate and should be included in the model designed with the DEO function.

The values of the "p" parameter presented in Table 6 show that majority of the analyzed factors as well as the interactions between them are statistically significant. In most of the factors, the value of the "p" parameter is greater than the assumed level of significance.

The verification model derived using ANOVA (Statgraphics Centurion XVI) for all analyzed pH values is shown in Fig 4.

As can be seen in Fig. 4, the mass of the precipitate can be measured with a fairly good accuracy when knowing the values of the aforementioned parameters.

XPS analysis results

XPS analysis of the sediment from the pilot plant installation was carried out for a solution with ammonium ions 1000 mg·dm^{-3}, phosphate ions 50 mg·dm^{-3} and pH = 9.5. The presence of several compounds with calcium ions, as well as with phosphate and magnesium ions has been suggested.

Table 6. The result of the ANOVA analysis of the impact of individual factors on the mass of the precipitate

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:pH	5.97548	1	5.97548	0.76	0.3840
B:Mg	0.000558026	1	0.000558026	0.00	0.9933
C:PO4	54.283	1	54.283	6.93	0.0095
D:NH4	27.752	1	27.752	3.54	0.0620
E:v	223.225	1	223.225	28.50	0.0000
AB	6.49158	1	6.49158	0.83	0.3643
AC	84.742	1	84.742	10.82	0.0013
AD	86.5222	1	86.5222	11.05	0.0012
AE	66.8032	1	66.8032	8.53	0.0041
BC	0.0531261	1	0.0531261	0.01	0.9345
BD	8.60223	1	8.60223	1.10	0.2966
BE	0.425535	1	0.425535	0.05	0.8161
CD	2.29933	1	2.29933	0.29	0.5889
CE	97.0833	1	97.0833	12.39	0.0006
DE	0.103265	1	0.103265	0.01	0.9088
Total error	1026.19	131	7.83354		
Total (corr.)	9121.78	146			

R – squared = 88.7501 percent
R – squared (adjusted for d.f.) = 87.4619 percent
Standard Error of Est. = 2.79885
Mean absolute error = 2.07072
Durbin-Watson statistic = 1.36782 (P=0.0000)
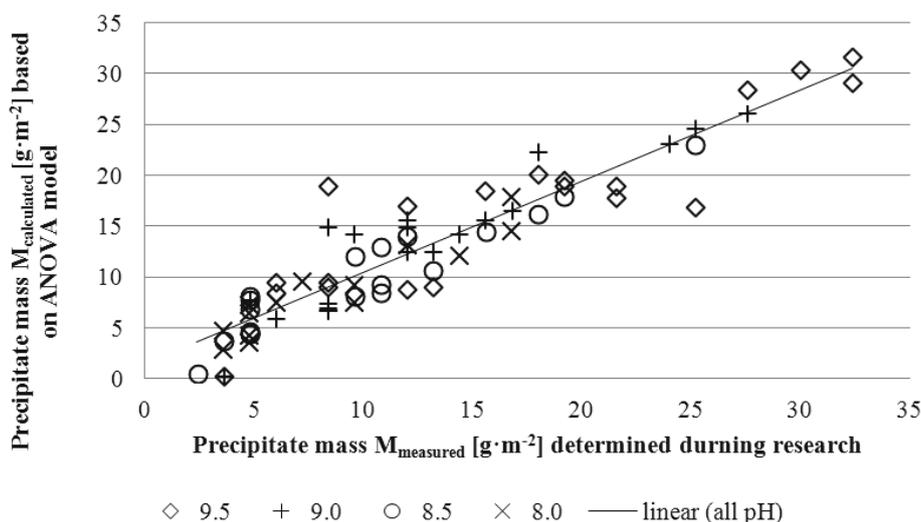Lag 1 residual autocorrelation = 0.312344

Fig. 4. Verification of the equation allowing the mass of the precipitates to be determined on the basis of ANOVA analysis of variance

Zinc ions that come from galvanized steel pipelines were also seen in quite significant amounts. The flow of the test solution caused the leaching of ions from the internal surface of the pipelines that were part of the analyzed precipitate.

In the pilot plant installation, a solution of reagents based on distilled water was used to minimize the presence of undesirable ions and particles, including calcium ions. Despite this fact, the analysis showed the presence of this ion in the sample under study. Therefore, a laboratory analysis of the distilled water used on the test bench was carried out, revealing the presence of calcium ions at a concentration of 4.44 mg·dm^{-3}. The ratio of mass concentrations of Mg:Ca in this sample was 1:1.11 (molar 1:0.69). Le Corre et al. (2005) found that, at such a ratio of magnesium to calcium, calcium compounds can be expected. Calcium ions may increase the time of formation of the first struvite crystals and may

co-create hydroxyapatite $Ca_5(PO_4)_3OH$ or calcium carbonate-calcite $(CaCO_3)$ (Mazierski and Kowalski 2008). When molar ratio of magnesium to calcium is 1:1, calcium phosphate, not struvite, is formed (Le Corre et al. 2005). Both the presence of calcite and calcium carbonate was suggested in the sample from the pilot plant installation.

The research described above referred to a special situation, i.e. laboratory conditions, which do not occur in the treatment plant. Firstly, the sediments from a WWTP contain different contaminations when compared to those assumed in laboratory and the pilot plant. In addition, a new portion of ingredients along with wastewater continues to flow in. That is why, for purposes of comparison, X-ray examinations were carried out for samples obtained from the working pipeline of the WWTP.

A sample of sediments from one of Poland's WWTPs was sent for XPS analysis. The analysis of the surface composition suggests the presence of complex compounds, which include $(NH_4)Mg(PO_4)$ – struvite. It is worth noting that the atomic percentage of phosphate compounds, among which struvite is classified, is less than 4%. Again, a large part of the sample contains oxides and free ions. These results therefore suggest that precipitates found in pipes of the sludge processing line of a WWTP are a mixture of various compounds.

According to Soczek (2003), the problem that occurs in WWTPs is the formation of struvite, but also, what was not always properly defined, calcium deposits. The result of the analysis of the sample from the WWTP indicates that the sediments are not only a mixture of struvite in its amorphous forms, but also calcium compounds. They occur both in the material collected from a WWTP and in the precipitates found in the pipes of the pilot plant, and are namely $CaCO_3$ and $Ca_3(PO)_2$. The obtained results are in line with the results of a study by Crutchik and Garrido (2011), who found that crystal struvite precipitates in sediments under certain conditions, whereas in other cases, crystals of magnesium phosphate as well as amorphous crystals of calcium and magnesium phosphates precipitate.

Conclusions

This paper presents the influence of physical (flow velocity) and chemical (ion concentration included in struvite, pH) factors on the mass of the precipitate on the inner walls of steel pipelines. Based on the results of the pilot plant, the ANOVA model was developed. Using this model, a WWTP operator familiar with the pH, flow velocity, concentration of ammonium, orthophosphate and magnesium ions can determine the mass of the precipitation per 1 m^2. It turned out that the weight of the precipitate increases with increasing concentration of ammonium ions and the pH of the solution. Along with an increase in the flow velocity and the concentration of orthophosphate ions, the mass of the sediments decreases. Therefore, in order to inhibit the precipitation of sediments in pipelines, the flow rate of the liquid, as well as the concentration of orthophosphate should be increased, whereas the concentration of magnesium as well as ammonium ions should be lowered. The above recommendations are of course related to the limitation of sediment formation, but can also have a negative effect. For example, increasing flow velocity will increase hydraulic losses.

Analysis of sediments precipitated on a pilot plant and samples of sediment from a WWTP, using the XPS method, showed the presence of various chemical compounds and free particles formed on the basis of solutions of specific salts.

The XPS surface analysis of sediment from the WWTP showed the possibility of struvite occurrence, but the share of the atomic percentage of bonds which struvite was classified is small and amounts to less than 4%. This means that sediment produced on technological devices is a mixture of various compounds, in which pure struvite may constitute only a small part.

XPS surface analysis did not give a definite answer as to the composition of precipitates. The spectra obtained makes it possible to state that sediments precipitating in WWTPs commonly referred to as struvite are actually a mixture of various compounds composed of ions found in solutions (Marchi et al. 2014, Mehrez et al. 2014). Taking into account the fact that the composition of the supernatant liquid is very diverse and significantly variable over time, the formation of sediments of a diverse composition applies to all WWTPs due to the removal of biogenic compounds.

Acknowledgement

References

Ali, M.I. & Schneider, P.A. (2006). A fed-batch design approach of struvite system in controlled supersaturation, *Chemical Engineering Science*, 61, pp. 3951–3961.

Bhuiyan, M.I.H., Mavinic, D.S. & Koch, F.A. (2008). Thermal decomposition of struvite and its phase transition, *Chemosphere*, 70, pp. 1347–1356.

Crutchik, D. & Garrido, J.M. (2011). Struvite crystallization versus amorphous magnesium and calcium phosphate precipitation during the treatment of a saline industrial wastewater, *Water Science and Technology*, 64, 12, pp. 2460–2467.

Czajkowska, J. & Siwiec, T. (2011). Crystallization of struvite in variable conditions of the reaction and concentrations of the analyzed components, *Infrastruktura i Ekologia Terenów Wiejskich*, PAN branch in Cracow, 7, pp. 145–154. (in Polish)

Czajkowska, J. (2012). Crystallization of struvite from solutions at pH 9.5 and varying concentrations of the analyzed components, *Przegląd Naukowy Inżynieria i Kształtowanie Środowiska*, 21, 1, pp. 38–45. (in Polish)

Czajkowska, J. (2013). Influence of flow velocity and concentrations of individual ions on struvite deposition from aqueous solutions on internal surfaces of steel pipelines at pH = 9.5, *Zeszyty Naukowe Uniwersytetu Zielonogórskiego, Inżynieria Środowiska*, 152, 32, pp. 105–112. (in Polish)

Huang, H., Liu, J., Xu, Ch. & Gao, F. (2016). Recycling struvite pyrolysate obtained at negative pressure for ammonia nitrogen removal from landfill leachate, *Chemical Engineering Journal*, 284, pp. 1204–1211.

Kim, T.-H., Nam, Y.-K. & Lim, S.J. (2014). Effects of ionizing radiation on struvite crystallization of livestock wastewater, *Radiation Physics and Chemistry*, 97, pp. 332–336.

Konieczny, P. (2002). Struvite. How to prevent it from forming? Seminar Kemipol Copenhagen, pp. 38–48. (in Polish)

Kuglarz, M., Grübel, K. & Bohdziewicz, J. (2014). Post-digestion liquor treatment in the method combining chemical precipitation with reverse osmosis, *Archives of Environmental Protection*, 40, 3, pp. 29–42.

Le Corre, K.S., Vaslami-Jones, E., Hobbs, P. & Parsons, S.A. (2005). Impact of calcium on struvite crystal size, shape and purity, *Journal of Crystal Growth*, 283, pp. 514–522.

Marchi, A., Geerts, S. & Weemaes, M. (2014). Full-scale phosphorous recovery as struvite from digested sludge: a return on experience. 2nd IWA Specialized International Conference ecoSTP 2014 Eco Technologies for Wastewater Treatment Technical, Environmental & Economic Challenges, Verona, Italy, 23–27 June 2014, pp. 110–114.

Mazierski, J. & Kowalski, E. (2008). Kinetics of struvite precipitation in a batch and flow reactor in a laboratory scale, *Przemysł Chemiczny*, 87, pp. 520–523. (in Polish)

Mehrez, H., Gras, M., Valderrama, C., Dosta, J., Cortina, J.L. & Batis, N.H. (2014). Hydroxyapatite precipitation from a highly concentrated phosphate solution. 2nd IWA Specialized International Conference eco STP 2014 Eco Technologies for Wastewater Treatment Technical, Environmental & Economic Challenges Verona, Italy, 23–27 June 2014, pp. 657–660.

Ohlinger, K.N., Young, T.M. & Schroeder, E.D. (1998). Predicting struvite formation in digestion, *Water Research*, 32, 12, pp. 3607–3614.

Petruzzelli, D., Dell'Erba, A., Liberti, L., Notarnicola, M. & Sengupta, A.K. (2004). Aphosphate-selective sorbent for REM NUT® process: field experience at Massafra, *Wastewater Treatment Plant. Reactive & Functional Polymers*, 60, pp. 195–202.

Siwiec, T., Reczek, L., Michel, M.M., Gut, B., Hawer-Strojek, P., Czajkowska, J., Jóźwiakowski, K., Gajewska, M. & Bugajski, P. (2018). Correlations between organic pollution indicators in municipal wastewater, *Archives of Environmental Protection*, 44, 4, pp. 50–57.

Soares, A., Czajkowska, J., Colprim, J., Gali, A., Johansson, S., Masic, A., March, A., McMeod, A., Nenov, V., Ruscalleda, M. & Siwiec, T. (2017). Nutrients recovery from wastewater streams, in: *Innovative Wastewater Treatment & Resource Recovery Technologies. Impacts on Energy, Economy and Environment*, Lema, J.M. & Suarez, S. (Eds.). IWA Publishing, London 2017, pp. 369–398.

Soczek, A. (2003). The use of polymers to eliminate struvite and calcium deposits, *Forum Eksploatatora*, 1, pp. 10–12. (in Polish)

Xue, T. & Huang, X. (2007). Releasing characteristics of phosphorus and another substances during thermal treatment of excess sludge, *Jurnal of Environmental Sciences*, 19, pp. 1153–1158.

Zou, H. & Wang, Y. (2017). Optimization of induced crystallization reaction, *Archives of Environmental Protection*, 43, 4, pp. 33–38.

Modelowanie wytrącania osadów zawierających struwity z roztworów wodnych na wewnętrznych ścianach rurociągów stalowych

Streszczenie: Złożoność i niekontrolowane powstawanie struwitu ($MgNH_4PO_4·6H_2O$) oraz jego osadzanie w urządzeniach technologicznych oczyszczalni ścieków jest nadal przedmiotem badań mających na celu zrozumienie przyczyn i zaproponowanie działań zaradczych. W celu zmniejszenia intensywności wytrącania struwitu w oczyszczalniach ścieków zalecano między innymi ograniczenie prędkości przepływu poniżej 1,5 m·s⁻¹. Analiza literatury wykazała, że nie ma badań dotyczących wytrącania struwitu w rurociągach stalowych. Większość badań koncentruje się na umyślnym wytrącaniu struwitu, na przykład w celu odzysku fosforu, doprowadzając do stosunku molowego 1:1:1 (NH_4:PO_4:Mg). W rzeczywistości w oczyszczalniach ścieków takie stężenia nie występują, ale zdarzały się przypadki wytrącania tego minerału (i jego mieszanin) w częściach osadowych. W pracy podjęto próbę określenia warunków występowania osadów z udziałem struwitu na wewnętrznych ścianach rur stalowych. Badanie przeprowadzono przy niestechiometrycznym stężeniu składników przy różnych wartościach pH, a także w warunkach dynamicznych z prędkością przepływu poniżej 1,5 m·s⁻¹. Opracowano wzór matematyczny (ANOVA), który można wykorzystać do określenia masy osadów w zależności od stężenia amonu, fosforanu, pH i prędkości przepływu. Opracowano modele obliczeniowe do badania wytrącania struwitu i jego mieszanin przy różnych poziomach pH (8,0–9,5) i stężeniach jonowych. Badania prowadzono na roztworach zawierających jony, w tym amonu (NH_4^+), fosforanu (PO_4^{3-}), magnezu (Mg^{2+}) oraz prędkości przepływu (0,4; 0,9 i 1,4 m·s⁻¹). Następnie wyznaczono formułę matematyczną w oparciu o badania wyzyskane w warunkach przepływowych na specjalnie skonstruowanej instalacji. Analiza powierzchniowe osadów mineralnych z oczyszczalni ścieków wykazała podobny skład z osadem uzyskanym w badaniach własnych. Sugerowano istnienie struwitu, ale procent udziału atomowego połączeń, do których sklasyfikowano struwite jest mały i wynosi mniej niż 4%. Oznacza to, że osady powstające w obiektach technologicznych oczyszczalni ścieków są mieszaniną różnych związków, w których czysty struwit może stanowić tylko niewielką część.