



Phosphate Elimination with Iron Salts

1. Phosphorus in wastewater and bodies of water

Phosphorus is an essential substance in foods and consumer goods, and corresponding quantities of it are left behind in wastewater.

Concentrations of 5 to 20 mg/l typically are detected at the inflow of raw sewage to municipal water treatment plants. Phosphorus as a fertilizer and nutrient in the farming industry promotes growth and thus production of biomass. In an aquatic environment, an oversupply

of phosphorus is expressed in the proliferation of floating and sessile algae. This phenomenon is referred to as eutrophication (from the Greek “eutroph,” meaning “well nourished”).

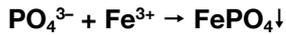
The decay of algal blooms strongly depletes the natural oxygen content in a body of water, to the detriment of various living organisms. This eutrophication often results in an increased incidence of fish kill. For this reason, steps have been taken to improve conditions in bodies of water and targeted phosphate elimination has been introduced in wastewater treatment plants.



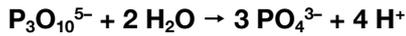
Fig. 1: Large water treatment plant in Köln-Stammheim

2. Chemical principles

Only orthophosphate can be chemically precipitated by trivalent metals.



The phosphates contained in wastewater consist of both structurally different phosphates (orthophosphates, metaphosphates, polyphosphates) and organically bound phosphates. Under the conditions prevailing on the way into and through a waste water treatment plant, the various phosphates (total phosphate) are converted almost entirely into precipitable orthophosphate, for instance by means of decomposition mechanisms. This reaction can be described by the example of polyphosphate hydrolysis:



This reaction equation for phosphate precipitation is greatly simplified. In practice, the phosphate ions are not present in the form of PO_4^{3-} , rather, it is a case of pH-dependent equilibria in accordance with Figure 2.

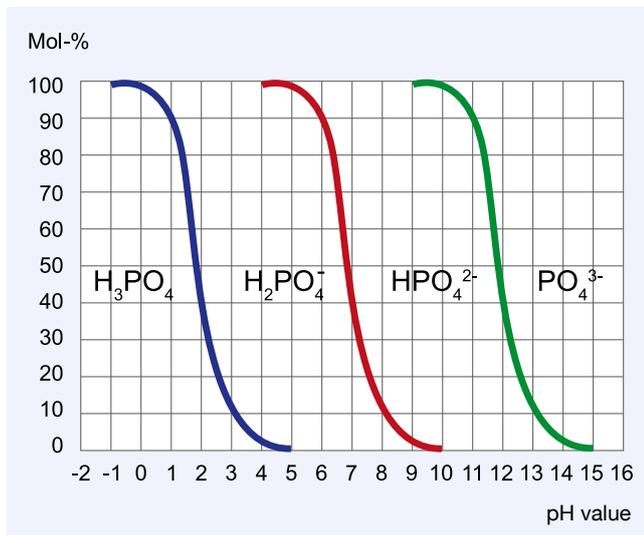


Fig. 2: Phosphate ion concentration as a function of pH value

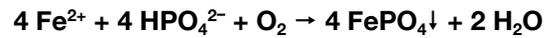
The figure shows that the phosphate ions in domestic sewage (pH 6-8) occur only in the form of hydrogen phosphates or dihydrogen phosphates and that PO_4^{3-} ions only exist at a pH value above 9.5.

The following precipitation reactions result from using iron (III) salts:

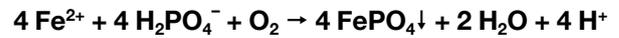


The use of bivalent iron salts results in simultaneous oxidation in the aeration tank. These products therefore are reserved for simultaneous precipitation:

pH > 7:



pH < 7:



This oxidation takes place in contact with the activated sludge and requires no measurable oxygen. The rate of oxidation at pH 7 amounts to a few minutes, where many of the substances contained in the wastewater catalyse the reaction.

3. Methods for eliminating phosphorus from wastewater

3.1 Phosphate separation in the primary sedimentation tanks

In wastewater treatment plants with mechanical/biological wastewater treatment, some of the phosphorus is removed in particulate form together with other solids in the primary sedimentation tanks. Separation efficiency at this stage is in the region of 10 to 20% of the influent load. Precipitants are only rarely used for pre-precipitation in the primary stream, because if nutrients are precipitated, they frequently are lacking in the downstream treatment process.

One variation of pre-precipitation is the treatment of high-load partial wastewater streams. This process is particularly suitable for wastewater from the food industry (e.g. dairies, slaughterhouses). Instead of the conventional sedimentation tanks, compact flotation tanks are used in these cases.

Pre-precipitation has become more significant in recent years, because the energy-rich primary sludge contributes to a considerably higher production of digester gas.

Furthermore, by unburdening the biodegradation stage, less energy is required to supply the aerobic biomass with oxygen.

3.2 Phosphate elimination in the aeration tank

3.2.1 Biological phosphorus elimination

Biological phosphate elimination is based on the capacity of some bacteria strains to take up phosphorus beyond the extent required for cell growth and to store it in the form of a polyphosphate. The bacteria take up increased phosphorus when exposed to rapidly alternating anaerobic and aerobic conditions. The phosphorus is discharged from the system via the excess sludge.

In targeted biological phosphate elimination, several processing problems have emerged, above all in downstream sludge treatment, including: A deterioration in sludge dewatering behaviour, a high P content in the returned (sludge) filtrate, and deposits in the region of sludge dewatering.

Increased biological phosphate elimination is not always sufficient for reliably meeting specified limit values in the effluent. Therefore, targeted biological phosphate elimination generally is combined with a dosing of precipitant that ensures compliance with these limit values.

3.2.2 Simultaneous precipitation

Simultaneous precipitation, i.e. chemical phosphate precipitation with simultaneous biodegradation, is the most commonly used process for chemical phosphate elimination. All turbulent zones in the biological stage are suitable metering points: Inlet to the aeration tank, outlet from the aeration tank, the aeration tank itself and the return sludge line.

Iron ions not involved in the precipitation reaction at the dosing point end up as iron hydroxide in the activated sludge circuit, where they repeatedly have the opportunity to participate in binding the phosphate. This is one of the major advantages of simultaneous precipitation and also explains the frequent use of this method.

It is also possible here to use bivalent iron salts, which means greater flexibility in product selection.

Simultaneous precipitation can also be used in aerated and non-aerated wastewater ponds, where the latter require a trivalent product.

3.3 Post-precipitation as flocculation filtration

To achieve very low effluent concentrations of e.g. $< 0.2 \text{ mg/l } P_{\text{tot}}$, not only do the dissolved phosphate compounds have to be eliminated, particulate wastewater constituents also have to be optimally retained. In this context, the wastewater is conducted through a filter layer, which removes any solids remaining in the wastewater after treatment.

The precipitant is added at the inlet to the flocculation filter. The phosphorus concentration at the inlet to the filter should not exceed 1 mg/l in order to extend the filter service life.

Because the filter should only be max. 4 g Fe/m^3 , it is recommended that this method always be combined with an upstream simultaneous precipitation stage.

3.4 Two-point/Multi-point precipitations

In two-/multi-point precipitation, different precipitation methods are combined, most frequently pre-precipitation and simultaneous precipitation; simultaneous precipitation and post-precipitation; or two-point simultaneous precipitation.

Two-point precipitation results in the following advantages among others:

1. Early alleviation of conditions in downstream treatment stages, e.g. flocculation filtration
2. Cost-efficient use of chemicals thanks to a higher degree of efficiency compared with dosing at a single point.

In two-point simultaneous precipitation, adding iron at the inlet to the aeration tank achieves 90% phosphate elimination with β -values of $1.0 - 1.2$.

If iron salt is then added at the outlet from the aeration tank, only a low residual concentration with relatively high β -values > 2.0 needs to be eliminated.

In contrast, with only one metering point (aeration tank), the entire phosphate concentration with β -values > 2.0 would have to be precipitated.

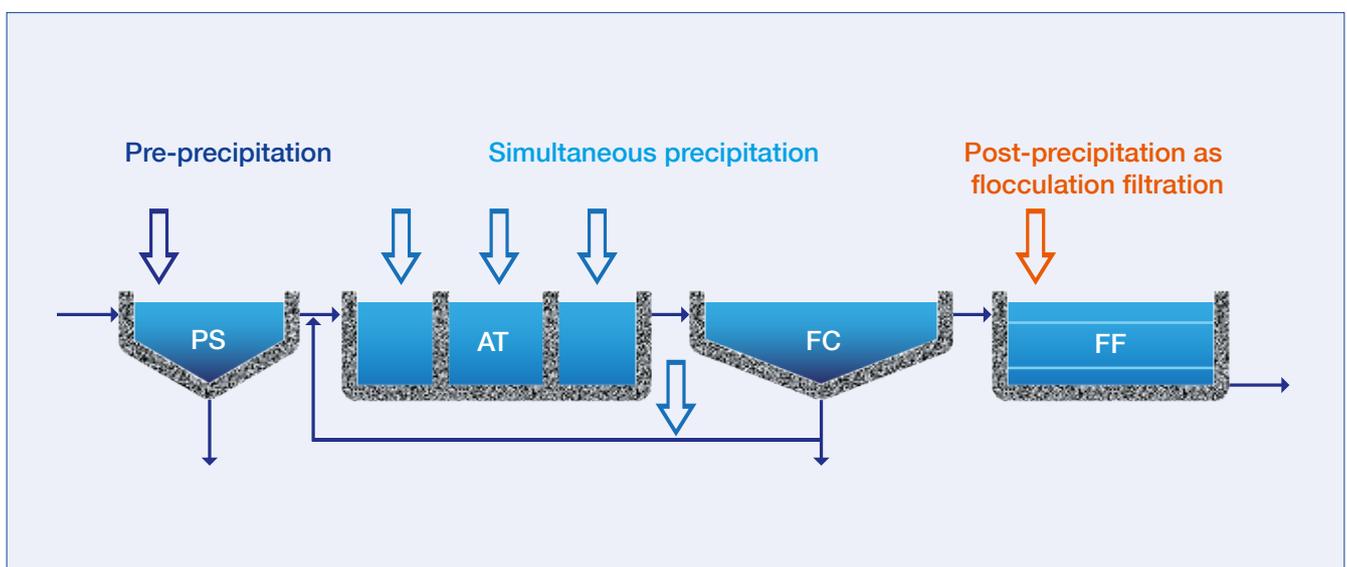


Fig. 3: Diagram of various metering options

Tab. 1: KRONOS iron salts for phosphate elimination

Product	Active substance	Specification
QUICKFLOC* Ferrous sulfate	17.8 % Fe ²⁺ \triangleq 3.19 mol/kg	Technical Information TI 1.01
FERROFLOC Ferrous chloride solution	8.6 % Fe ²⁺ \triangleq 1.54 mol/kg 0.6 % Al ³⁺ \triangleq 0.22 mol/kg	Technical Information TI 1.04
KRONOFLOC Ferrous chloride solution	8.7 % Fe ²⁺ \triangleq 1.56 mol/kg	Technical Information TI 1.05
FERRIFLOC Ferric chloride sulfate solution	12.3 % Fe ³⁺ \triangleq 2.20 mol/kg	Technical Information TI 1.06

* Moist salt

4. KRONOS iron salts

The user has a choice of four classical KRONOS ecochem phosphate precipitants based on iron salts (Tab.1):

QUICKFLOC, FERROFLOC, KRONOFLOC and FERRIFLOC.

The key elements of a chemical phosphate precipitation system are the storage, dissolving and metering equipment for the precipitant. Different storage, dissolving and metering equipment is used, depending on the requirements of the respective form in which the precipitant is supplied (see Technical Information TI 2.01 and TI 2.03 from KRONOS ecochem). Diaphragm pumps usually are used to meter the precipitant solution and transport it to the metering point.

5. Quantity added

The precipitant demand is primarily governed by the phosphate content of the wastewater and the quantity of phosphate eliminated biologically.

β -values of roughly 1.2 to 1.5 are necessary to achieve phosphate contents of less than 1 mg P_{tot}/l in the effluent. β -values between 1.1 and 1.3 are generally sufficient for values below 2 mg P_{tot}/l.

Because of surges, such as flush surges, many wastewater treatment plants strive for effluent values of up to 50% of the control value. To achieve this operating mean, significantly higher β -values must be applied when estimating the precipitant demand.

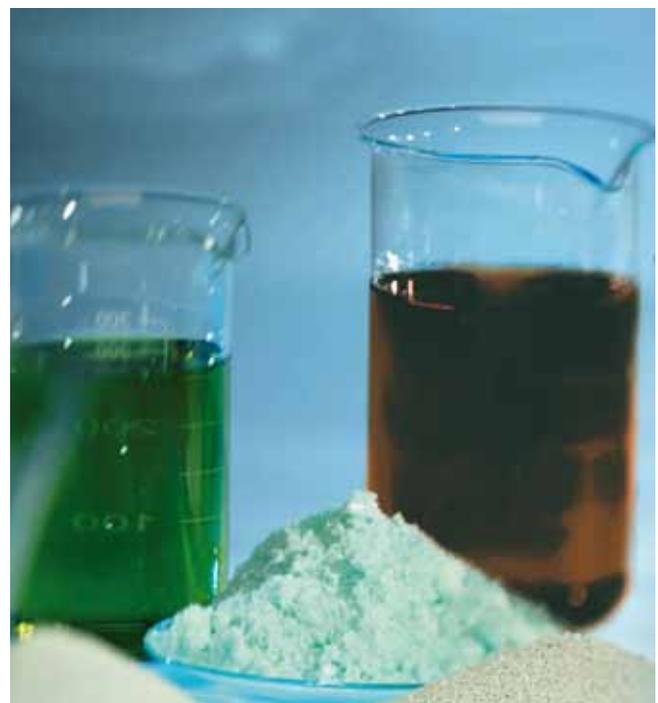


Fig. 4: KRONOS ecochem iron salts

Table 2: β -values for effluent values

Effluent value mg PO ₄ -P/l	β -value
1.5	1,2
1.0	1.5
0.5	2- 2.5
0.2 (flocculation filtration)	> 2.5

Example for calculating the necessary quantity of Fe to be added

The following parameters apply for an example wastewater treatment plant with nitrification and denitrification:

Inlet to biological stage	10 g P/m ³ 280 g DBO ₅ /m ³
Control value	2.0 g P/m ³
Effluent value	1.0 g P/m ³

Calculation of the phosphate concentration to be precipitated for the example wastewater treatment plant

Inlet aeration tank	10.0 g PO ₄ -P/m ³
Effluent value	-1.0 g PO ₄ -P/m ³
P bound by Nitri/DeNi (A202): 1.5 % of 280 g BOD ₅ /m ³	-4.2 g PO ₄ -P/m ³
PO ₄ -P concentration to be precipitated	= 4.8 g PO₄-P/m³

Molar masses:	1 mol Fe \triangleq 55.85 g 1 mol P \triangleq 30.97 g
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β -value (Tab. 2)	1.5
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Precipitating 1 mol P requires 1.5 mol Fe, resulting in

$$m_{\text{Fe}} = \frac{M_{\text{Fe}}}{M_{\text{p}}} \cdot \beta\text{-value} \cdot m_{\text{p}} = \frac{55.85}{30.97} \cdot 1.5 \cdot 4.8 \text{ g P/m}^3$$

Necessary quantity to be added for **1 m³ wastewater with 4.8 g P/m³ = 13.0 g Fe/m³**

Referred to the form supplied, the quantities required are as follows:

73.0 g	QUICKFLOC Ferrous sulfate/m³ \triangleq 183 ml saturated QUICKFLOC solution/m ³ (400 g/l)
99.4 ml	FERROFLOC Ferrous chloride solution/m³
109.5 ml	KRONOFLOC Ferrous chloride solution/m³
69.5 ml	FERRIFLOC Ferric chloride sulfate solution/m³

6. Acid capacity

Acid capacity in mmol/l is defined as the quantity of 0.1 mol/l HCl required to achieve a pH value of 4.3 during titration in water. Wastewater has an acid capacity in the region of 4 to 8 mmol/l. It is partially consumed during elimination of the nitrogen and phosphorus compounds, where consumption is 5 to 10 times higher during nitrogen elimination.

An excessively low residual acid capacity in the effluent of a wastewater treatment plant can have the following negative effects, among others: Disruption of nitrogen elimination, redissolved phosphate, concrete corrosion and floc breakup. Detailed information on the effect of acid capacity is provided in Technical Information 3.05 from KRONOS ecochem.

7. Metering control

A simple day/night circuit for the metering pumps is an effective first step in adapting to changing influent P loads. Another step towards adapting added quantities to phosphate load is to control metering on the basis of 24-hour profiles.

In addition, the online P measurement and control equipment available today permits optimum adaptation of the metering equipment to the effective demand.

The question of which control strategy should be used depends primarily on the size of the system, the existing measurement equipment and the targeted or required control values.



Fig. 5: Storage and metering station for liquid iron salts



Fig. 6: Metering unit

8. Determining phosphate content

Operators of wastewater treatment plants can use practical, compact photometers to determine the phosphate concentration in wastewater. As a rule, the methods and instruments are designed to directly display mg P_{tot}/l. If this is not the case, the following points must be kept in mind:

1. The total phosphate content (P_{tot}) can only be determined by prior acid-oxidative digestion. "Boiling" is particularly indispensable for measuring influent phosphate.
2. Only orthophosphate (P_{ortho}) is detected in direct analysis of effluent samples.
3. Although reference constantly is made to phosphate precipitation and phosphate content, the unit used is the phosphorus content per litre. Phosphate is converted into phosphorus using a factor of 0.326:

$$3 \text{ mg PO}_4/\text{l} \approx 1 \text{ mg de P/l.}$$

9. Secondary benefits

Activated sludge with accumulated iron compounds displays improved thickening properties compared to sludges from other phosphate elimination processes.

This results in a number of positive effects from the use of iron salts:

- Improved purification efficiency
- Improved effluent COD values
- Improved sludge structure
- Improved sludge liquor separation
- Improved sludge dewatering properties
- Increased digester gas yield
- Digester gas free of hydrogen sulfide
- Less redissolved phosphate than with biological phosphate elimination
- Lower risk of MAP crystallisation in sludge treatment.

10. Sludge production

Sludge is a by-product of wastewater treatment. This also applies to phosphate elimination, regardless of the method used. The following example of chemical phosphate elimination with iron salts demonstrates how the amount of excess sludge is calculated:

Sludge from precipitation	
Specific sludge production (iron)	2.5 g DM/g Fe
Precipitant demand (see Section 5)	13 g Fe/m ³
Precipitated sludge	32.5 g DM/m ³
Sludge from wastewater	
Per resident and day	50 g DM
Wastewater volume per resident and day	120 l
Sludge production	416.7 g DM/m ³
Sludge production from precipitation	Approx. 8%

The increase in DM (dry matter) amounts to about 5 to 10% and should be taken into account particularly when the sludge is incinerated.

The added cost of increased sludge production is offset by the savings that result from the improved thickening and dewatering properties.



Fig. 7: Aeration tank

Source: Stadtentwässerung Dresden GmbH

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KRONOS INTERNATIONAL, Inc.

KRONOS ecochem

Peschstr. 5 · D-51373 Leverkusen

Telephone +49 214 356-0 · Fax +49 214 44117

E-mail kronos.ecochem@kronosww.com

www.kronosecochem.com

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