GERMAN
ATV-DVWK RULES AND STANDARDS

STANDARD
ATV-DVWK-A 202E
Chemical-Physical Methods for the Removal of Phosphorus from Wastewater

April 2004

Sponsored by the
German Federal Environmental Foundation
DBU
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The German Association for Water, Wastewater and Waste, DWA (former ATV-DVWK), is the spokesman in Germany for all universal questions on water and is involved intensely with the development of reliable and sustainable water management. As politically and economically independent organisation it operates specifically in the areas of water management, wastewater, waste and soil protection.

In Europe the DWA is the association in this field with the greatest number of members and, due to its specialist competence it holds a special position with regard to standardisation, professional training and information of the public. The ca. 14,000 members represent the experts and executive personnel from municipalities, universities, engineer offices, authorities and businesses.

The emphasis of its activities is on the elaboration and updating of a common set of technical rules and standards and with collaboration with the creation of technical standard specifications at the national and international levels. To this belong not only the technical-scientific subjects but also economical and legal demands of environmental protection and protection of bodies of waters.

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Foreword

The first edition of Standard A 202 "Methods for the Removal of Phosphorus from Wastewater" [Not available in English], which was elaborated by the then ATV Specialist Committee 2.8 "Advanced Treatment of Wastewater following Biological Treatment", was published in 1992. Through wide application, in particular of the chemical precipitation/flocculation, further knowledge was elaborated and experiences gathered which made it appear to be sensible to revise Standard ATV-A 202. The revised edition is now presented here.

As a result of the legally laid down limitation of phosphates in detergents in the middle of the seventies and the extensive introduction of P-removal in municipal wastewater treatment plants since the end of the eighties of the last century, the loading of surface waters from municipal sources has reduced by some 80 %. Today's contribution by wastewater treatment plants is ca. 30 % and can be most easily further reduced as point source. Today's loading of surface waters originates primarily from diffuse sources and from combined wastewater overflow facilities.

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This Standard was elaborated by the ATV-DVWK Specialist Committee KA-8 "Methods of Advanced Treatment following Biological Treatment".

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User Notes

This Standard is the result of honorary, technical-scientific/economic collaboration which has been achieved in accordance with the principles applicable therefore (statutes, rules of procedure of the ATV-DVWK and the Standard ATV-DVWK-A 400). For this, according to precedents, there exists an actual presumption that it is textually and technically correct and also generally recognised.

The application of this Standard is open to everyone. However, an obligation for application can arise from legal or administrative regulations, a contract or other legal reason.

This Standard is an important, however, not the sole source of information for correct solutions. With its application no one avoids responsibility for his own action or for the correct application in specific cases; this applies in particular for the correct handling of the margins described in the Standard.

1 Area of application

This Standard is concerned with the removal of phosphorus from municipal wastewater through the employment of precipitation/flocculation. For the biological removal of phosphate attention is drawn to the Standard ATV-DVWK-A 131E. The combination of biological P-removal using simultaneous precipitation is dealt with in detail in Section 4.2.2.

In surface waters phosphorus is usually the limiting factor for the growth of algae (primary production) or can made this most easily using technical measures.

2 Definitions and Symbols

The unified system of Standard ATV-DVWK-A 198E is adopted for all symbols. Accordingly the respective main term e.g.:

- *Q* for volume flow,
- *C* for concentration (homogenised sample),
- *S* for concentration (filtered sample, 0.45 µm membrane filter),
- *X* for concentration (filter residue) and
- *B* for loads

Is followed by an index or indices separated by commas.

Symbol		Unit	Designation
English	German		
β_{Prec}	[$\beta_{\text{Fäll}}$]	mol Me/mol $X_{P,Prec}$	Relative quantity of precipitant (Beta value)
ρ_{PS}	[ρ_{FML}]	kg/m^3 solution	Density of the precipitant solution
AM_{Al}		g/mol	Relative atomic mass of aluminium
AM_{Fe}		g/mol	Relative atomic mass of iron (Fe)
AM_P		g/mol	Relative atomic mass of phosphorus
AM_x		g/mol	Relative atomic mass of a parameters *x*
$B_{d,BOD}$	[$B_{d,BSB}$]	g/(I · d)	Inhabitant-specific daily BOD_5 load
$B_{d,PQ}$	[$B_{d,FM}$]	g/d	Mean dosed absolute precipitant quantity per day in delivered form
$B_{d,P}$		g/(I · d)	Inhabitant-specific daily phosphorus load in the homogenised sample as P
$B_{h,PQ}$	[$B_{h,FM}$]	g/h	Mean dosed absolute precipitant quantity per hour in delivered form
C_{BOD}	[C_{BSB}]	mg/l	Concentration of BOD_5 in the homogenised sample
C_{PS}	[C_{FML}]	kg/m^3	Precipitant concentration of a solution using a powder or granulate precipitant (kg precipitant/m^3 solution)
C_P		mg/l	Concentration of phosphorus in the homogenised sample as P
$C_{P,aM}$		mg/l	Concentration of phosphorus in the homogenised sample as P as annual mean
DR	[*TR*]	kg/m^3	Dried solids content (evaporation residue)
DS	[*TS*]	kg/m^3	Dry solids
$K_{A4.3}$	$K_{S4,3}$	mmol/l	Acid capacity up to pH 4.3
$PE_{XXX;ZZ}$	[$EGW_{XXX;ZZ}$]	I [E]	Population equivalents, e.g. for the characterisation of industrial wastewater, always with reference parameter and associated inhabitant-specific load, e.g. $PE_{COD,120}$, i. e. depending on the parameter, various PE can result for one operation
PT	[*EW*]	I [E]	Total number of inhabitants and population equivalents (*PT* = *P* + *PE*), depending on parameter possibly different *PT*
P	[*EZ*]	I [E]	Number of inhabitants
f_p		-	Peak factor to cover peaks in the phosphorus content in the inflow by the precipitant quantity
PB		-, %	Phosphorus bonding in the activated sludge as share of the BOD added to the biological reactor ($C_{BOD,INB}$)
PB_{Ana}		-, %	Phosphorus bonding in the activated sludge as share of the BOD added to the biological reactor ($C_{BOD,INB}$) with existing anaerobic tank or selector
PB_{BM}		-, %	Phosphorus bonding in the activated sludge as share of the BOD added to the biological reactor ($C_{BOD,INB}$) with the degradation of carbon and, possibly, with nitrification
PB_{Deni}		-, %	Phosphorus bonding in the activated sludge as share of the BOD added to the biological reactor ($C_{BOD,INB}$) with denitrification
$Q_{d,PQ}$	[$Q_{d,FM}$]	l/d	Volume flow of the precipitant to be dosed per day
Q_{PQ}	[Q_{FM}]	l/s	Volume flow of the precipitant to be dosed
$Q_{h,PQ}$	[$Q_{h,FM}$]	l/h	Volume flow of the precipitant to be dosed per hour
$Q_{DW,d}$	[$Q_{T,d}$]	m^3/d	Daily dry weather flow
$WS_{d,BioP}$	[$\ddot{U}S_{d,BioP}$]	kg/d, g/d	Daily sludge production from the biological phosphorus removal (BioP-waste active sludge) in kg or. g DS per day
$WS_{d,Chem}$	[$\ddot{U}S_{d,Chem}$]	kg/d, g/d	Daily sludge production from the chemical phosphorus removal (chemical waste sludge) in kg or g DS per day
$WS_{d,P}$	[$\ddot{U}S_{d,P}$]	kg/d, g/d	Daily sludge production from the phosphorus removal (BioP-waste active sludge + chemical waste active sludge) in kg or g DR per day
$w_{ww,d}$	[$w_{S,d}$]	I/(I · d)	Inhabitant-specific daily wastewater yield
AS_{Al}	[WS_{Al}]	kg Al/kg precipitant	Aluminium active substance of the precipitant as delivered

Symbol		Unit	Designation
English	German		
AS_{Fe}	[WS_{Fe}]	kg Fe/kg precipitant	Iron (Fe) active substance of the precipitant as delivered
AS_{Me}	[WS_{Me}]	kg Me/kg precipitant	Metal active substance of the precipitant as delivered
$X_{P,BioP}$		mg/l	Phosphorus biologically bonded with biological P-Removal
$X_{P,BM}$		mg/l	Phosphorus incorporated in the biomass
$X_{P,Prec}$	[$X_{P,Fäll}$]	mg/l	Phosphorus eliminated through precipitation
z		kg Me/kg precipitant	Interaction coefficient of the precipitant used
Indices for the site and purpose of the sampling (always as last index)			
EB	[AB]		Sample from the effluent of the aeration tank (biological stage), e.g. $S_{NO3,EB}$
EF	[AF]		Sample from the effluent of a filter e.g. $S_{NO3,EF}$
ESST	[AN]		Sample from the effluent of the secondary settling stage e.g. $C_{BOD,ESST}$, $X_{SS,ESST}$
EP	[AT]		Sample from the effluent of a pond, e.g. $S_{NO3,EP}$
ED	[DB]		Sample from the effluent of the denitrification tank, e.g. $S_{NO3,ED}$
EN	[NB]		Sample from the effluent of the nitrification stage, e.g. $S_{NO3,EN}$
RS			Sample from the return sludge
WS	[ÜS]		Sample from the waste (activated) sludge
In	[Z]		Sample from the inflow to the wastewater treatment plant, e.g. $C_{BOD,IN}$, $X_{SS,IN}$
InB	[ZB]		Sample from the inflow to the biological stage, e.g. $C_{COD,INB}$
Other symbols			
BM			Biomass
PQ	[FMM]*		Precipitant quantità [*Translator's note: In the German original it appears that FMM (Fällmittelmenge) is used only as a symbol. Fallmittelmenge as an index is FM. In English PQ is used to translate both symbol and index.]
SDM	[STM]		Sludge dry mass
MV	[ÜW]		Monitoring value

3 General Principles of Chemical-Physical Phosphate Removal

3.1 Phosphorus Compounds and Phosphorus Loads in Wastewater

Due to the limitation of phosphates in detergents the inhabitant-specific phosphorus yield of ca. 1.8 g/(I · d) has reduced. Depending on the wastewater produced and the infiltration water component, phosphorus concentrations from 5 mg/l to 20 mg/l result.

The greater part of the overall phosphorus, to be determined according to EN 1189, is available in inorganically dissolved form and consists essentially of orthophosphate and possibly condensed phosphates. On the other hand, there is a small part of the phosphorus available both organically dissolved and non-dissolved. To these also belong phosphonates, less degradable P-compounds which are employed in the textile industry and in the area of combined heat and power generation.

Condensed phosphates and organic phosphorus fractions are already extensively converted into orthophosphate in the sewer network and during wastewater treatment processes.

Only orthophosphate can be removed from the wastewater through precipitation using chemical-physical processes.

3.2 Description of the Procedures using Chemical-Physical Phosphate Removal

The chemical-physical phosphate removal consists of five consecutive processes:

- dosing and completely mixing of a precipitant into the wastewater flow,
- forming of particular bonding of the precipitant cations (Fe^{3+}, Al^{3+}, Ca^{2+}) and phosphate anions (PO_4^{3-}) as well as other anions (precipitation reaction),
- destabilisation of the colloides contained in the wastewater and combination into micro-flocs (coagulation),
- formation of flocs, i.e. formation of easily separable macro-flocs from the micro-flocs, With this suspended solids and colloids, including the organically bonded phosphorus in the flocs, can be incorporated (co-precipitation and co-flocculation),
- separation of the macro-flocs from the wastewater. Separation can be effected by sedimentation, flotation, filtration or combination of these processes.

The processes taking place with chemical-physical phosphate removal (precipitation) are essentially described under the second bullet point, while the physical sub-processes (flocculation and floc separation) are listed under the three subsequent bullet points.

3.3 Precipitants

Many types of polyvalent metal ions, following addition to the wastewater, form insoluble compounds with the phosphate ions dissolved therein. Fe^{3+}, Al^{3+}, Fe^{2+} und Ca^{2+} are employed for phosphate precipitation for economic reasons (see Table 1). Fe^{2+} can be used successfully only if it is oxidised to Fe^{3+} in water containing oxygen. In practice, for this, it is dosed into the aerated grit chamber or into the area of the aeration. Then the same results can be expected as for the application of Fe^{3+}. The oxygen necessary for the oxidation of iron is insignificant for the dimensioning of the aeration facilities for the aeration tanks.

As a result of using metal salts there is an exchange of anions in the water. PO_4^{3-} forms insoluble compounds with the metal ions and is removed; the anions of the precipitant (Cl^- or SO_4^{2-}) get into the water. The addition of Cl^-- or SO_4^{2-} anions can be tolerated.

Table 1 gives a summary of the precipitants usually used in the treatment of wastewater.

Requirements on the purity of precipitants

The precipitants are in part by-products or waste products of industrial processes. In these cases impurities such as, for example, heavy metals and organic halogen compounds can appear, which are conditioned by production or the natural properties of the initial raw materials.

It is to be assumed that the impurities are taken up in the precipitation sludge and appropriately increase the loads in the sewage sludge produced. With a view to phosphate recycling these impurities should as far as possible be avoided.

Table 1: Common precipitants

Product description	Chemical formula	Typical form of delivery and density or bulk weight in t/m^3	Storage and dosing	Effective cation for P-precipitation	Normal active substance content in g/kg and mol/kg delivery form	pH value of the (saturated) solution
Aluminium chloride	$AlCl_3$	Solution 1.3	Tank Acid-resistant pump	Al^{3+}	58 – 60 2.2	1
Aluminium-iron(III)-chloride	$AlCl_3 + FeCl_3$	Solution 1.15	Tank Acid resistant pump	Al^{3+} Fe^{3+}	19 10 0.9	1
Aluminium sulphate	$Al_2(SO_4)_3$	Granulate, powder 1 Solution 1.27	Silo Screw Tank Pump	Al^{3+}	40 1.5 24 0.9	3
Aluminium-iron(III)-sulphate	$[Al_2(SO_4)_3 + Fe_2(SO_4)_3] \cdot n\ H_2O$	Granulate 0.95	Silo Screw and eccentric pump	Al^{3+} Fe^{3+}	82 10 3.2	2
Iron(II)-chloride	$FeCl_2$	Solution 1.24 – 1.37	Tank Acid resistant pump	$Fe^{2+} \rightarrow Fe^{3+}$	86 – 135 1.5 – 2.4	1
Iron(III)-chloride	$FeCl_3$	Solution 1.41 – 1.43	Tank Acid resistant pump	Fe^{3+}	135 – 138 2.4 – 2.5	1
Iron(III)-chloride sulphate	$FeClSO_4$	Solution 1.43 – 1.52	Tank Acid resistant pump	Fe^{3+}	123 2.2	1
Iron(II)-sulphate	$FeSO_4 \cdot 7\ H_2O$	Residual moisture (green) salt 1	Ponding bunker Pump	$Fe^{2+} \rightarrow Fe^{3+}$	178 – 195 3.2 – 3.5	2
Iron(II)-sulphate	$FeSO_4 \cdot n\ H_2O$	Granulate 0.8	Silo Screw and eccentric pump	$Fe^{2+} \rightarrow Fe^{3+}$	195 3.5	3
Iron(III)-sulphate	$Fe_2(SO_4)_3$	Solution 1.5	Tank Acid resistant pump	Fe^{3+}	118 2.1	1
Calcium hydroxide White lime hydrate (slaked lime) Stabilised milk of lime (20 % by wt.)	$Ca(OH)_2$	Powder 0.45 Suspension 1.15	Silo Screw Tank Eccentric pump	Ca^{2+}	376 9.4 75 1.9	12.5
Sodium aluminate	$NaAl(OH)_4$	Solution 1.3 – 1.5	Tank Pump	Al^{3+}	62 – 105 2.3 – 3.9	14
Polyaluminium (hydroxide)-chloride (PAC)	$[Al(OH)_{3-x}Cl_x]_n$	Solution 1.2 – 1.37	Tank Acid resistant pump	Al^{3+}	70 – 90 2.6 – 3.3	1 - 3
Polyaluminium-(hydroxide)-chloride-sulphate	$Al_x(OH)_yCl_z(SO_4)_k$	Solution 1.4	Tank Acid resistant pump	Al^{3+}	52 – 90 1.9 – 3.3	1
Polyaluminium iron(III)-chloride	$[Al(OH)_{3-x}Cl_x]_n + FeCl_3$	Solution 1.3	Tank Acid resistant pump	Al^{3+} Fe^{3+}	59 6 – 15 2.3 – 2.5	1

According to model calculations by the German Federal Environmental Office (UBA, 1997) for the addition of heavy metal into sewage sludge with which, on average, a β-value of 1.2 and an adsorption rate in the sewage sludge of 90 % were assumed, no limiting values but rather standard values (Table 2) were formulated due to the marginal increase with the inputs of heavy metal via the path of precipitation and flocculation salts. In comparison with the positive effects (P, COD, and AOX reduction) the increase in metal is tolerable.

Table 2: Standard values for precipitation and flocculation agents containing iron or aluminium (UBA, 1997)

	Standard value [mg/kg STM]	Standard value [mg/kg Fe]	Standard value [mg/kg Al]
Lead (Pb)	90	260	427
Cadmium (Cd)	1	2.9	4.7
Chrome (Cr)	90	260	427
Copper (Cu)	80	230	380
Nickel (Ni)	20	58	95
Mercury (Hg)	0.8	2.3	3.8
Zinc (Zn)	250	720	1190
AOX		100	100

Some precipitants contain metals (e.g. barium), which are not listed in the Klärschlammverordnung (German Sewage Sludge Ordinance), but which, with dilution of the precipitant using water, lead to operating problems (incrustation).

A regular quality control is to be ensured by manufacturers and suppliers of the precipitants. A production data sheet should be provided with each delivery. In addition, a test certificate with analyses of the delivery should be attached.

3.4 Chemical Reactions

3.4.1 Precipitation Reaction

Phosphate removal using metal salts is based essentially on the precipitation of the PO_4^{3-} through Me^{3+}, i. e. through the formation of the only slightly soluble phosphate compounds $FePO_4$ and $AlPO_4$, according to the reaction equation

$$Me^{3+} + PO_4^{3-} \rightarrow MePO_4$$

As precipitants, Fe^{3+} and Al^{3+} behave similarly. It is, however, to be noted that with iron the pH value optimum for precipitation is lower by ca. one unit (see 3.6.1). The iron flakes are in general heavier, compacter and more resistant to shear than aluminium flakes. This is of significance with the design of the separation system.

With calcium phosphate precipitation there are various known possible reactions. It is, however, not predictable which of these reactions will take place in the wastewater. The most important precipitation product with the bonding of phosphate is hydroxyl apatite

$$5Ca^{2+} + 3PO_4^{3-} + OH^- \rightarrow Ca_5(PO_4)_3OH$$

As – with the exception of soft water - calcium is always sufficiently available, the purpose is primarily not the input of calcium ions Ca^{2+}, but much more an increase of the pH value with precipitation treatment through the dosing of slaked lime $Ca(OH)_2$. Therefore, with water of high hardness, a precipitation can also be carried out following input of another alkaline solution.

In particular, in connection with biological P-removal, a reaction of magnesium and ammonium with phosphorus can result under the formation of magnesium-ammonium-phosphate (MAP) This spontaneous MAP formation can lead to incrustation in pipelines and machine components. A deliberate precipitation of MAP is too cost-intensive due to the necessary high dosing of magnesium.

3.4.2 Competing Reactions

Simultaneously with the phosphate precipitation reaction several competing reactions occur which, seen technically, lead to an increased consumption of precipitants and thus lead to an increase in the quantity of sewage sludge. Essentially the following are to be differentiated:

- hydroxide formation $Me^{3+} + 3OH^- \rightarrow Me(OH)_3$,
- carbonate formation $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$,
- complexing with organic substances,
- adsorption reactions.

The most important competing reactions with Fe^{3+} and Al^{3+} are precipitation using the hydroxyl ion OH^- and, with Ca^{2+}, formation of carbonate.

Organic substances can be removed through precipitation reactions to a minor degree only. The decisive mechanisms of the removal of organic substances with chemical-physical phosphate removal are, on the other hand, the coagulation of organic colloids as well as the inclusion of the suspensa in flocs, whereby organic phosphorus is also removed. Furthermore, with precipitation, surfaces capable of adsorption are formed on a large scale so that the addition of adsorbing materials can be significant.

3.5 Type of and Requirement for Precipitants

Considered chemically, iron and aluminium salts are very similar in their effectiveness. With practical employment, however, in part significant differences occur which, primarily, are to be explained by the composition of the wastewater and the thus related secondary reactions. A first orientation on the effectiveness of precipitants is provided by laboratory tests (see for example DVGW[1] Standard W 218 „Flockentestverfahren" [Floc test procedures]).

The necessary requirement for precipitant for the maintenance of a monitoring value with precipitants containing iron and aluminium salts is influenced by:

- the dosing point
- the phosphate load of the wastewater taking into account the type and concentration of the phosphorus,
- the extent of the biological phosphorus bonding,
- the size of the monitoring value,
- the pH value of the raw wastewater,
- the concentration of substances which, together with the precipitants used, form complexes, e.g. between iron ions and humic matter,
- the concentration of compounds which can attach to solid matter as a type of "protective layer" sheathing and thus make the effect of floc-promoting chemicals more difficult.

On the other hand, attention must be paid that other treatment objectives, in particular nitrification, are not affected negatively through the dosing of precipitants. In particular, the reduction of pH values and acid capacity is significant. In individual cases remedial measures have to be taken (see 3.6.1, 3.6.2, 3.6.4 and in particular ATV-DVWK-A 131E, Section 5.2.9).

The required quantity of precipitant to be dosed is estimated for practical reasons via the β-value. This is defined as:

$$\beta_{Prec} = \frac{X_{Me}/AM_{Me}}{X_{P,Prec}/AM_{P}} \quad \text{in} \quad \frac{\text{mmol/l}}{\text{mmol/l}}$$

with

X_{Me}	required quantity of precipitant (metal) in mg Me/l wastewater
$X_{P,Prec}$	phosphorus to be precipitated in mg P/l wastewater
AM_{Me}	atomic mass of the metal in mg/mmol and
AM_{P}	atomic mass of the phosphorus in mg/mmol

The phosphorus to be precipitated $X_{P,Prec}$ corresponds with the phosphorus in the inflow minus the phosphorus in the effluent of the respective stage, reduced by the heterotrophic phosphorus and by the phosphorus bonded through a biological phosphate removal (see calculation example, Appendix A.4.1, Equation A.10).

As reference value for β_{Prec} with pre-precipitation, simultaneous precipitation and post-precipitation β_{Prec} is to be set as = 1.2. To be noted is that the necessary β values increase with tighter monitoring values and reducing phosphate concentrations, which have to be precipitated. Accordingly, with flocculation filtration and post-precipitation as second stage, a β_{Prec} of at least 2.5 is to be applied.

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[1] German Technical and Scientific Association for Gas and Water (DVGW)

3.6 Influencing Factors on Precipitation

3.6.1 *pH Value*

The solubility of the meal phosphates formed with the chemical-physical phosphate removal is dependent on the pH value. The smallest solubility of $FePO_4$ lies in the pH range 5.0 to 5.5, and that of $AlPO_4$ in the pH range 6.0 to 7.0. In these ranges, the best precipitation results are, theoretically, to be expected. The floc formulation required in addition to the chemical-physical phosphate removal, however, possibly does not run satisfactorily in these pH ranges.

In general therefore, an effective phosphate removal is achieved in practice with pH values of 6.5 to 8.5. Under certain circumstances an increase of the pH value through the input of an alkaline solution or lime is necessary.

If no precipitants containing metals are used but rather lime, it is not the quantity of lime added but rather the pH value which is thus achieved which is decisive for the success of the precipitation.

With pre-precipitation using slaked lime and with soft water, only a small amount of slaked lime is required in order to achieve a high pH value. Heavily buffered wastewater, on the other hand, requires higher quantities of slaked lime; here the simultaneously occurring calcium carbonate precipitation with pH values > 9 can lead to the formation of crusts and thus to considerable operating difficulties.

3.6.2 *Acid capacity*

The extent of the pH modification depends on the quantity of the precipitant added and the buffer capacity of the wastewater, characterised by its acid capacity $K_{A4.3}$. With soft wastewater with low acid capacity a too low a pH value can easily arise with the dosing of Al and Fe salts, which, for example, is a disadvantage for nitrification.

Then the employment of alkaline Al compounds or the combination of acid salts and slaked lime is advantageous.

3.6.3 Further Chemical Influencing Variables

With otherwise identical wastewater compositions the requirement for precipitant increases with:

- increasing turbidity (suspended solids and colloids) – due to flocculation occurring in parallel,
- increasing content of dissolved organic matter – due to competing complex formation reactions.

3.6.4 Physical Influencing Variables

With phosphate precipitation and flocculation the following physical constraints are to be maintained:

- The thorough mixing of the precipitant must be guaranteed in the shortest time so that the direct reaction of the metal ion with the phosphate ion is encouraged. In practical application this phase, as a rule, is coupled with that of the formation of micro-flocs. The detention time of the wastewater in the mixing zone/in the mixing reactor should be ca. one minute. The energy input is to be so adjusted that a power density in the range of 100 W/m³ to 150 W/m³ is achieved.
- Although the energy density in the phase of flocculation formation must be sufficiently high in order to enable the necessary collision of the particle and micro-flocs it must, however, not be so high that the flocs already formed are not destroyed again. Technically this is effected through scheduling a multi-phase floc formation (micro-floc formation, chronologically coupled with the precipitant mixing; macro-floc formation which, on their part, can be conceived again using staged power density). The reaction time of the macro-floc formation should be ca. 20 to 30 minutes. The power density is, on average , set at ca. 5 W/m³ (for multi-stage floc formation these values are to be divided and graduated). The formation of easily separable macro-flocs can also be supported through the addition of polymers as flocculation aid (see ATV-M 274 [Not available in English]). The possible input of contaminants (polyacrylamides and dithio-carbonates) is to be noted.

With multi-stage flocculation the flocculation stages are operated with reducing power density in the direction of flow, while the detention time in the substage remains ca. the same size.

3.6.5 Influence of the Biological Phase on the Precipitant Requirement

In general, with nitrification/denitrification, an increased biological phosphate removal occurs. Through this the precipitant requirement becomes smaller (see Section 3.5). The increased biological phosphorus bonding in the form of polyphosphates causes an increased yield of surplus sludge of ca. 3 g DS/g bonded phosphorus.

3.7 Storage and Dosing of Precipitants

Precipitants are supplied as a solid, a solution or as a suspension (see Table 1). Facilities for storage and, possibly, solution and dosing are to be designed dependent on the condition at delivery and on the aggressiveness, danger of forming lumps, flow ability and abrasion through undissolved components. Storage containers are made from steel, concrete or plastic. With steel and concrete, corrosion protection through appropriate, approved coatings is required. With liquid precipitants dosing can be direct from these containers; with solid precipitants additional facilities for solutions are to be planned, with quicklime also a quenching facility. If required, the facilities or parts thereof are to be accommodated in buildings. Pipelines, as a rule, are manufactured from corrosion resistant plastic.

Precipitants are water-hazardous substances within the meaning of § 19g of the [German] Water Resources Management Law (in German = WHG) and must meet the requirements of §§ 19g to 19l WHG. Furthermore, the water laws of the German Federal States apply as well as the respective Ordinance for Facilities for Handling Water-hazardous Substances and on Special Operations (in German = VAwS).

Complete and prescribed dosing stations are offered by relevant specialist firms and suppliers of precipitants. Attention is to be paid that the containers have a nationally technically approved suitability certificate, i.e. either suitable in accordance with the [German] Construction Regulation List A, Part 1, No. 15 or in accordance with a National General Technical Approval. Precipitants are hazardous substances within the meaning of § 3 of the [German] Law on Protection against Hazardous Substances (Chemical Law – [in German = ChemG]) and of § 4 of the [German] Ordinance on Protection against Hazardous Substances (Hazardous Substance Ordinance – [in German = GefStoffV]). With the handling of precipitants Section 5 of the [German] Hazardous Substance Ordinance "General Regulations for the Handling of Hazardous Substances" is to be noted in particular.

The storage containers are to be so dimensioned that the complete load of a silo- or tank vehicle can be accepted (> 25 m³). Attention is to be paid to a sufficient reserve corresponding with the requirement at weekends and holidays.

The arrangement of the dosing station and the dosing of the precipitant are dependent on method. Appropriate explanations are given in Section 4 with the description of the individual dosing method.

Control or regulation of the precipitant dosing can be carried out dependent on time taking into account measured hydrograph curves (small scale wastewater treatment plants), proportional to quantities of water (medium-sized wastewater treatment plants) or proportional to phosphorus load (large wastewater treatment plants). In addition, a dosing proportional to the phosphate concentration has also proved successful.

With dosing proportional to water quantities an increased combined wastewater inflow can lead to overdosing if a limitation of the dosing is not planned.

With lime precipitation dosing must be undertaken via a pH value regulation.

Advisory Leaflet ATV-DVWK-M 206E deals in detail with continuous measurement, with automation concepts as well as storage and dosing technology.

4 Methods

Various methods are defined depending on the point of application of the precipitant:

- pre-precipitation,
- simultaneous precipitation,
- post-precipitation and
- flocculation filtration.

With pre-precipitation the precipitation products are separated out in the primary settlement tank and with simultaneous precipitation in the secondary settlement tank. The precipitation products with post-precipitation and with flocculation filtration are separated using independent stages (sedimentation, flotation or filtration). Fundamentally these methods can also be combined (two-stage precipitation), e.g. pre-precipitation and simultaneous precipitation or simultaneous precipitation and post-precipitation. In each case attention is to be paid to sufficiently thorough mixing and flocculation (see 3.6.4). If no position with sufficient turbulence is available (hydraulic jump, drop structure), the efficiency can be improved considerably through increasing the power density by mixing the precipitant thoroughly at the dosing point.

Preferred dosing points which satisfy these conditions are the inverted siphon inlet to a circular primary or secondary settlement tank with high turbulence in the inverted siphon and small turbulence in the central structure.

In channels the thorough mixing can be improved through the installation of a baffle or the operation of a submerged pump or propeller. If the wastewater at the dosing point contains no coarse materials which can lead to blockages, a static mixer is also suitable.

The methods and their performance are drawn up in Table 3.

4.1 Pre-precipitation

With the pre-precipitation method (Figure 1) the precipitants are added before the primary settlement tank or before the grit chamber.

With this method, in addition to the phosphates, organic and filterable substances are also removed. The subsequent nitrification is made easier through this, the denitrification more difficult. Slaked lime up to pH values of 9.5 is employed, iron(II)-salts only in combination with an aerated grit chamber.

With biofilters as main stage, pre-precipitation is the only possibility to remove phosphates, possibly also as two point precipitation (pre-precipitation and flocculation filtration).

Table 3: Precipitation methods – dosing points, performance, floc separation

	Pre-precipitation	Simultaneous precipitation	Post-precipitation	Flocculation filtration
Observable monitoring value * (mg/l P)	2	1	1	0.5
Dosing point(s)	Before primary settlement tanks (e.g. venturi, aerated grit chamber)	Before / in / after aeration tanks, after biological filters or contactors	After secondary settlement tanks	Twofold as with simultaneous and post-precipitation
Thorough mixing	Points of higher turbulence	Points of higher turbulence	Mixer	As with simultaneous and post-precipitation
Place of floc separation	Primary settlement tanks	Secondary settlement tanks	Additional sedimentation or flotation tanks	1st Stage: existing secondary settlement tanks 2nd Stage: additional filters

* Under favourable conditions and optimum operating conditions even lower values can be observed.

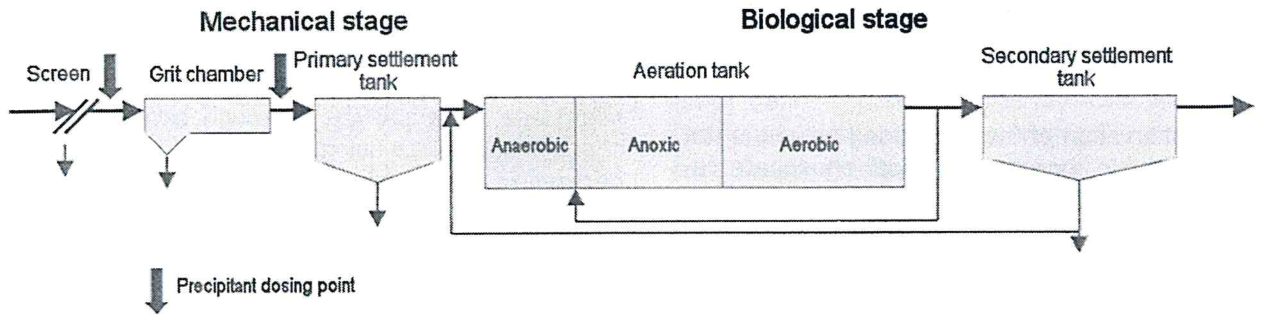

Figure 1: **Dosing points *pre-precipitation***

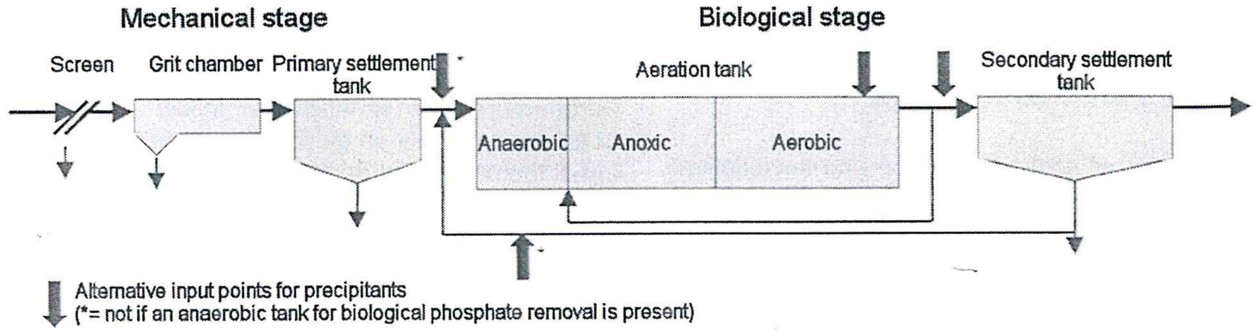

Figure 2: **Dosing points *simultaneous precipitation***

4.2 Simultaneous Methods

4.2.1 Simultaneous Precipitation

With simultaneous precipitation (Figure 2) the addition of the precipitant takes place, as selected, before the aeration tank, in the aeration tank, in the inlet to the secondary settlement tank or in the return sludge. The two dosing points: inlet aeration tank and return sludge, are not to be recommended if an anaerobic tank is available for the biological phosphate removal (Section 4.2.2).

With the employment of trivalent iron salts the inlet to the secondary settlement tank has shown itself to be favourable as dosing point.

Through the addition of precipitants the inorganic part of the solid content increases in the aeration tank (Section 5.1).

With the biological filter method the precipitant is dosed exclusively into the inlet to the biological filter trough, with rotating biological contactors the dosing can take place both in the inlet to the biological contactor trough and into the secondary settlement tank.

The precipitant and the resultant product remain in the aeration tank for the duration of the sludge age and can in this period buffer high phosphate peaks. The buffer capability can be ensured through a minimum base load dosing.

Simultaneous precipitation can also be applied with aerated and unaerated ponds. With unaerated ponds the use of lime (avoidance of the formation of iron sulphide) is recommended. It is, however also pointed out that, with many unaerated ponds, a significant precipitation of calcium phosphate occurs, at least temporarily, even without the addition of precipitant, as a result of the increase in pH with the formation of algae.

4.2.2 *Simultaneous Precipitation for the Supplementing of Biological Phosphate Removal*

As the observation of the monitoring values is not always possible through biological phosphate removal alone, facilities for the supplementing of simultaneous precipitation are to be supplied.

The addition of precipitant for the supplementary simultaneous precipitation to the biological phosphate removal should take place either in the inlet to the secondary settlement tank (trivalent precipitants only) or into the aeration tank or in the return sludge (see Figure 2).

4.3 Downstream Stages

The methods of post-precipitation and flocculation filt ration are characterised in that the precipitation and flocculation as well as the separation of the flocculated substances take place in a separate stage downstream from the biological treatment.

4.3.1 *Post-precipitation*

The precipitants with post-precipitation (Figure 3) are added into the inlet to the downstream separation stage, whereby the thorough mixing in the channel takes place using appropriate baffles (static or dynamic mixers) or in separate flocculation tanks. A flocculation area is required for the formation of the separable flocs (see Section 3.6.4).

The flocs are separated by sedimentation in a settlement tank or through lamination separators or through flotation. With sedimentary separation methods the flocculation process can be improved by feeding return sludge into the flocculation stage.

The post-precipitation stage forms its own process unit and barely influences the upstream processes. Furthermore, the variations in inflow concentrations are relatively small and thus a better matching of the precipitant dosing is possible.

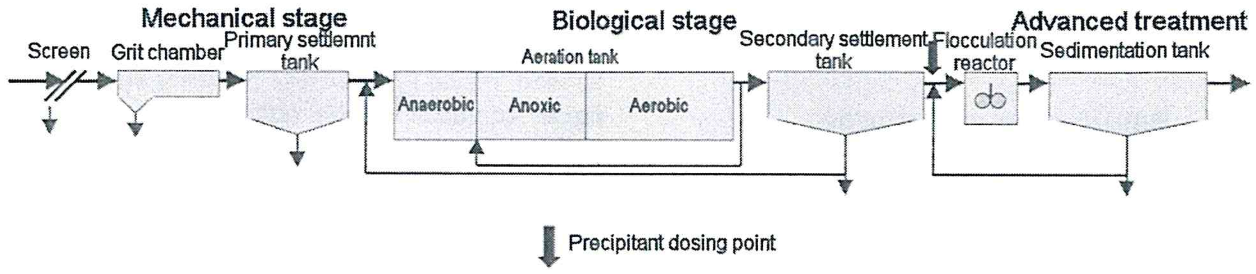

Figure 3: Dosing points *post-precipitation*

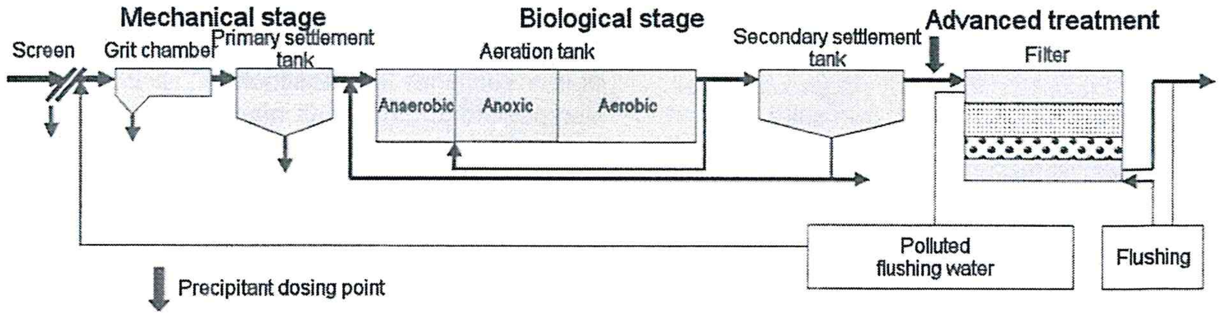

Figure 4: Dosing points *flocculation filtration* (in combination with BioP, with pre- and simultaneous precipitation see Figures 1 and 2)

4.3.2 Flocculation Filtration

Flocculation filtration (Figure 4) can be employed as second stage only, for example following pre- or simultaneous precipitation or biological phosphate removal.

The dosing of the precipitant takes place in the inlet of the flocculation filter. According to available experience monitoring values of 0.5 mg/l P can be maintained using flocculation filtration. Lower monitoring values can also be maintained with favourable constraints. With a β_{Prec} of ≥ 2.5 necessary here, the phosphate concentration in the inflow should not be higher than ca. 1 mg/l in order to achieve still tolerable filter service lives. For the ecological aspects of the employment of organic polymers as flocculation aid, attention is drawn to Advisory Leaflet ATV-M 274 „Einsatz organischer Polymere in der Abwasserreinigung“ [Employment of Organic Polymers in Wastewater Treatment (Not available in English)], Section 8.

With flocculation filtration the flocculation takes place in the filter. The adjustable energy input with intensive mixing, above all, however, the type and quantity of precipitant, must be matched very carefully to the filter. From experience not more than 4 mg/l Fe or 2.5 mg/l Al are added. The dosing of polymers should be done without in order to avoid operational problems (sticking) and because, as a rule, the effect is insignificant.

The mixing processes occurring with the flow through the filter encourage the formation of flocs. Size, shape and structure of the filter grain as well as the structure, loading and filtration rate of the filter determine the pressure loss. The efficiency, the required energy input into the filter for macro-filter formation and a practical filter service life limit the possible filtration rates. For vertically downward streamed open filters this allows a dimensioning for the case of dry weather ($Q_{DW,h,max}$) with a filter rate of 6 m/h up to 8 m/h, whereby the plant with rainy weather can be fed with 2 $Q_{DW,h,max}$. Within this range the treatment performance achievable using flocculation filtration is almost independent of the filtration rate. Further information on flocculation filtration is contained in Standard ATV-A 203 [Not available in English].

4.4 Two-stage Precipitation

With two-stage precipitation two of the processes described in the previous sections are combined, e.g. as simultaneous precipitation and flocculation filtration, and also pre- and simultaneous precipitation or as simultaneous- and post-precipitation. This takes place for the following reasons:

- early relief of the following process stages,
- economical use of chemicals (from experience the overall degree of effect with two-point precipitation is greater than with the dosing of the total amount of precipitants at one input point),
- specifically for the protection of the filter with flocculation filtration.

A regulation or control of the dosing can be limited to the second stage.

5 Influence of Precipitation/Flocculation on the Treatment of Wastewater and Sludge

5.1 Influence of Phosphate Precipitation on the Biological Processes

The biological degradation of organic substances and the biochemical oxidation and reduction of nitrogen are influenced

- with pre-precipitation (see 4.1): through increase of the N/BOD_5 ratio and modification of the acid capacity of the wastewater as well as through raising the sludge age,
- with simultaneous precipitation (see 4.2): as a rule, through improvement of the settling and thickening characteristics as well as the increase of the inorganic part of the activated sludge, through increased yield of surplus (waste) sludge and a lowering of the sludge age, abatement of the acid capacity and, depending on the type of precipitant, the stimulating or inhibiting effect on the nitrification,
- with post-precipitation (see 4.3.1): no or only insignificant influencing with the return feed of sludge from the post-precipitation stage into the plant inlet.

With all methods of precipitation it is important that a subsequent biological stage remains supplied with sufficient phosphorus (0.7 mg/l P to 1 mg/l P per 100 mg/l BOD_5).

The change of the N/BOD_5 ratio as a result of pre-precipitation, through the abatement of the BOD_5-loading of the biological stage, has positive effects on the nitrification, however, usually negative results for the denitrification.

The specific reduction of the acid capacity is referred normally to a kilogramme of metal ions, although it is really dependent on the content of the acid residues in the precipitant. It is 54 mol/kg with iron and 111 mol/kg with aluminium. In order to avoid an inhibition of the nitrification, for reasons of safety, an acid capacity of 1.5 mmol/l should be maintained. In critical cases an alkaline precipitant should be employed, possibly combined with slaked lime. With dosing of slaked lime the pH value may not be increased too heavily so that no return solution of aluminium takes place and a calcium carbonate precipitation is avoided (see 3.6.1).

The inorganic part of the activated sludge increases as a result of the simultaneous precipitation. The additional surplus sludge produced must be taken into account with the dimensioning of the activated sludge plant. With pre- and post-precipitation also one can reckon with the same order of this chemical sludge production.

5.2 Influence of Phosphate Precipitation on the Sludge

5.2.1 Solid Matter Load

Through the transfer of dissolved and suspended substances in settleable flocs the share of solid matter is increased. The additional solid matter load results from the quantity of the precipitant added, from the compounds formed as well as from the quantity of solid matter removed.

In practice the phosphates, hydroxides and other substances also precipitated formed from the precipitants give a dry solid matter content of:

- 2.5 g/g, referred to iron, and
- 4 g/g, referred to aluminium.

The overall increase in solid matter can be calculated from the above specific values and the dosed active substance (see calculation example in the Appendix). With increased biological P-removal one must reckon with an increase of the solid matter load of ca. 3 g/g referred to phosphorus removed.

With the addition of slaked lime as precipitant one has to reckon with an increase of solid matter of ca. 1.35 times the dosed quantity. The specific growth of solid matter is, with:

- pH values of about 9.5 up to ca. 50 g/(l · d),
- pH values of about 11 up to 200 g/(l · d).

5.2.2 *Sludge Volumes*

The additional sludge volumes produced with phosphate removal result from the solid matter load and the water content or solid matter content. If a higher solid matter content is achieved, despite increased solid matter yield from the precipitation/flocculation reaction, smaller sludge volumes of activated sludge are possible.

The selected method of operation (pre-, simultaneous or post-precipitation) and type and quantity of precipitant employed have a significant influence on the solid matter content of the flocs formed.

With pre-precipitation the solid matter content of the primary sludge increases with increasing input of precipitants. In the case of an originally lower solid matter content of the secondary sludge with simultaneous precipitation a slight increase with increasing dosing occurs. Through this the formation of bulking sludge can also be combated. With post-precipitation the share of water-rich hydroxide flocs increases with increasing dosing. Through this the solid matter content in the tertiary sludge is abated.

If metal salts (β>2) are also employed for the formation of the macro-flocs (see Section 3.2), the solid matter content is reduced as a result of hydroxide floc formation. These can be countered through addition of organic flocculants (polyelectrolytes) in place of additional metal salts (see ATV-M 274)

Appendix A Calculation Examples

A.1 Basic Elements of Calculation

With the following calculations of precipitant requirements and yield of solid matter the relative atomic masses (AM_X) of the elements phosphorus (AM_P = 31.0 g/mol P), iron (AM_{Fe} = 55.8 g/mol Fe) and aluminium (AM_{Al} = 27.0 g/mol Al) are employed. The data sheet belonging to each precipitant contains details of the content of active substance in delivery form (AS_{Me}) in one of the following forms (see also Table 1):

- kg Me per kg precipitant = AS_{Me} (Definition used here)
- % Me (mass percentage) = $100 \cdot AS_{Me}$
- g Me per kg precipitant = $1000 \cdot AS_{Me}$
- mol Me per kg precipitant for Fe^{2+} and Fe^{3+}: = $1000 \cdot AS_{Me}/AM_{Fe}$
  = $1000 \cdot AS_{Me}/55.8$
  = $17.9 \cdot AS_{Me}$
- for Al^{3+}: = $1000 \cdot AS_{Me}/AM_{Al}$
  = $1000 \cdot AS_{Me}/27.0$
  = $37.0 \cdot AS_{Me}$
- Density of the precipitant solution ρ_{PS} (kg/m³ solution)

From the respectively specified data the active substance content AS_{Me} (kg/kg) of a precipitant used in an example can be calculated using the above equations.

From the details for the content of iron AS_{Fe} and aluminium AS_{Al} an interaction coefficient z is calculated with the aid of the relative atomic masses (AM_X):

$$z = \frac{AM_P}{AM_{Fe}} \cdot AS_{Fe} + \frac{AM_P}{AM_{Al}} \cdot AS_{Al} = 0.555 \cdot AS_{Fe} + 1.148 \cdot AS_{Al} \quad \text{(A.1)}$$

The average quantity of precipitant to be dosed $B_{d,PQ}$ (g/d precipitant) then results as:

- $Q_{DW,d}$ the daily wastewater quantity with dry weather (m³/d),
- $X_{P,Prec}$ phosphorus (mg/l) eliminated through precipitation, to be calculated,
- β_{Prec} of the relative quantity of precipitant to be selected (mol Me/mol $X_{P,Prec}$)

as

$$B_{d,PQ} = X_{P,Prec} \cdot \beta_{Prec} \cdot \frac{Q_{DW,d}}{z} \quad \text{(g/d precipitant) (A.2)}$$

To cover the peaks of the phosphorus content in the inflow – similarly as with nitrogen (ATV-DVWK-A 131E, f_N in Table 8) – a peak factor f_P dependent on the size of the plant and the sludge age (peak load adjustment as a result of tank volume) is applied, which is involved for the design of the dosing facility(ies). With pre-precipitation the greatest value from Table 8, ATV-DVWK-A 131E, is recommended; with post-precipitation, as a result of the previous peak load adjustment, the smallest. With this the maximum hourly dosing is:

$$B_{h,PQ} = X_{P,Prec} \cdot \beta_{Prec} \cdot \frac{f_P \cdot Q_{DW,d}}{24 \cdot z} \quad \text{(g/h precipitant)} \quad \text{(A.3)}$$

In general the precipitant is dosed as a solution. If the precipitant solution is delivered by the manufacturer with a density of ρ_{PS}, then the volume flow to be dosed is Q_{PQ} of the dissolved precipitant:

$$Q_{d,PQ} = \frac{B_{d,PQ}}{\rho_{PS}} \ \text{(l/d)} \quad \text{or} \quad Q_{h,PQ} = \frac{B_{h,PQ}}{\rho_{PS}} \ \text{(l/h)} \quad \text{(A.4)}$$

A powder or granulate formed precipitant is applied on site and leads to a solution with a precipitant concentration of C_{PS} (kg/m³ precipitant); a dry dosing is often also possible. The solution applied lies in the area of 10 % precipitant content and the solution density c_{PS} (100 kg/m³) which results can be monitored using a hydrometer. The volume flows of precipitant solution are the:

$$Q_{d,PQ} = \frac{B_{d,PQ}}{C_{PS}} \ \text{(l/d)} \quad \text{or} \quad Q_{h,PQ} = \frac{B_{h,PQ}}{C_{PS}} \ \text{(l/h)} \quad \text{(A.5)}$$

The delivery of the pump(s) is to be designed at max. Q_{PQ}.

The on average solid matter yielded (chemical waste sludge) $WS_{d,Chem}$ (g/d DR) from precipitation and flocculation are calculated in accordance with the statement in Section 4.2.1 on the basis of the dosed quantity of iron or aluminium. Basis for this with powder or granulate-formed precipitants, the calculated mean precipitant quantity $B_{d,PQ}$ in accordance with Equation A.2 and the content of active substance of the precipitant AS_{Me}:

$$WS_{d,Chem} = B_{d,PQ} \cdot (2.4 \cdot AS_{Fe} + 4.0 \cdot AS_{Al}) \text{ (g/d DR)} \quad (A.6)$$

If the precipitant is delivered from the manufacturer as solution and is then dosed, the mean solid matter $WS_{d,Chem}$ (g/d DR) produced is determined through the combination of Equations A.5 and A.6 as:

$$WS_{d,Chem} = B_{d,PQ} \cdot (2.4 \cdot AS_{Fe} + 4.0 \cdot AS_{Al}) \text{ (g/d DR)} \quad (A.7a)$$

or

$$WS_{d,Chem} = Q_{d,PQ} \cdot c_{PS} \cdot (2.4 \cdot AS_{Fe} + 4.0 \cdot AS_{Al}) \text{ (g/d DR)} \quad (A.7b)$$

With the treatment process using denitrification and biological phosphorus removal, in addition to the chemical surplus sludge, also addition solid matter is produced as a result of biological phosphorus compounds. These ($WS_{d,BioP}$ in g/d DR) are calculated in accordance with ATV-DVWK-A 131E, Section 5.2.4 as follows:

$$WS_{d,BioP} = 3.0 \cdot Q_{DW,d} \cdot X_{P,BioP} \text{ (g/d DR)} \quad (A.8)$$

A.2 Treatment Methods Investigated and Monitoring Values P_{tot}

Below are the wastewater treatment methods investigated together with the monitoring values applied. The mean operating values used as basis for the calculation are given respectively in brackets. For flocculation filtration a lower mean operating value of the upstream activated sludge process of 1.0 mg/l is required.

Treatment method investigated

1. Activated sludge process with simultaneous precipitation
   Selected mean operating value:
   C_P = 1.5 mg/l P
   Monitoring value: C_P = 2.0 mg/l P

1.1 and nitrification
1.2 and denitrification
1.3 and biological P-removal

2. Activated sludge process with simultaneous precipitation
   Selected mean operating value:
   C_P = 1.0 mg/l P
   plus flocculation filtration
   Selected mean operating value:
   C_P = 0.2 mg/l P
   with a monitoring value of : C_P = 0.3 mg/l P

2.1 and nitrification
2.2 and denitrification
2.3 and biological P-removal

A.3 Load and Dimensioning Assumptions

Plant capacity: PT = 15,000 I

Specific wastewater yield	$w_{ww,d}$	= 180 l/(I·d)
Dry weather flow	$Q_{DW,d}$	= 2,700 m³/d
Specific wastewater load BOD₅	$B_{d,BOD}$	= 60 g/(I·d)
After primary settlement (in the example)	$B_{d,BOD}$	= 40 g/(I·d)
Specific wastewater load P_{tot}	$B_{d,P}$	= 1.8 g/(I·d)
After primary settlement (in the example)	$B_{d,P}$	= 1.6 g/(I·d)

Phosphorus bonding in the activated sludge:

The bonding of phosphorus in the activated sludge (biomass) X_P is calculated as share [PB (-, %)] of the BOD_5 $C_{BOD,InBio}$ fed in. Bonding takes place via the biological cell build up in the activated sludge with nitrification (PB_{BM}) and via the increased P-Bonding, which is dependent on the denitrification (PB_{Deni}) and a possibly existing anaerobic primary settlement tank:

Cell build-up only

$$X_{P,BM} = PB_{BM} \cdot C_{BOD,InB} \quad (A.9a)$$

With denitrification

$$X_{P,BioP} = PB_{Deni} \cdot C_{BOD,InB} \quad (A.9b)$$

With anaerobic tank

$$X_{P,BioP} = (PB_{Deni} + PB_{Ana}) \cdot C_{BOD,InB} \quad (A.9c)$$

Types of bonding:

1. Nitrification (cell build-up) of the $C_{BOD,InB}$ fed in	PB_{BM}	= 1.0 %
2. Denitrification additional biological P-bonding of the $C_{BOD,InB}$ fed in	PB_{Deni}	= 0.5 %
3. additional biological P-removal with anaerobic primary settlement tank additional biological P-bonding of the $C_{BOD,InB}$ fed in	PB_{Ana}	= 1.0 %

Selected relative precipitant quantities β_{Prec}:

With simultaneous precipitation

With mean operating value	C_P	= 1.5 mg/l P
	β_{Prec}	= 1.2
With mean operating value	C_P	= 1.0 mg/l P
	β_{Prec}	= 1.5
With flocculation filtration	β_{Prec}	= 2.5

Selected precipitant:

1. Aluminium-Iron(III)-Sulphate as granulate $[Al_2(SO_4)_3 + Fe_2(SO_4)_3] \cdot n\,H_2O$

with 1.0 % Fe^{3+} and 8.2 % Al^{3+}
i.e. AS_{Fe} = 0.010 kg Fe/kg granulate and
AS_{Al} = 0.082 kg Al/kg granulate

with this an interactive coefficient results:

$$\begin{aligned} z &= 0.555 \cdot AS_{Fe} + 1.148 \cdot AS_{Al} \\ &= 0.555 \cdot 0.010 + 1.148 \cdot 0.082 \\ &= 0.0056 + 0.0941 = 0.0997 \end{aligned}$$

From this granulate a solution with $\rho_{PS} = 100\ kg/m^3$ is produced and dosed.

2. **Iron(III)-chloride** ($FeCl_3$) liquid, with 13.8 % Fe^{3+} and a density of 1.430 kg/m^3 with this an interaction coefficient results:
$z = 0.555 \cdot AS_{Fe} = 0.555 \cdot 0.138 = 0.0766$

Selected peak factors:

Simultaneous precipitation $f_P = 2.0$
Flocculation filtration $f_P = 1.5$

A.4 Calculations

A.4.1 Calculation of the Phosphorus to be Precipitated

The phosphorus to be precipitated $X_{P,Prec}$ (mg/l) results from the following phosphorus balance (*C* for phosphorus in the homogenised sample; *X* for filterable phosphorus; in each case mg/l P):

$$X_{P,Prec} = C_{P,InB} - C_{P,aM,ESST} - X_{P,BM} - X_{P,BioP} \quad \text{(mg/l)} \qquad \text{(A.10)}$$

with

$X_{P,Prec}$	(mg/l)	Concentration of the phosphorus to be precipitated,
$C_{P,InB}$	(mg/l)	Concentration of the phosphorus in the homogenised sample in the inflow to the activated sludge plant (after primary settlement),
$C_{P,aM,ESSS}$	(mg/l)	Concentration of the phosphorus in the homogenised sample in the effluent of the secondary settlement tank, annual mean value (mean operating value),
$X_{P,BM}$	(mg/l)	Phosphorus required for cell build-up with carbon removal and nitrification,
$X_{P,BioP}$	(mg/l)	Phosphorus removed through biological P-removal (denitrification and anaerobic primary settlement tank).

In the above sections assumptions are made and calculation information is given with regard to these values ($C_{P,aM,ESST}$). The calculation of $X_{P,Prec}$ for the six methods investigated took place with the aid of Equations A.9 and A.10. The calculation process and the results are summarised in Table A.1. The table also contains the β-values and the relevant product $X_{P,Prec} \cdot \beta_{Prec}$ required for the calculation of the precipitant quantity. The calculation process is explained using the treatment process 1.2 (activated sludge process with nitrification and denitrification):

The content of total phosphorus $C_{P,InB}$ and of $C_{BOD,InB}$ in the inflow to the activated sludge tank with all treatment processes investigated was:

$C_{P,InBio} = 1000 \cdot (1.6/180) = 8.9$ mg/l P
(Column 2, Table A.1)

$C_{BOD,InB} = 1000 \cdot (40/180) = 222$ mg/l

The annual mean value for total phosphorus in the effluent of the secondary settlement tank is selected as:

$C_{P,aM,ESST} = 1.5$ mg/l P (Column 3).

The phosphorus required for cell build-up in Column 4 with 1 % of the inflow BOD_5 ($C_{BOD,InB}$) is:

$X_{P,BM} = PB_{BM} \cdot C_{BOD,InB} = 0.01 \cdot 222 = 2.2$ mg/l P

For process 2.2 in Appendix A.2 (denitrification) 0.5 % of $C_{BOD,InB}$ is biologically bonded (Column 5):

$X_{P,BioP} = PB_{Deni} \cdot C_{BOD,InBo} = 0.005 \cdot 222 = 1.1$ mg/l P

while with denitrification and anaerobic primary tank (additional 1.5 %)

$$\begin{aligned} X_{P,BioP} &= (PB_{BM} + PB_{Ana}) \cdot C_{BOD,InB} \\ &= (0.005 + 0.01) \cdot 222 \\ &= 3.3 \text{ mg/l P} \end{aligned}$$

Were additionally bonded (Appendix A.2: Process 1.3 and 2.3).

From these phosphorus concentrations $X_{P,Prec}$ is calculated in accordance with Equation A.10 (Column 6). The product in Column 8 is formed from the selected β_{Prec} (Column 7; see also Section A 3) and $X_{P,Prec}$.

A.4.2 Calculation of the Precipitant Quantities

The necessary precipitant quantities for both the selected products are determined with the aid of Equations A.2 to A.5. The necessary parameters for this ($X_{P,Prec} \cdot \beta_{Prec}$; $Q_{DW,d}$; z; f_P; ρ_{PS}; C_{PS}) are given or calculated in the previous sections. The results are summarised in Table A.2 for the processes investigated. With processes using flocculation filtration, in addition to the individual steps of the two-stage precipitation, the precipitant demand of the total process is given at the foot of the table.

Table A.1: Calculation of the phosphorus content to be precipitated $X_{P,Prec}$ and β-values

Process	$+ C_{P,InB}$	$- C_{P,aM,ESST}$	$- X_{P,BM}$	$- X_{P,BioP}$	$= X_{P,Prec}$	β_{Prec}	$X_{P,Prec} \cdot \beta_{Prec}$
Unit:	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
Column:	2	3	4	5	6	7	8
Activated sludge process (Compare Appendix A.2 "Treatment processes investigated"							
1.1	8.9	1.5	2.2	0.0	5.2	1.2	6.24
1.2	8.9	1.5	2.2	1.1	4.1	1.2	4.92
1.3	8.9	1.5	2.2	3.3	1.9	1.2	2.28
2.1	8.9	1.0	2.2	0.0	5.7	1.5	8.55
2.2	8.9	1.0	2.2	1.1	4.6	1.5	6.90
2.3	8.9	1.0	2.2	3.3	2.4	1.5	3.60
Flocculation filtration – downstream of the activated sludge process in Group 2							
2	1.0	0.2	0.0	0.0	0.8	2.5	2.00

Table A.2: Calculated precipitant quantities (*PQ*) for average and peak demand

Process	Aluminium-Iron(III)-sulphate				Iron(III)-chloride solution			
	Average *PQ*		Peak demand		Average *PQ*		Peak demand	
	$B_{d,PQ}$	$Q_{d,PQ}$	$B_{h,PQ}$	$Q_{h,PQ}$	$B_{d,PQ}$	$Q_{d,PQ}$	$B_{h,PQ}$	$Q_{h,PQ}$
	kg/d	l/d	kg/h	l/h	kg/d	l/d	kg/h	l/h
Column	2	3	4	5	6	7	8	9
Activated sludge process (compare Appendix A.2 "Treatment processes investigated")								
1.1	169	1.690	14.1	140.8	220	154	18.3	12.8
1.2	133	1.332	11.1	111.0	173	121	14.5	10.1
1.3	62	617	5.1	51.5	80	56	6.7	4.7
2.1	232	2.315	19.3	193.0	301	211	25.1	17.6
2.2	187	1.869	15.6	155.7	243	170	20.3	14.2
2.3	97	975	8.1	81.2	127	89	10.6	7.4
Flocculation filtration – downstream of the activated sludge process in Group 2								
2	54	542	3.4	33.9	70	49	4.4	3.1
Total requirement for aeration with flocculation filtration								
2.1	286	2.857	22.7	226.8	372	260	29.5	20.6
2.2	241	2.410	19.0	189.6	314	219	24.7	17.3
2.3	152	1.517	11.5	115.1	197	138	15.0	10.5

A 4.3 Calculation of the Increased Yield of Solid Matter

The increased yield of solid matter as a result of precipitation and flocculation ($WS_{d,Chem}$) is determined through the application of the active substances AS_X (see Section A.3 "Selected precipitant") and the calculated precipitant quantities $B_{d,PQ}$ (kg/d) in Table A.2, Columns 2 and 6, in Equation A.6 (granulate or powder formed precipitant) or A.7 (precipitant solutions). The employment of $B_{d,PQ}$ in kg/d also gives $WS_{d,Chem}$ in kg/d. The results for the processes investigated are summarised in Table A.3. With the processes with flocculation filtration, in addition to the individual steps of two-stage precipitation the sludge yield of the complete process is given at the foot of the table.

The additional sludge yielded with processes with denitrification and anaerobic primary tank $WS_{d,BioP}$ is calculated using equation A.8 as well as the $X_{P,Prec}$ values from calculated from Table A.1 and are also listed in Table A.3. In addition the total sludge quantities are determined.

Table A.3: Sludge quantities yielded

	Aluminium-Iron(III) sulphate			Iron(III) chloride solution		
Process	$WS_{d,Chem}$	$WS_{d,BioP}$	$WS_{d,P}$ (total)	$WS_{d,Chem}$	$WS_{d,BioP}$	$WS_{d,P}$ (total)
	kg/d	kg/d	kg/d	kg/d	kg/d	kg/d
Column	2	3	4	5	6	7
Activated sludge process (compare "Treatment processes investigated")						
1.1	72.8	0.0	72.8	59.5	0.0	59.5
1.2	57.4	8.9	66.3	46.9	8.9	55.8
1.3	26.6	26.7	53.3	21.7	26.7	48.5
2.1	99.8	0.0	99.8	81.5	0.0	81.5
2.2	80.6	8.9	89.5	65.8	8.9	74.7
2.3	42.0	26.7	68.8	34.3	26.7	61.0
Flocculation filtration – downstream of the activated sludge process in Group 2						
2	23.3	0.0	23.3	19.1	0.0	19.1
Total requirement for aeration with flocculation filtration						
2.1	123.2	0.0	123.2	100.6	0.0	100.6
2.2	103.9	8.9	112.8	84.8	8.9	93.8
2.3	65.4	26.7	92.1	53.4	26.7	80.1

Laws, Standard Specifications and Directives

RL 86/278 EEC Sewage Sludge Directive, Directive of the Council 86/278/EEC on the protection of the environment and in particular the soil with the employment of sewage sludge in agriculture dated 12 June 1986. [In Germany ABl. EC dated 04 July 1986 No. L 181 p. 6]

Klärschlammverordnung (AbfKlärV) vom 15. April 1992, BGBl. I Nr. 21 vom 28. 04. 1992 S. 912; zuletzt geändert durch Art. 2 der Verordnung zur Änderung abfallrechtlicher Nachweisbestimmungen [German Sewage Sludge Ordinance dated 15 April 1992. Last amended by Art. 2 of the Ordinance on the Amendment of Verification Regulations under Water Law] dated 25 April 2002, BGBl. I No. 28 dated 30.04.2002, p. 1488

Chemikaliengesetz (ChemG): Gesetz zum Schutz vor gefährlichen Stoffen. Neugefasst durch Bek. v. 20.06.2002, BGBl. I, S. 2090; zuletzt geändert durch Art. 183 Verordnung [German Chemical Law: Law on the Protection from hazardous Substances. New edition by Bek. Dated 20.06.2002. Last amended by Art. 183 dated 25.11.2003], BGBl. I p. 2304

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