

Precipitation assessment in wastewater treatment plants operated for biological nutrient removal: A case study in Murcia, Spain

R. Barat ^{a,*}, A. Bouzas ^b, N. Martí ^b, J. Ferrer ^a, A. Seco ^b

^a *Departamento Ingeniería Hidráulica y Medio Ambiente, Universidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain*

^b *Departamento Ingeniería Química, Universidad de Valencia, Doctor Moliner 50, 46100 Burjassot, Valencia, Spain*

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Abstract

The Murcia Este Wastewater Treatment Plant is the largest wastewater treatment plant in Murcia (Spain). The plant operators have continuously found pipe blockage and accumulation of solids on equipment surfaces during the anaerobic digestion and post-digestion processes. This work studies the precipitation problems in the Murcia Este Wastewater Treatment Plant in order to locate the sources of precipitation and its causes from an exhaustive mass balance analysis.

The DAF thickener and anaerobic digester mass balances suggest that most of the polyphosphate is released during excess sludge thickening. Despite the high concentrations achieved in the thickened sludge, precipitation does not occur at this point due to the low pH. The increases in ammonium and pH during anaerobic digestion cause precipitation to take place mainly inside the digesters and in downstream processes. This study shows that 50.7% of the available phosphate is fixed in the digester of which 52.0% precipitates as ammonium struvite, 39.2% precipitates as hydroxyapatite and the remaining 8.8% is adsorbed on the surface of the solids. Thermodynamic calculations confirm the precipitation of struvite and hydroxyapatite and also confirm that potassium struvite does not precipitate in the anaerobic digesters.

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1. Introduction

Phosphate is the limiting component for growth in most ecosystems. The discharge of phosphates in surface waters may lead to eutrophication and blooming of algae. Therefore, it is essential to control phosphate emissions. Nowadays, biological phosphorus removal is often the preferred technology to achieve effluent standards (typically in the range of 0.5–1 gP/m³).

In biological nutrient removal processes (BNR), phosphates and metal cations are taken up and stored as polyphosphates (Poly-P) inside the bacterial cells. These polyphosphates are removed from the system in the excess sludge. During the sludge treatment, especially anaerobic digestion, these Poly-P are

released to the liquid phase (Wild et al., 1997), which significantly increases the phosphate concentration in the system. The concentration of other ions also increases in the digester: soluble magnesium concentration mainly increases due to Poly-P hydrolysis, and ammonium concentration increases as protein is degraded. The hardness of the influent wastewater also controls the precipitation processes of phosphorus inside the digester since it determines Ca²⁺ and Mg²⁺ concentrations in the wastewater. Both the increase in the concentrations of dissolved components and the high pH achieved during anaerobic digestion increase the phosphorus precipitation potential in this stage of the treatment system. Different magnesium and calcium phosphates are likely to precipitate in the sludge treatment system causing significant operational problems. Accumulation of struvite (MgNH₄PO₄·6H₂O) on pipe walls and equipment surfaces of anaerobic digestion and post-digestion processes has been reported as a frequent problem in the wastewater treatment industry (Ohlinger et al., 1998).

* Corresponding author. Tel.: +34 96 387 96 18; fax: +34 96 387 76 17.

E-mail address: rababa@dihma.upv.es (R. Barat).

Dewatering of the anaerobic digested sludge by centrifugation was found to be a critical stage for precipitation in many wastewater treatment plants in Germany (Heinzmann and Engel, 2005). The solid that was formed was mainly struvite and small portions of different calcium phosphate compounds. Downstream of the centrifugation of the sludge, precipitation was so significant that the outgoing pipes were fully blocked.

Struvite precipitation is not simply a problem of BNR treatment works (Parsons and Doyle, 2004). However, Enhanced Biological Phosphorus Removal (EBPR) processes, which produce a Poly-P rich waste sludge, exacerbate struvite and calcium phosphate deposit problems in anaerobic sludge digestion. Therefore, in these cases, special attention must be paid to control the formation of these deposits.

Precipitation problems lead to great increases in the cost of sludge management operations (Neethling and Benisch, 2004). Furthermore, these precipitation processes can be very important in the composition of the recycled streams from the sludge treatment, which cause variations in the dissolved phosphorus concentration that might affect the efficiency of the EBPR process (Nyberg et al., 1994).

The aim of this work is to study the precipitation problems in a large-scale wastewater treatment plant in order to locate the sources of precipitation and its causes from an exhaustive mass balance analysis. This work is a first step in finding solutions to minimize the uncontrolled precipitation in the sludge treatment system.

2. Materials and methods

This study was performed in the Murcia Este Wastewater Treatment Plant (WWTP) to determine the type and extent of phosphate fixation in the waste activated sludge line.

2.1. Murcia Este WWTP

Murcia Este WWTP was established in the year 2000 and is the largest treatment plant in Murcia (Spain), with a capacity of 100 000 m³/d. The water line consists of an activated sludge process operated for biological nitrogen and phosphorus removal (A₂O configuration) following preliminary treatment and primary sedimentation. This water line consists of three identical lines each of which is divided into anaerobic, anoxic and aerobic zones. The total volume is 41 405 m³ (6429 m³ anaerobic, 4850 m³ anoxic, and 30 146 m³ aerobic).

The primary and the secondary excess sludges are concentrated in two gravity thickeners and two dissolved air flotation (DAF) thickeners, respectively. Once thickened, both sludges are mixed before being anaerobically digested. The anaerobic digestion is carried out in three digesters of 6103 m³ per unit. The digested sludge is stored in a secondary digester and finally dewatered by centrifugation. The effluents from centrifuges and sludge thickeners are recycled to the water line before the primary settler.

The plant operators have continuously found precipitation problems in the sludge line, especially during anaerobic digestion and post-digestion processes, which cause pipe blockage

and accumulation on the surfaces of different devices of the sludge management system such as centrifuge, pumps and digested sludge or supernatant pipes (Fig. 1).

2.2. Analytical campaign

To identify the precipitation problems, an intensive analytical campaign was carried out under normal operating conditions at different points of the sludge line. Fig. 2 shows the WWTP configuration with the sampling points marked with grey dots. The influent sludge line composition to the anaerobic digestion (line 8) was obtained from the mass balance between the primary thickened sludge (line 4) and the excess floated sludge (line 7). Each line was sampled four times in 2 weeks. The parameters analysed were: total suspended solids, volatile suspended solids, total phosphorus, phosphate, ammonium, alkalinity, pH, and total and soluble concentrations of calcium, magnesium and potassium. All the analyses were carried out according to the Standard Methods (APHA, 1998). Furthermore, the flow rates were measured in all the sludge lines sampled.

2.3. Mass balance

Phosphorus, potassium, magnesium and calcium mass balances can be used to understand the chemical fixation mechanisms in the sludge treatment system. However, in order to perform these balances, several assumptions must be taken into account:

- Phosphorus stored as Poly-P is hydrolyzed during anaerobic digestion (Wild et al., 1997).
- During Poly-P hydrolysis, the release of phosphorus is followed by a release of potassium and magnesium at the same ratio as observed during the phosphorus uptake (Jardin and Pöpel, 1994). Values of 0.354 gK/gP and 0.283 gMg/gP determined in previous studies (Barat et al., 2005) were used.
- Organic matter degradation produces a release of phosphorus (P), potassium (K), magnesium (Mg), and calcium (Ca) associated with the content of each element in the organic matter. This release must be quantified when the mass balances are performed.
- There is no chemical fixation of the potassium released in the digester due to the high concentration of ammonium reached in it. Only in the case of low ammonium concentrations different authors (Schuiling and Andrade, 1999; Wilsenach et al., 2006) have pointed out that potassium struvite (K-MAP, KMgPO₄·6H₂O) could precipitate instead of ammonium struvite (MAP).

According to the assumptions listed above, mass balances under steady state conditions can be carried out using the following equations:

- From the potassium mass balance (Eq. (1)), the potassium released by polyphosphate accumulating organisms (PAO)

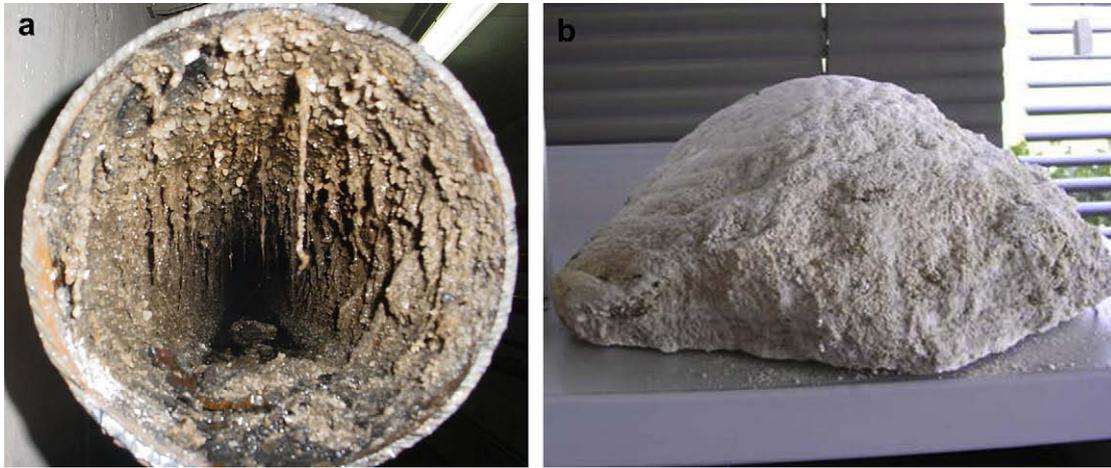


Fig. 1. Deposits of precipitates: (a) sludge pipes, (b) struvite deposit.

(K_{PAOrel} , M/T) can be calculated, considering that K_{ORGrel} (M/T) represents the potassium released from organic matter degradation, Q_{in} and Q_{out} (L^3/T) the influent and effluent flow rates, and K_{in} and K_{out} (M/L^3) the influent and effluent soluble potassium concentrations.

$$P_{PAOrel} = \frac{K_{PAOrel}}{0.354} \quad (2)$$

$$P_{fix} = \sum Q_{in}P_{in} + P_{ORGrel} + P_{PAOrel} - \sum Q_{out}P_{out} \quad (3)$$

$$\%P_{fix} = \frac{P_{fix}}{\sum Q_{in}P_{in} + P_{ORGrel} + P_{PAOrel}} 100 \quad (4)$$

$$K_{PAOrel} = K_{TOTrel} - K_{ORGrel} \\ = \left(\sum Q_{out}K_{out} - \sum Q_{in}K_{in} \right) - K_{ORGrel} \quad (1)$$

- The phosphate released by PAO (P_{PAOrel} , M/T) can be calculated (Eq. (2)) bearing in mind the mass of potassium released per mass of phosphate released. Then, from the phosphate mass balance, the phosphate fixed (P_{fix} (M/T) $\%P_{fix}$) by precipitation or adsorption can be obtained (Eqs. (3) and (4)): with P_{ORGrel} (M/T) being the amount of organic phosphate hydrolyzed, and P_{in} and P_{out} (M/L^3) being the influent and effluent phosphate concentrations.

- The magnesium mass balance can be applied to determine the magnesium precipitated (Mg_{prec} , M/T, and $\%Mg_{prec}$) (Eqs. (5) and (6)): Mg_{PAOrel} (M/T) represents the magnesium released by PAO; Mg_{ORGrel} (M/T) represents the magnesium released by organic matter degradation, Q_{in} and Q_{out} (L^3/T) represent the influent and effluent flow rates; and Mg_{in} and Mg_{out} (M/L^3) represent the influent and effluent soluble magnesium concentrations.

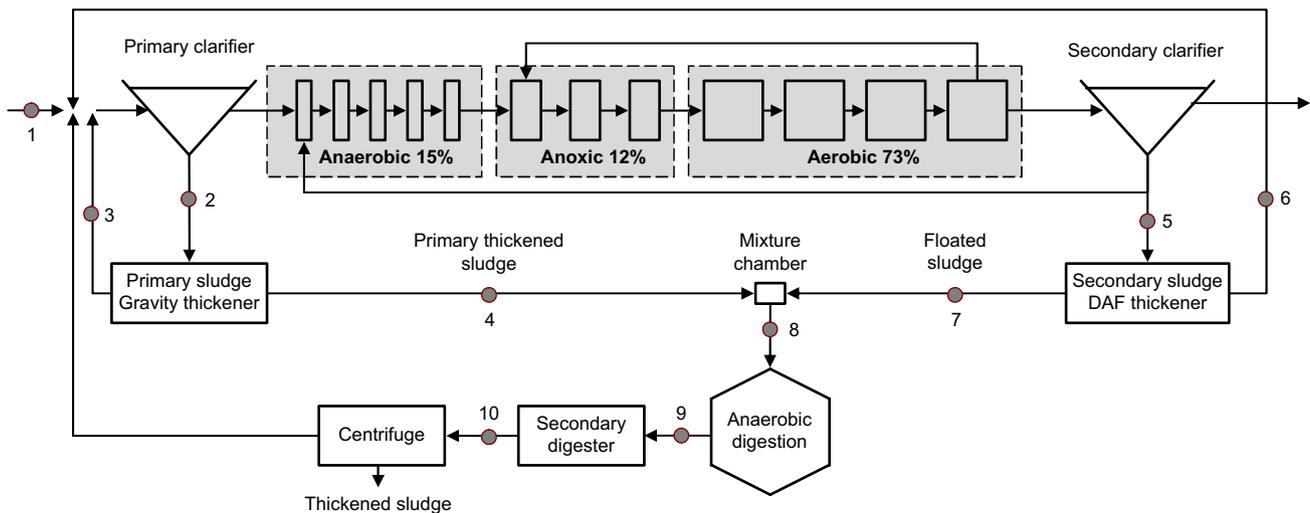


Fig. 2. Wastewater treatment plant flow chart and sampling points.

$$Mg_{\text{prec}} = \sum Q_{\text{in}} Mg_{\text{gin}} + Mg_{\text{ORGrel}} + Mg_{\text{PAOrel}} - \sum Q_{\text{out}} Mg_{\text{out}} \quad (5)$$

$$\%Mg_{\text{prec}} = \frac{Mg_{\text{prec}}}{\sum Q_{\text{in}} Mg_{\text{gin}} + Mg_{\text{ORGrel}} + Mg_{\text{PAOrel}}} 100 \quad (6)$$

- Finally, the precipitated calcium (Ca_{prec} , M/T, and $\%Ca_{\text{prec}}$) can be obtained from the calcium mass balance (Eqs. (7) and (8)), with Ca_{ORGrel} (M/T) being the calcium release due to organic matter degradation, Q_{in} and Q_{out} (L^3/T) being the influent and effluent flow rates, and Ca_{in} and Ca_{out} (M/L^3) being the influent and effluent soluble calcium concentrations.

$$Ca_{\text{prec}} = \sum Q_{\text{in}} Ca_{\text{in}} + Ca_{\text{ORGrel}} - \sum Q_{\text{out}} Ca_{\text{out}} \quad (7)$$

$$\%Ca_{\text{prec}} = \frac{Ca_{\text{prec}}}{\sum Q_{\text{in}} Ca_{\text{in}} + Ca_{\text{ORGrel}}} 100 \quad (8)$$

3. Results and discussion

Table 1 shows the average values of the parameters analysed and the average flow rate for each line. Standard deviations are also provided.

3.1. Influent wastewater

As Table 1 shows, the influent wastewater characterization (line 1) showed high concentrations of total phosphorus and phosphate (15.8 and 7.3 mgP/l, respectively), and soluble calcium (165.9 mg/l) and soluble magnesium (73.9 mg/l), which indicated the hardness of the water and suggested possible precipitation problems throughout the WWTP. Furthermore, there was an important difference between total and soluble influent calcium concentrations (201.6 and 165.9 mg/l, respectively). This difference could be the result of calcium carbonate precipitation in the sewage network induced by the high influent alkalinity (729 mgCaCO₃/l).

3.2. P, K, Mg and Ca content in the organic matter

As stated above, to properly perform the mass balances, P, K, Mg and Ca release due to organic matter hydrolysis should be considered. This makes it necessary to determine the P, K, Mg and Ca content in the primary sludge and in the excess sludge.

The amount of P, K and Mg in the organic fraction of the primary sludge was estimated from experimental analysis (line 2, Table 1) assuming that suspended P, K, and Mg were mainly associated to organic matter. This assumption can be made because the presence of P, K and Mg precipitates in the influent wastewater is negligible and no precipitation of P, K and Mg is expected in the primary settler. Nevertheless, an accurate determination of the calcium content in the organic matter of primary sludge was not possible due to the

high calcium carbonate concentration in the influent wastewater which is accumulated in the primary sludge. The obtained values for primary sludge (Table 2) were used to perform the mass balances in the gravity thickening units.

For the secondary sludge it is not easy to distinguish between the organic P, Mg, and K content and the P, Mg, and K content associated with Poly-P structure. Hence, reported values for biomass composition were assumed. These values (Table 2) were used to carry out the mass balances in the DAF thickening stage.

Once the organic P, K, Mg, and Ca content in the primary and secondary sludge was determined, the organic content of these elements in the mixed influent sludge (line 8) was calculated taking into account the proportion of primary and secondary sludge fed to the digester (i.e. 51–49%, respectively).

3.3. Mass balance across Murcia WWTP sludge line

Mass balances for phosphate and soluble potassium, magnesium and calcium were performed under steady state conditions in different operation units, such as gravity thickeners, secondary sludge DAF thickeners, anaerobic digesters and secondary digester.

3.3.1. Gravity thickening

As Table 1 shows, the soluble phosphorus, calcium, magnesium and potassium concentrations increased during the thickening process. No PAO presence was expected in gravity thickeners, so the organic release due to the degradation of solids in the gravity thickener accounted for the increase in phosphate, magnesium and potassium concentrations. This organic matter degradation led to a release of 82.6 kgP/d, 21.4 kgMg/d, and 26.7 kgK/d. The phosphate and magnesium mass balances did not reveal a significant precipitation of these elements in the gravity thickener.

The rise in calcium concentration was the most significant, increasing from 177.5 mgCa/l in the primary sludge (line 2) to 1099.2 mgCa/l in the thickened sludge (line 4). The soluble calcium mass balance showed a release of 218.7 kgCa/d. This high release may be attributed not only to the organic release, as mentioned above, but also to a possible calcium carbonate dissolution forced by the pH decrease.

3.3.2. DAF thickening

With regard to the phosphorus dynamic in the DAF thickener, an important phosphate release took place in the thickened sludge. As can be seen in Table 1, the phosphate concentration increased significantly from 120.3 mgP/l in the excess sludge (line 5) to 1291.4 mgP/l in the floated sludge (line 7). The amount of phosphate released in the DAF thickener was 222.4 kgP/d of which 206.9 kgP/d was from Poly-P hydrolysis and only 15.5 kgP/d was from organic matter degradation.

This phosphate release can be attributed to the formation of anaerobic zones inside the thickener. Under anaerobic conditions and in the presence of volatile fatty acids (VFA), PAO release the internal Poly-P to the bulk solution. These VFA are produced by organic matter fermentation, which gives

Table 1
Average analytical measurements and flow rates

		Sampling points									
		1	2	3	4	5	6	7	8 ^a	9	10
TSS	mg/l	343	5165	224	59 500	9875	44	45 500	51 727	36 333	33 750
	s.d.	74	1708	34.1	5066	854	9	7047	5162	382	5852
VSS	mg/l	298	3200	204	41 650	7700	38	36 000	38 513	23 958	22 250
	s.d.	68	896	29.9	92	683	9	5354	2050	260	3948
Ammonium	mgNH ₄ -N/l	49.9	51.4	57.8	195.8	3.1	1.0	93.8	139.2	922	928.5
	s.d.	13.7	11.1	14.7	72.7	0.3	0.2	12.4	20.4	87.8	115.7
Total P	mgP/l	15.8	86.7	23.1	908.5	323.9	11.7	1553.1	1266.4	1152.2	1124
	s.d.	3.9	24.1	1.6	80.1	124.1	3.3	39.6	55.0	38.9	72.4
Phosphate	mgPO ₄ -P/l	7.3	9.6	13.4	176.4	120.3	7.2	1291.4	755.2	598.3	491.3
	s.d.	1.1	4.5	3.8	42.1	7.9	4.9	71.9	53.1	3.4	71.6
Alkalinity	mgCaCO ₃ /l	729	875.8	837.9	11 340	412	409	2370	6360	6464	4273
	s.d.	96	122.8	168.4	4879	62	31	298	2066	685	2971
pH		7.5	7.7	7.6	6.9	7.2	7.4	6.7	6.8	7.5	7.4
	s.d.	0.1	0.1	0.1	0.1	0.2	0.3	0.1	0.1	0.1	0.3
Soluble Ca	mg/l	165.9	177.5	158	1099.2	152.3	212.4	417.1	720.4	228.3	248.7
	s.d.	13.8	4.9	26.9	70.9	53.2	23.9	133.0	20.3	18	99.6
Total Ca	mg/l	201.6	440.9	225.2	3620.8	367.4	250.1	810.3	2060.4	1827.5	2047.2
	s.d.	68.1	94.4	66.8	834.9	141.1	45.9	30.8	293.6	217	356.1
Soluble Mg	mg/l	73.9	88.3	80.2	243.8	98.9	67.8	348.7	302.0	172.9	144.8
	s.d.	9.3	14.9	7.5	19.1	33.7	19.9	27.6	18.5	28.8	51.4
Total Mg	mg/l	86.6	108.3	89.4	313.2	165.1	88.7	406.9	365.2	331.2	335.3
	s.d.	7.1	43.1	6.3	61.2	26.3	10.3	32.3	41.8	13.4	103.3
Soluble K	mg/l	33.1	46.8	49.1	84.2	105.8	35.6	562.9	350.0	470.4	461.8
	s.d.	3.6	2.5	1.4	13.4	49.1	4.6	28.4	11.7	16.4	17.1
Total K	mg/l	38.3	52.6	48.8	140.0	184.5	42.2	793.3	502.7	481.1	444.1
	s.d.	3.1	4.4	4.7	9.5	16.6	3.4	29.6	18.1	25.3	9.2
Flow rate	m ³ /d	89 500	6110	5751	359	2204	1695	448	807	807	807
	s.d.	4139	1066	677	59	622	595	123	142	142	142

s.d., Standard deviation.

^a Obtained from mass balance between lines 4 and 7 (excepting pH value).

rise to a pH decrease as a consequence of the acid formation. This pH decrease was confirmed by the experimental pH values obtained during the analytical campaign. As can be seen in Table 1, the pH value decreased in the DAF thickener from 7.2 in the influent to 6.7 in the floated sludge.

The soluble calcium concentration also increased in the DAF thickener. As Table 1 shows, the calcium concentration increased from 152.3 mg/l in the DAF influent (line 5) to 417.1 mg/l in the thickened sludge (line 7). The soluble calcium mass balance showed a release of 214.3 kgCa/d. This release

was mainly caused by the calcium carbonate dissolution forced by the pH decrease during organic matter fermentation since the organic matter degradation in the DAF thickeners is much lower than in the gravity thickeners.

Nevertheless, despite the high concentration of phosphate, calcium and magnesium achieved in the DAF thickener and according to the results obtained in the mass balances, no precipitation was detected. The lack of precipitation probably stems from the sludge pH decrease in the DAF thickener, which decreased from 7.2 to 6.7 (Table 1).

Table 2
Organic P, K, Mg and Ca in primary and secondary sludge

	Primary sludge ^a	Biomass ^b
P (mgP/mgTVS)	0.024	0.020
K (mgK/mgTVS)	0.002	0.008
Mg (mgMg/mgTVS)	0.006	0.004
Ca (mgCa/mgTVS)	—	0.004

^a Experimental data.

^b Metcalf and Eddy (2003).

3.3.3. Digestion

The average organic loading rate (OLR) during the experimental period was 1.9 gTVS/l/d. The average value for TVS removal was 38%, which was slightly lower than the typical values observed in the literature (Zhao and Viraraghavan, 2004). pH and alkalinity in the digester (Table 1) showed normal values for a well-stabilized digester.

Table 3 shows the results of the mass balances carried out in the anaerobic digester. The results obtained show a lower

Table 3
Results of the anaerobic digester mass balances

K_{TOTrel}	97.1 kgK/d
K_{ORGrel}	57.8 kgK/d
K_{PAOrel}	39.3 kgK/d
P_{PAOrel}	111.1 kgP/d
P_{ORGrel}	258.9 kgP/d
P_{fix}	496.5 kgP/d
$\%P_{fix}$	50.7 %
Mg_{PAOrel}	39.3 kgMg/d
Mg_{ORGrel}	59.0 kgMg/d
Mg_{prec}	202.5 kgMg/d
$\%Mg_{prec}$	59.2 %
Ca_{ORGrel}	22.9 kgCa/d
Ca_{prec}	419.8 kgCa/d
$\%Ca_{prec}$	69.5 %
$\%P-MAP$	52.0 %
$\%P-HAP$	39.2 %
$\%P_{ads}$	8.8 %

release of phosphorus due to Poly-P hydrolysis (P_{libPAO}) than due to organic solid degradation (P_{libORG}). This result confirmed that Poly-P degradation had begun in a previous stage of the sludge line. Considering that all the remaining Poly-P was released during the digestion process, the amount of Poly-P released in the digester (111.1 kgP/d) was lower than the amount of Poly-P released during the excess sludge thickening (206.9 kgP/d).

The mass phosphate balance shows significant phosphate precipitation. The results indicate that 50.7% of the available phosphate in the digester was fixed. Moreover, magnesium and calcium precipitation was detected. These results suggested that the conditions reached in the digestion process enhanced the precipitation. The high concentration of ammonium (922.0 mgNH₄-N/l in the digested sludge versus 139.2 mgNH₄-N/l before the digestion) and the increase in the pH value (from 6.8 to 7.5) during the anaerobic digestion process gave rise to the formation of struvite in that stage of the sludge treatment line.

Finally, the results obtained in the secondary digester (using the experimental values showed in Table 1) confirmed that there was no more release of potassium from Poly-P. The magnesium and phosphate mass balances suggested a slight precipitation in the secondary digester.

3.4. Distribution of precipitates in the digester

Struvite (MgNH₄PO₄·6H₂O) and newberyte (MgHPO₄·3H₂O) can easily precipitate in the anaerobic digester conditions. Moreover, as mentioned above, struvite deposits are quite common and are actually found at just about every municipal WWTP where anaerobic digestion is carried out (Neethling and Benisch, 2004). Therefore, magnesium was considered to precipitate in the digester mainly as struvite, which made it possible to estimate the amount of phosphate precipitated as struvite (%P-MAP) from its stoichiometry.

Calcite precipitation was not considered due to the high phosphate concentrations in the digester. Several authors have reported that the presence of phosphates inhibits calcite growth due to the adsorption of phosphates on the calcite surface, which enables the formation of calcium phosphates (Plant and House, 2002; Lin and Singer, 2005). Therefore, the calcium precipitated in the digester was considered to be in the form of calcium phosphates.

Calcium phosphate precipitation is a very complex subject that involves several parameters. In particular, it depends on calcium and phosphate ions' concentrations, as well as on supersaturation, ionic strength, temperature, ion types, pH and also on time (solid–solid transformation) as noted in the literature (Boskey and Posner, 1973; Baronne and Nancollas, 1977; Van Kemenade and de Bruyn, 1987). The calcium phosphate precipitation follows the Ostwald rule, which states that the least thermodynamically stable phase is the first one formed, which works as a precursor of the most stable phase which, in this case, is hydroxyapatite (HAP). The most common precursors for the HAP formation are brushite (DCPD, CaHPO₄·2H₂O), octacalcium phosphate (OCP, Ca₄H(PO₄)₃·2.5H₂O), and amorphous calcium phosphate (ACP, Ca₃(PO₄)₂·xH₂O) (Montastruc et al., 2003). Barat (2004) observed the formation of ACP as a precursor for HAP in an activated sludge process. Hence, in this work, hydroxyapatite (HAP) was considered as the calcium phosphate that was formed due to the high process retention time, which allows precursors to transform into HAP. Then, assuming that calcium precipitates with phosphate as HAP, the amount of phosphate precipitated with calcium (%P-HAP) can be calculated using a molar ratio Ca/P of 1.67. The rest of the phosphorus fixed in the digester was considered to be adsorbed on the surface of solids (P_{ads}). Although phosphate adsorption during anaerobic digester is still not a well-understood process, it is considered as a possible mechanism for phosphorus fixation (Jardin and Pöpel, 1994; Wild et al., 1997).

The precipitation of aluminium and iron phosphates was not considered in this work due to the negligible soluble iron and aluminium concentrations in the digester influent and effluent streams.

The results obtained show that 52.0% of the phosphate precipitates as struvite, 39.2% as hydroxyapatite, and the remaining 8.8% is adsorbed on the surface of solids. The magnesium mass balance in the secondary digester indicated a slight precipitation of phosphate as struvite.

In order to confirm the precipitates formed in the digester conditions, the Saturation Index values (SI) for the most

Table 4
SI values in the anaerobic digester

Mineral	pKps	Reference	SI
Struvite	13.26	Ohlinger et al. (1998)	2.325
Newberyte	5.8	Taylor et al. (1963)	−11.35
Hydroxyapatite (HAP)	48.6	Murray and May (1996)	17.836
Amorphous calcium phosphate (ACP)	24	Mamais et al. (1994)	2.199
Calcite	8.3	Mamais et al. (1994)	1.8

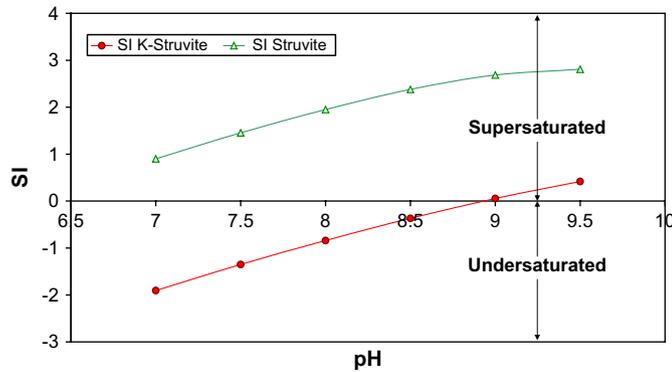


Fig. 3. K-struvite and struvite SI in the influent line to anaerobic digestion at different pH.

common precipitates were calculated. The SI is used to describe the saturation state of the aqueous phase composition versus different solids (Eq. (9)). When $SI = 0$, the solution is in equilibrium; when $SI < 0$, the solution is undersaturated and no precipitation occurs; when $SI > 0$, the solution is supersaturated and precipitation occurs spontaneously. Therefore, the SI values can be used to evaluate the effect of the solution conditions on the tendency and extent of the precipitation, according to the following equation:

$$SI = \log \frac{IAP}{K_{SP}} \quad (9)$$

where IAP represents the ion activity product, and K_{SP} represents the thermodynamic solubility product.

As Table 4 shows, the digester sludge composition is supersaturated with regard to MAP, HAP and its precursor ACP, which confirms the possible formation of these precipitates in the digester. With regard to calcite formation, the results obtained in the geochemical study show that the solution is supersaturated for calcite. Nevertheless, as explained above, calcite formation was considered to be inhibited due to the high phosphate concentrations in the digester (Plant and House, 2002; Lin and Singer, 2005). The SI for newberyite confirmed that this precipitate was not formed in the anaerobic digester.

3.5. K-struvite precipitation

The potential precipitation of K-struvite was evaluated through thermodynamic calculations according to the composition of the influent to the anaerobic digestion. The SI value was evaluated in this line because that is the point where the concentration of phosphate, magnesium and potassium achieved the highest values with low ammonium concentration. Therefore, this point shows the best conditions for K-struvite formation. The value of K_{SP} used was 2.4×10^{-11} for K-struvite (Taylor et al., 1963). Fig. 3 shows the SI for K-struvite and for struvite in the influent line to anaerobic digestion at different pH (from 7 to 9.5). As can be seen, the influent sludge composition was undersaturated with regard to K-struvite; therefore, its precipitation was not expected until very high pH values. The SI values for struvite formation at this point show that the influent sludge composition was supersaturated for struvite formation in the entire pH range studied. Finally, the presence of struvite in the solid deposits found

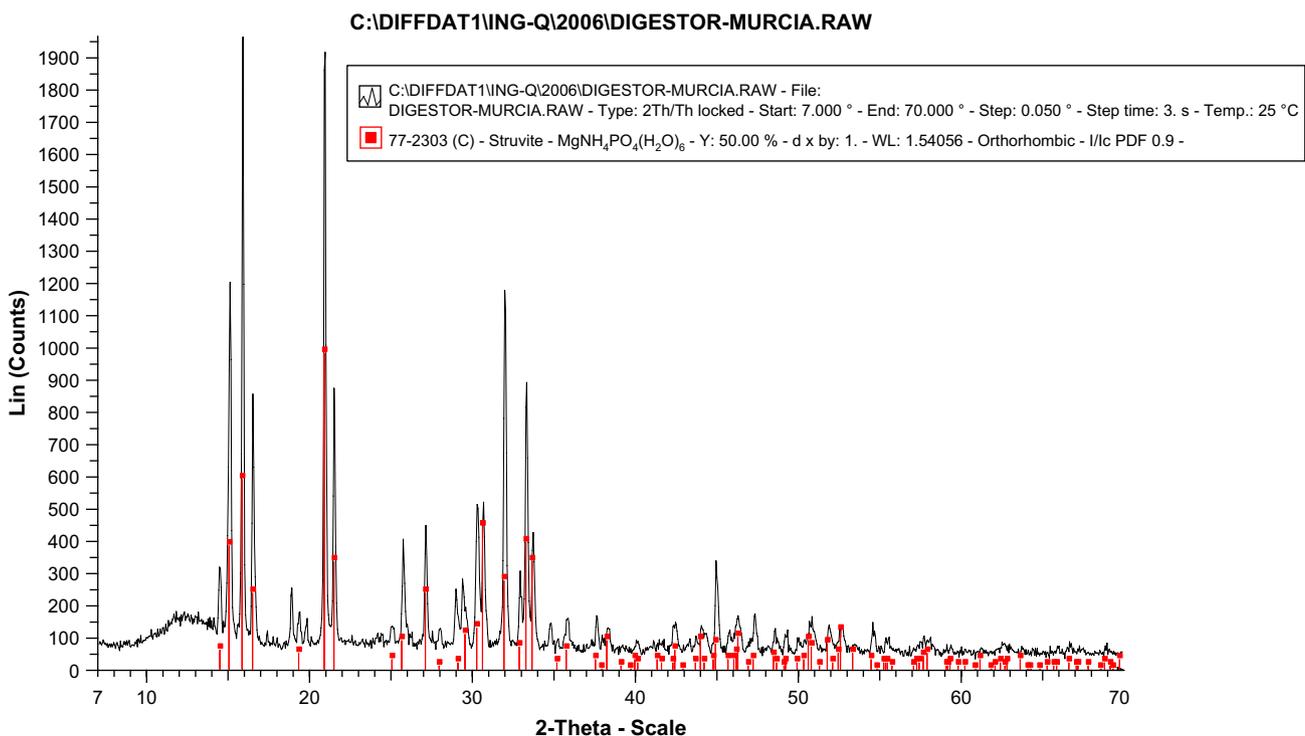


Fig. 4. XRD analysis of the precipitates found in Murcia WWTP.

in the Murcia WWTP (Fig. 2) was confirmed by means of XRD analysis (Fig. 4).

4. Conclusions

Analytical determinations of soluble P, K, Mg and Ca and mass balances were used to easily identify precipitation problems throughout the sludge treatment line of the Murcia Este WWTP.

The influent wastewater characterization showed the hardness of water and its potential to spontaneously precipitate different solids during waste sludge treatment.

The mass balances carried out in the DAF thickener and anaerobic digester showed that most of the polyphosphate was released during the excess sludge thickening, which was probably due to the formation of anaerobic zones inside the thickener. However, despite the high concentrations achieved in the thickened sludge, precipitation did not occur at this point due to the pH decrease.

Precipitation problems were mainly found in the digestion stage. The results show that 50.7% of the available phosphate was fixed in the digester of which 52.0% precipitates as ammonium struvite, 39.2% precipitates as hydroxyapatite, and the remaining 8.8% was adsorbed on the surface of the solids. The increase in soluble P, K, Mg, $\text{NH}_4\text{-N}$ and Ca availability in the digester as well as the increase in pH were pointed out as the main causes of precipitation problems.

Thermodynamic calculations confirmed the precipitation of MAP, HAP and ACP and also confirmed that K-struvite did not precipitate under the conditions achieved during the sludge treatment.

This study confirms the importance of precipitation problems in the sludge management of a wastewater treatment plant with EBPR. Other studies in different WWTP also indicate that this problem is especially important on the Mediterranean Coast due to significant saline intrusion in the sewage network, which increases the magnesium content in the influent wastewater.

The results obtained in this study will be used in future works to minimize phosphorus precipitation, in order to reduce maintenance problems at the Murcia Este WWTP.

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