

# 11. PRECIPITATION

## 11.1 Principles of Precipitation

Precipitation in a strictly chemical sense is the transition of a substance from the dissolved state to the non-dissolved state upon the addition of other (dissolved) reagents that lead to the formation of precipitates.

However, if chemicals causing precipitation are added to water, other reactions may also take place such as for instance coagulation. Thus, in any practical application of the precipitation process it is often very difficult to distinguish between these reactions. Only on the basis of a detailed knowledge of the composition of the (waste-) water matrix is it possible to describe the direction into which the process advances, i.e., which reaction is favored or which reaction is suppressed.

*Precipitation is accomplished by a reaction between a specific metal ion and an anion, for instance:*

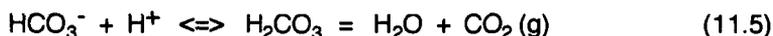


In surface water, and in the pore water, there is a predominance of the following anions: chloride, sulfate, carbonate, hydrogen carbonate, hydroxide, and under reducing conditions anionic species derived from hydrogen sulfide. The chlorides and sulfates of the common metals are readily soluble, whereas the carbonates, hydroxides and sulphides only dissolve with difficulty.

Hydroxides precipitate in several forms, which may behave quite differently with respect to the effects of co-precipitation or later redissolution. Precipitates may persist in metastable equilibrium with the solution and may slowly convert into the aged forms, thereby becoming more stable and inactive.

The solubility is highly dependent on pH, as the concentration of the precipitating anions hydroxide, carbonate or sulfide, decreases with decreasing pH due to reaction with the hydrogen ion:





With increasing pH, first carbonates and then hydroxides become the stable phase for many metal ions. For negative values of the reduction potential, the sulfide remains the stable phase over a wide pH range for many metal ions.

The various interacting processes, which determine the solubility at different pH values can conveniently be illustrated in a graphical double logarithmic representation; see below.

The concentrations of proteolytic species are characterized by the total alkalinity A, and pH. The total alkalinity is determined by adding an excess of a standard acid (e.g., 0.1 M), boiling off the carbon dioxide formed and back titrating to a pH of 6. During this process all the carbonate and hydrogen carbonate are converted to carbon dioxide which is expelled and all the borate is converted to boric acid. The amount of acid used (i.e., the acid added minus the base used for back titration) then corresponds to the alkalinity, Al, and the following equation is valid:

$$\text{Al} = C_{\text{H}_2\text{BO}_3^-} + 2C_{\text{CO}_3^{2-}} + C_{\text{BO}_3^-} + (C_{\text{OH}^-} - C_{\text{H}^+}) \quad (11.7)$$

where C = the concentration in moles per liter for the indicated species.

In other words the alkalinity is the concentration of hydrogen ions that can be taken up by proteolytic species present in the sample examined. Obviously, the higher the alkalinity, the better the solution is able to maintain a given pH value if acid is added. The buffering capacity and the alkalinity are proportional (see e.g. Stumm and Morgan, 1981).

Each of the proteolytic species in an aquatic system has an equilibrium constant. If we consider the acid HA and the dissociation process:



we have:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (11.9)$$

where  $K_a$  = the equilibrium constant.

It is possible, when the composition of the aquatic system is known, to calculate both the alkalinity and the buffering capacity, using the expression for the equilibrium constants. However, these expressions are more conveniently used in logarithmic form. If we consider the expression for  $K_a$  for a weak acid, the general expression (11.9), may be used in a logarithmic form:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = pK_a + \log [A^-] - \log [HA] \quad (11.10)$$

multiplying both sides of the equation by -1 and using the symbol p for -log and pH for -log  $H^+$ .

It is often convenient to plot concentrations of HA and  $A^-$  versus pH in a logarithmic diagram. If C denotes the total concentrations  $C=[HA]+[A^-]$ , we have at low pH:

$$[HA] \approx C \quad (11.11)$$

$$\log[A^-] = pH - pK_a + \log C \quad (11.12)$$

This means that  $\log[A^-]$  increases linearly with increasing pH, the slope being +1. The line goes through  $(\log C, pK_a)$  as  $pH=pK_a$  gives  $\log[A^-] = \log C$ .

Correspondingly, at high pH,  $[A^-] = C$  and

$$\log [HA] = pK_a - pH + \log C \quad (11.13)$$

which implies that  $\log[HA]$  decreases with increasing pH, the slope being -1. This line also goes through  $(\log C, pK_a)$ .

At  $\text{pH} = \text{pK}_a$ ,  $[\text{A}^-] = [\text{HA}] = C/2$  or  $\log [\text{A}^-] = \log [\text{HA}] = \log C - 0.3$

Table 11.1 and Fig. 11.1 show the result of these considerations for a single acid-base system.

Note that for  $\text{H}_2\text{A}$  the slope will be  $-2$  at  $\text{pH} > \text{pK}_2$ , corresponding to the dissociation of  $2\text{H}^+$ :

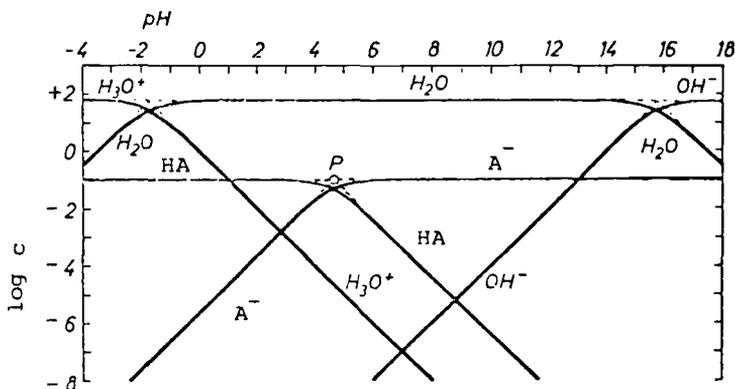
$\text{H}_2\text{A} = 2\text{H}^+ + \text{A}^{2-}$  and for  $\text{A}^{2-}$  the slope will be  $+2$  at  $\text{pH} < \text{pK}$ . This is demonstrated in Fig. 11.2.

$\beta$ , the buffer capacity, is defined as  $dC / d\text{pH}$ , where  $C$  is the added acid or base in moles of hydrogen or hydroxide ions respectively.

It can hence be shown that:

$$\log \left( \frac{\beta}{2.3} \right) = \log \left( [\text{H}_3\text{O}^+] + [\text{OH}^-] + \sum \frac{[\text{A}^-][\text{HA}]}{C} \right) \quad (11.14)$$

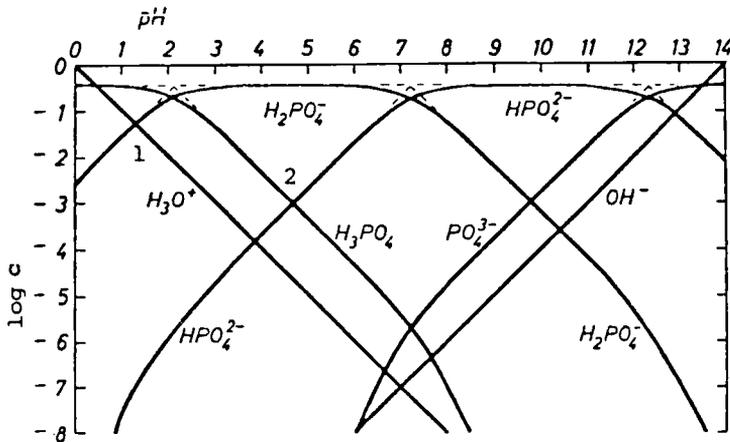
At  $\log \text{pH} [\text{HA}] = C$ , and only  $[\text{H}_3\text{O}^+]$  plays a role.



**Figure 11.1.**  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ ,  $\text{HA}$  and  $\text{A}^-$  are plotted versus  $\text{pH}$  for a weak acid with  $\text{pK}_a = 4.64$  and  $C = 0.1 \text{ M}$ .

**Table 11.1**  
**[HA] and [A-] at various pH-values**

pH	log [HA]	log [A-]
$\ll pK_a$	log C	pH - pKa + log C
$\gg pK_a$	-pH + pKa + log C	log C
= pKa	log C/2 = log C - 0.3	log C/2 = log C - 0.3



**Figure 11.2.** pH - log C diagram for phosphoric acid.

At higher pH, also  $\frac{[A^-][HA]}{C} = [A^-]$  contributes to  $\frac{\beta}{2.3}$

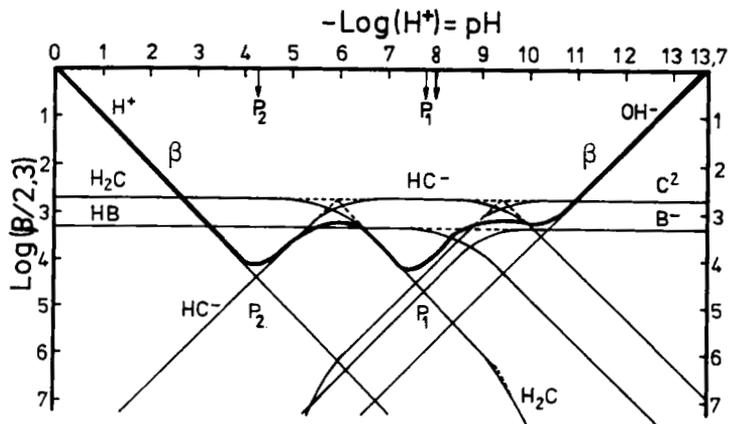
where  $[H_3O^+] = [A^-]$ ,  $\log\left(\frac{\beta}{2.3}\right) = \log(2[H_3O^+]) = -pH + 0.3 = \log(2[A^-])$ .

At still higher pH, but with values of  $pH < pK_a$ ,  $\log [A^-]$  dominates.

At  $pH = pK_a$   $\log \frac{\beta}{2.3} = \log \frac{\frac{C}{2} \frac{C}{2}}{C} = \log \frac{C}{4} = \log C - 0.6$

At  $pH > pK_a$ ,  $[A^-] = C$  and  $\log [HA]$  contributes the most to  $\frac{\beta}{2.3}$

At very high pH,  $\log [OH^-]$  will dominate. These considerations are used in the construction of Fig. 11.3



**Figure 11.3.** Buffering capacity of sea water as function of pH.

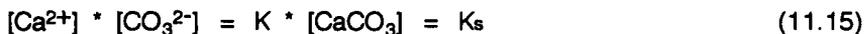
If one is dealing with waters containing very few components, then it is frequently possible to refer to precipitation processes in a stricter sense. Precipitation is a chemical reaction with a relatively fast rate. Thus, in most instances the rate itself is of no direct concern, and there exist no models to describe the rate aspects of the process. The application of the process depends to a large degree upon the equilibrium situation that characterizes this process. Thus, the precipitation process is described by use of the equilibrium or the end-point of the reaction for specified boundary conditions. However, it must be pointed out that for most practical applications such equations derived from thermodynamic principles, have to be modified.

If precipitation is defined as the transformation of two or more dissolved components to a non-dissolved substance, the so-called precipitate, then dissolution processes and precipitation processes are similar reactions but of opposite directions. The solubility of a product, or vice versa the degree to which precipitation will control the dissolved species, is determined by the capacity of the solute to accommodate specific ions. This capacity is controlled by:

- the energy of bonding between the ions under consideration
- the dielectric characteristics of the solute
- the type and number of ions present in the system

The solubility of certain species or the relationship between two or more precipitating partners is furthermore controlled by third partners which lead to so-called side reactions. The solubility is also determined by temperature and ambient pressure.

The **mass law** describes the solubility and the corresponding precipitation reaction in terms of a solubility product. As seen from the example below the solubility product,  $K_s$ , describes the equilibrium concentrations of the precipitating ions, in particular the ion to be removed by precipitation.



**The stoichiometric relationship** describes how many atoms, molecules or ions of one reaction partner react with corresponding forms of the other partner. Using the above example:

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = [\text{CaCO}_3]_{\text{prec}} \quad (11.16)$$

The **reaction rate** with which the precipitation occurs, or with which a disturbed solubility / precipitation equilibrium is balanced again, is finite. However, in most instances of interest for the practical application of this process, the reaction rate is so large that the available detention time, or reaction time, suffices to reach the equilibrium. It has been indicated above that either in the stage of mixing of chemicals with the waste water stream, or in the transport of the precipitating system from one reactor (mixing reactor) to the next one (in most cases a reactor for the liquid-solid separation) the flow or detention time is large enough. However, there are situations where a change in the stoichiometric parameters in terms of an overdosing of the precipitation causing reagent leads to improved reaction rates and to increased efficiency. Efficiency in this instance is interpreted as reduced remaining concentrations of the ion to be precipitated.

The *stoichiometric parameters* for practical purposes can also be formulated as a quotient of concentration values. This is indicated in the example below:

$$Q_u = \text{Al}^{3+} / \text{PO}_4^{3-} \quad (11.17)$$

On the basis of thermodynamic arguments this quotient should have a value of 1 in this instance shown above. However, practical observations have indicated that increased quotients may increase the reaction rate and the separation of the precipitate. Usually each precipitation reaction is followed in its practical application by a liquid-solid separation step. Depending upon the specific gravity of the solids formed or upon the amount of solids formed, such separation steps can be sedimentation, flotation or filtration.

It has been indicated that the equilibrium concentrations are a function of ambient pressure and temperature. Similarly the reaction rate is strongly affected by these parameters.

One further variable needs be described or defined: *the pH value* of the precipitating system which is of utmost importance. In aqueous solutions. The role of the process variables presented about will be treated in more detail in Section 11.2.

The application of precipitation as waste water treatment process involves a combination of three unit operations:

1. *Addition* of chemicals to obtain a precipitation. The process conditions determine the stoichiometric coefficient and thereby the amount of chemicals needed to produce a proper precipitation.
2. *Mixing and flocculation* of the chemicals to produce flocs, which settle or float readily.
3. A *separation process*, whereby the precipitated components are removed from the water. It might be performed either by sedimentation, flotation, centrifugation or filtration.

The first operation has been treated in details above, while the two following processes are presented below.

Colloidal particles often possess an electrical charge, which creates a repelling force and prevents aggregation. Stabilizing ions are adsorbed to an inner fixed layer, which gives its particles its electrical charge, the latter varying with the valence and number of adsorbed ions. Ions of an opposite charge are held near the surface by electrostatic forces. The psi potential is defined as the gradient between the interface of the colloidal particles and the solution, while the zeta potential is defined as the gradient between the slipping plane and the solution. The zeta potential is related to the particle charge and to the thickness of the double layer. It is not possible to measure the psi potential, but the zeta potential can be determined and expressed.

The zeta potential can be used as an expression for the stability. It is possible to measure it on the basis of the following equation:

$$\text{zeta potential} = \frac{4 p \mu}{X * E} U \quad (11.18)$$

where

- E = the dielectric constant of the medium
- $\mu$  = the viscosity of the medium
- X = the thickness of the double layer
- U = the electrophoretic mobility.

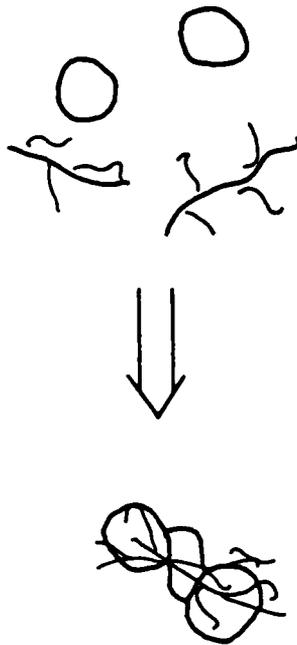
The zeta potential is determined by measuring the mobility of the colloidal

particles across the electrophoresis cell, viewed through a microscope. Several types of zeta meters are commercially available.

La Mer (1964) distinguished between two types of particle destabilization: coagulation and flocculation.

According to La Mer, coagulation results from compression of the electric double layer surrounding the colloids, while flocculation refers to a destabilization by adsorption of large organic polymers with a subsequent formation of bridges between particles and polymers. These definitions of the two terms - coagulation and flocculation - are not universally accepted, but are useful because they have a practical significance.

Fig. 11.4 is a schematic presentation of destabilization by flocculation.



**Figure 11.4** Destabilization by flocculation.

Lawler et al. (1983) has presented a mathematical model describing changes in the particle size (PSD) immediately below the solid/liquid interface in gravity thickening based upon Brownian motion, fluid shear, and differential sedimentation. Although the model predicted trends for the coagulation and differential sedimentation for changes in time, solids concentration, particle stability, and the subsidence velocity at the interface, the model was limited because the subsidence velocity cannot be predicted and a simplified approach to the hydrodynamics of differential sedimentation was used. Several mathematical models were developed by Babenkov (1983) to describe the relation between the density and the size of the flocs formed during coagulation. The characteristics of the final flocs depended on the size and density of the micro-flocs. Aluminum sulfate and cationic polymers provided efficient coagulation for coal processing waste waters.

In many cases agitation is used to accelerate the aggregation of colloidal particles. When particles follow a fluid motion they have different velocities, so that opportunities exist for interparticle contacts. When a contact between particles is caused by fluid motion the process is sometimes called ortho-kinetic flocculation (Overbeck, 1962).

The following equation describes the rate of change in the concentration of particles:

$$\frac{dN}{dt} = \frac{-2h \cdot \bar{G}d^3 \cdot N^2}{3} \quad (11.19)$$

where

- h = collision efficiency factor
- $\bar{G}$  = velocity gradient
- N = concentration of particles (number/vol.)
- d = diameter of particles
- t = time.

—  
G can be calculated (Camp and Stein, 1943) and (Camp, 1955) from

$$\bar{G} = \left( \frac{\bar{P}}{V m} \right)^{1/2} \quad (11.20)$$

where

$\bar{P}$  = the power input to the fluid

$V$  = the volume

$m$  = the viscosity of the fluid

Agitation will not increase the aggregation rate of particles smaller than about  $1 \mu$  diameter, whereas particles with a diameter of  $1 \mu$  or more will grow as a result of fluid motion. Since  $1 \mu$  particles do not settle well, a flocculation tank to allow aggregation must be included in a treatment system which uses sedimentation tanks at a later stage to separate solids from water. Flocculation tanks are designed to provide interparticle contact by orthokinetic flocculation. Design data include selection of velocity gradients, reactor configuration, reactor data and detention time necessary to produce sufficient aggregation. It is difficult to base the design on equations because such parameters as  $h$  and  $P$  are almost impossible to measure, and even the velocity gradient  $G$  can be difficult to determine. It is therefore necessary to provide information for design based on laboratory and pilot plant experiments. However, the interpretation of such an experiment is only possible using a mathematical description of the orthokinetic flocculation.

Suspended matter is removed from water by various separation processes, including sedimentation or settling. The principles of this process will be presented here, while other possible separation processes will be touched upon in Section 11.3, dealing with the design problems. Precipitates and coagulates might settle. Settling rates depend on the difference in density between the suspended matter and the water, the size and shape of the matter, the viscosity of water, the turbulence and velocity of the flow field. In addition, the physiological state of the phytoplankton cells also plays an important role.

In most cases it is not difficult to describe the sedimentation itself, but it is far more difficult to account for the influence of the hydrological flow pattern. Therefore theoretical approaches based upon physical considerations should almost always

be accompanied by measurements of sedimentation rates, either directly or indirectly. This latter determination is often carried out by use of tracers, for instance by use of isotopes.

Removal by settling is most often described as a first order reaction:

$$\frac{dm}{dr} = -s * m \quad (11.21)$$

where m is the concentration of suspended matter and s is the rate of removal by sedimentation, s is thereby also the ratio between the settling rate, Vs, and the depth D:

$$s = \frac{Vs}{D} \quad (11.22)$$

### **Discrete settling**

The settling of a discrete non-flocculating particle in a dilute suspension can be described by means of classical mechanics. Such a particle is not affected by the presence of other particles, and settling is therefore a function only of the properties of the fluid and the characteristics of the particles. As shown in Fig. 11.5 the particle is affected by three forces:

(1) Gravity, Fg; (2) the buoyant force, Fb and (3) the frictional force, Ff.

In accordance with Newton's second law of motion, the following equation can be set up:

$$m \frac{dvs}{dt} = Fg - Fb - Ff \quad (11.23)$$

where vs = the linear settling velocity of the particles, m = the mass of the particles and t = time.

The gravity effect is given by:

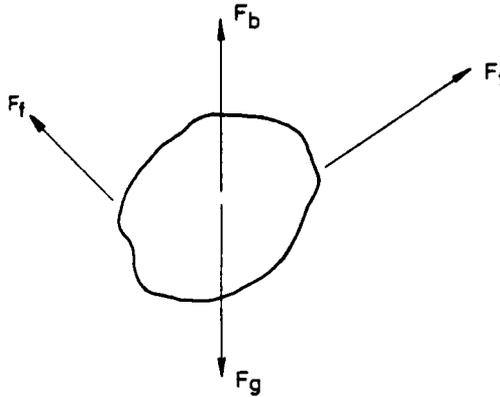
$$Fg = p * V * g \quad (11.24)$$

where  $p$  = the particle density,  $V$  = the particle volume and  $g$  = the acceleration due to gravity.

The buoyant force is:

$$F_b = p_e * V * g \quad (11.25)$$

where  $p_e$  = the fluid density.



**Figure 11.5.** The settling particle is affected by three forces: The gravity,  $F_g$ , the buoyant force,  $F_b$  and the frictional force,  $F_f$ .

The frictional force is a function of different particle parameters, such as roughness, size, shape and velocity of the particle, and of the density and viscosity of the fluid. It can be described by the following relationship:

$$F_f = \frac{C_d * A * p_e * v_s^2}{2} \quad (11.26)$$

where  $C_d$  = Newton's dimensionless drag coefficient and  $A$  = the projected particle area in the direction of the flow.  $C_d$  varies with the Reynolds number.

By substituting the equations (11.24), (11.25) and (11.26) in equation (11.23), an expression for the dynamic behavior of the particles is obtained:

$$m \cdot \frac{dv_s}{dt} = g(p - p_e) V - \frac{C_d \cdot A \cdot p_e \cdot v_s^2}{2} \quad (11.27)$$

After an initial transient period the acceleration becomes zero and the velocity is constant. This velocity can be obtained from equation (11.27):

$$v_s = \left( (2g(p - p_e) \cdot V) / (C_d \cdot p_e \cdot A) \right)^{1/2} \quad (11.28)$$

If the particles are spherical and the diameter is  $d$ , the  $V/A$  is equal to  $2/3 \cdot d$  and equation (6.8) becomes:

$$v_s = \left( (4g(p - p_e) \cdot d) / (3C_d \cdot p_e) \right)^{1/2} \quad (11.29)$$

Newton's drag coefficient  $C_d$  is, as mentioned, a function of the Reynolds number and of the shape of the particle. The relationship between  $C_d$  and the Reynolds number for spheres and cylinders is given in Fig. 11.6.

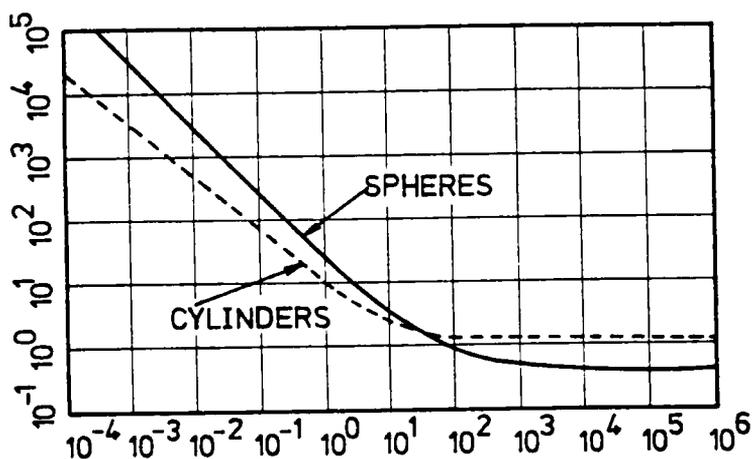
When the Reynolds number is below 1, the relationship between  $C_d$  and  $Re$  can be approximated by  $C_d = 24/Re$ , where  $Re$  = Reynolds number defined as:

$$\frac{d \cdot p_e \cdot v_s}{\mu}$$

where  $\mu$  = the viscosity

In this case (11.29) conforms with Stokes law:

$$v_s = \frac{g}{18\mu} (p - p_e) \cdot d^2 \quad (11.30)$$



**Figure 11.6.** Experimental variation of the drag coefficient with Reynolds number. After Fair et al. (1968).

From Fig. 11.6 it can be seen that  $C_d$  is approximately constant for turbulent flow in the range for Reynolds number between 1000 and 250,000. For this region the velocity  $v_s$  is given by:

$$v_s = 1.82 \left( \frac{(\rho - \rho_e) \cdot d \cdot g}{\rho_e} \right)^{1/2} \text{ (for spheres only)} \quad (11.31)$$

Stokes law can be modified to account for non-spherical flocs by use of an "equivalent radius" and shape factor in the formulation:

$$V_s = \frac{2}{9} \frac{g R^2 (\rho_p - \rho_w)}{v \cdot F_s} \quad (11.32)$$

where

- $V_s$  = settling velocity, length/time
- $g$  = acceleration due to gravity, length/time<sup>2</sup>
- $R$  = equivalent radius (based on a sphere of equivalent volume), length
- $\rho_p$  = density of the cell, mass/length<sup>3</sup>

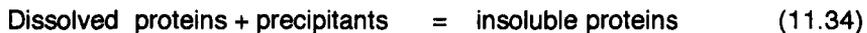
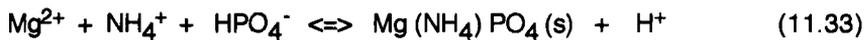
$\rho_w$  = water density, mass/length<sup>3</sup>

$\nu$  = kinematic viscosity

$F_s$  = shape factor

The shape factor has a value  $< 1.0$  and accounts for all factors, reducing the settling velocity.

Most nitrogen components are unfortunately readily dissolved in water, which implies that precipitation cannot be used as an easy solution to the problem of nitrogen removal, in contrast to phosphorus, which is widely removed from waste water by the use of chemical precipitation. Nitrogen removal by use of precipitation may, however, be carried out by the following two processes:



Process (11.33) looks at the first glance as a very attractive solution, as phosphate and ammonium are precipitated simultaneously. The stoichiometric ratio between the two components in municipal waste water is however not favorable for the precipitation. The concentration of phosphate is about 10 mg / l or 0.3 mmol / l, while ammonium is normally present as ammonium-N in a concentration of about 30 mg / l or about 2 mmol/l.

This implies that phosphate must be added to assure a proper precipitation. This makes the process much more expensive, although the product magnesium-ammonium-phosphate is an appreciated fertilizer. The process has therefore not been used for removal of nitrogen from municipal waste water except in pilot plant experiments in Bari, Italy. It might be more attractive to utilize the process, where the stoichiometric ratio between N and P is more favorable, but the ratio in most industrial waste waters is even more unfavorable than in municipal waste water.

The precipitation of proteins by use of various precipitants such as ligno-sulfonic acid, iron (III) chloride, calcium hydroxide, glucose-tri-sulfate or just pH-adjustment has been widely used. The precipitation is carried out at the isoelectric point of the proteins, where the destabilization is most easily performed. As waste

water often contains a wide range of proteins, it is not possible to adjust the pH for all proteins at the same time, so that precipitation of proteins never can become 100 % effective.

## 11.2. Process Variables

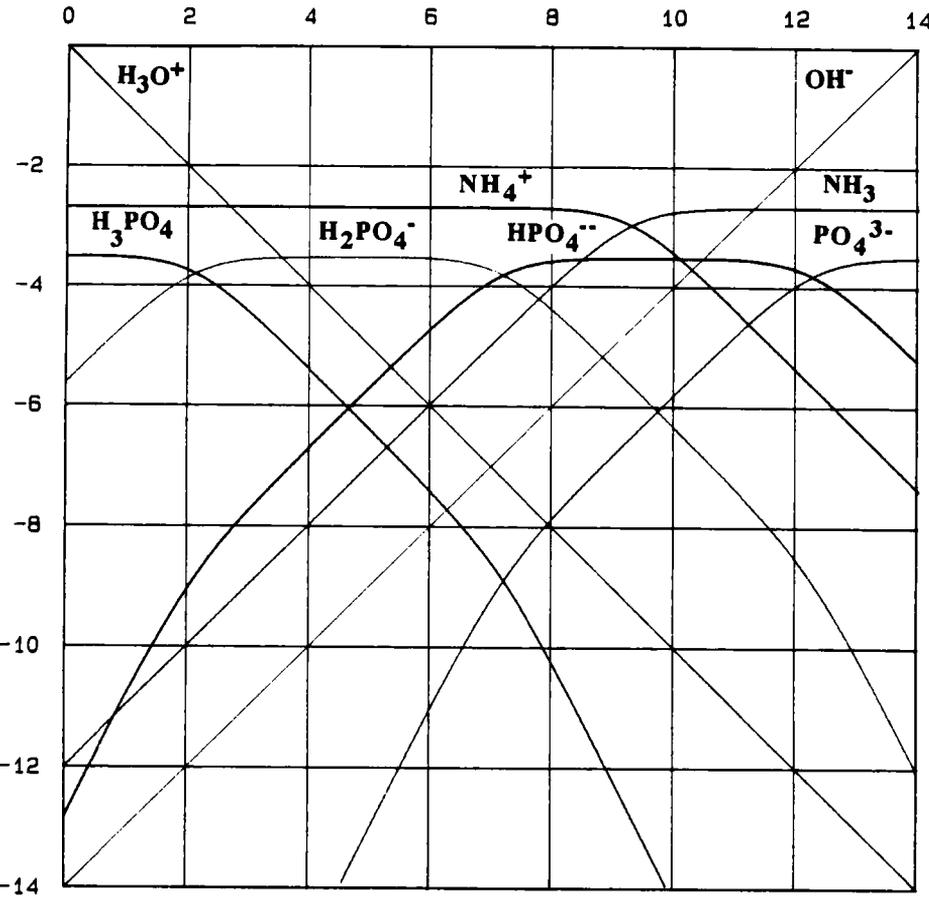
It is possible to play on two variables to optimize the application of precipitation by nitrogen removal: the stoichiometric coefficient and pH. The composition of the waste water determines the possibilities of finding a good solution to a particular waste water problem by the use of these two variables.

The optimum pH for precipitation of magnesium-ammonium-phosphate may be found by use of double logarithmic diagrams, as presented in Section 11.1. The method is best illustrated by presentation of a concrete case study. Let us consider a waste water with the concentration of ammonium at 2mmol/l and of phosphate at 0.3 mmol/l, corresponding to municipal waste water. Let us furthermore presume that we use 0.02 mol/l magnesium for the precipitation. What, under these circumstances, is the optimum pH? Several processes are interacting: the acid-base reactions of phosphate. Phosphoric acid has three pKa-values: 2.1, 7.2 and 12.3; see also Fig. 11.2. Ammonium has a pKa-value of 9.25. The solubility product of magnesium-ammonium-phosphate is  $10^{-12.6}$ . Let us also assume that the ionic strength is too small to have any significant influence on the equilibrium constants.

Figure 11.7. is a double logarithmic diagram of phosphate and ammonium in the actual concentrations. It can be seen on the diagram that the product of ammonium and phosphate reaches its highest value at about pH = 10.7, which is the optimum for the precipitation, when the concentrations of free magnesium ions are accounted for.

Figure 11.8 is constructed from 11.7. The product of the phosphate and ammonium concentrations are plotted versus pH and on the diagram shows, where the product exceeds  $10^{-10.6}$ , corresponding to a magnesium concentration of 10 mmol/l. It is possible to obtain an effective precipitation but the stoichiometric ratio between phosphate and ammonium must of course be 1:1 to assure that both components are readily precipitated. It implies, that if 1.7 mmol/l phosphate and 10

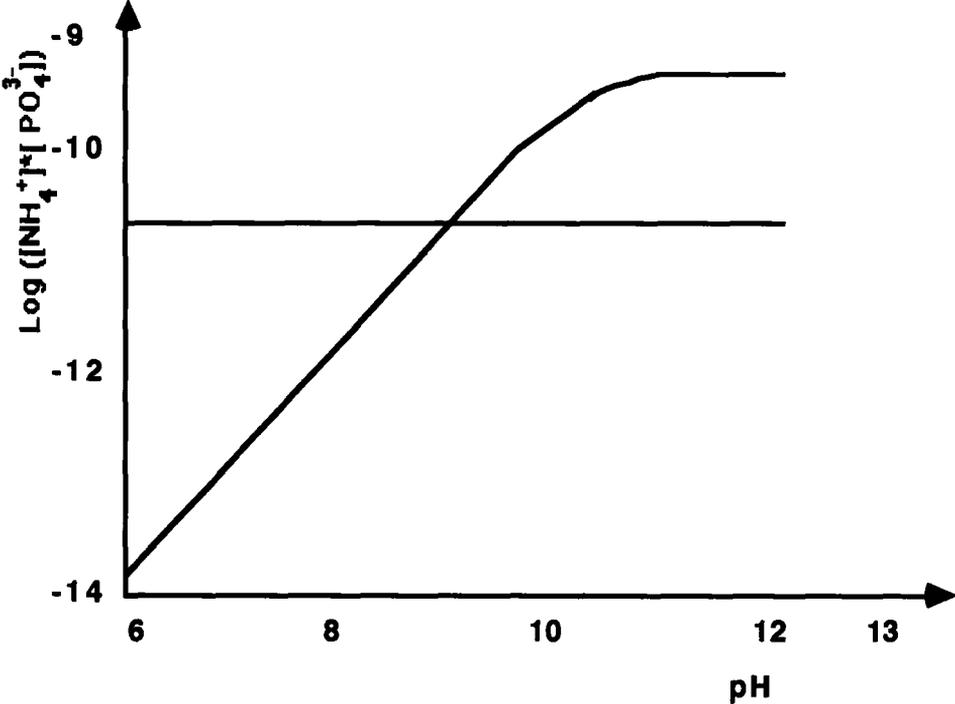
mmol / l magnesium are added, an almost complete removal of ammonium and phosphate is possible.



**Figure 11.7.** Double logarithmic plot of ammonium and phosphate in the concentrations found generally in municipal waste water.

It is not possible theoretically to calculate the optimum condition for precipitation of proteins. It is necessary to make laboratory experiments to arrive at the relationship between removal efficiency on the one hand and pH, the amount and type of precipitant on the other; see for instance Jørgensen (1989). Several precipitants in combinations with at least a few polyfloculants must be tested at 3 or more different pH values. The settling rate is observed and used, as will be

shown in Section 11.3, to design the sedimentation unit, while plots of the type shown in Figs. 11.9 -10 are used to determine which precipitant to use, in which amount and at which pH to obtain the best precipitation. As seen in Fig. 11.9 the obtained COD of the effluent is plotted versus the amount of precipitant added for three different precipitants. BOD5 or the permanganate number or the total nitrogen concentration could of course also be used.

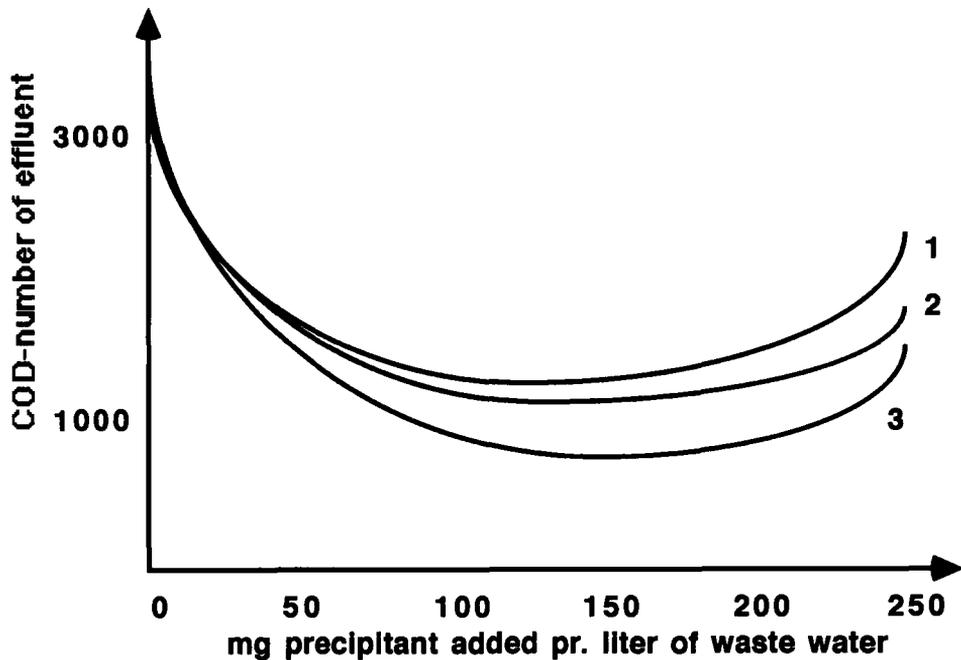


**Figure 11.8.**The product of phosphate and ammonium concentration, taken from Fig. 11.7, is plotted versus pH in a double logarithmic diagram.

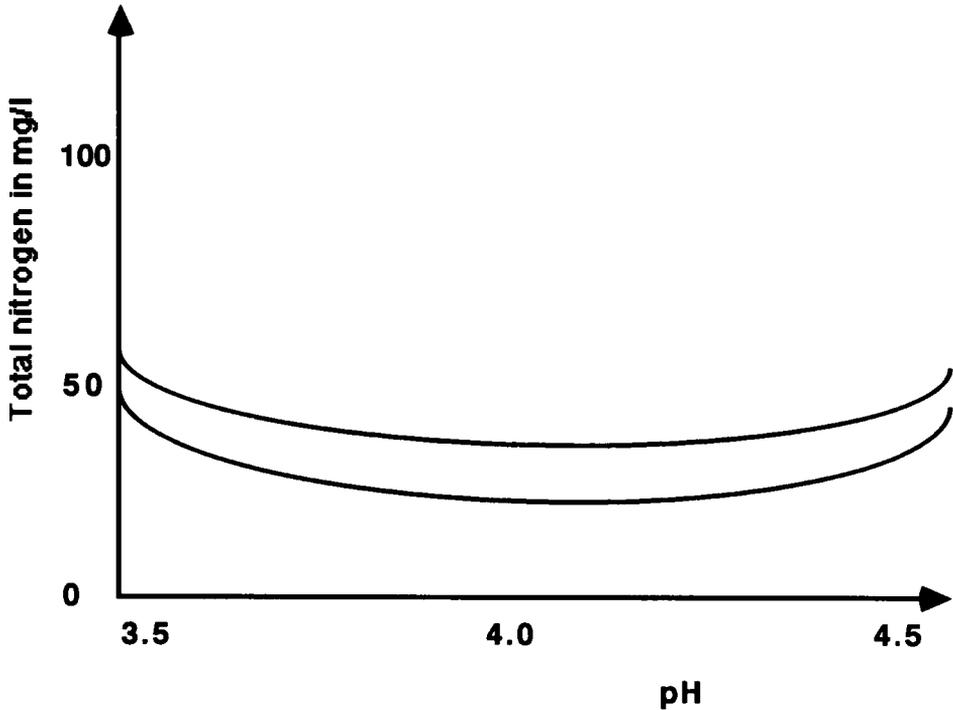
The effluent quality at optimum dosage is plotted versus pH for each of the selected precipitants to find the optimum pH; see Fig. 11.10. Here the nitrogen concentration of the effluent is used as quality parameter.

Another question to raise is of course: what is the economic optimum? An answer to this question requires that the relationship between the cost of waste water discharge and the effluent quality is known and can be compared with the cost of the added chemicals (precipitant, polyfloculant) and acid (to obtain the

right pH). Recovery of proteins might, on the other hand give an income, which should be included in the financial calculations on the various alternatives. The experience gained from such calculations shows that the economic optimum very often is close to the technical optimum, i.e. it pays to utilize the technical possibilities to obtain the best effluent quality with the lowest nitrogen concentration.



**Figure 11.9.** COD (mg/l) of effluent versus dosage of three different precipitants used on waste water from a brewery are shown. 1. corresponds to the use of iron III chloride at pH = 4.2, 2 the use of glucose-tri-sulfate at the same pH and 3 the use of lignosulphonic acid at pH = 4.5. Note that the initial COD is 3300 mg/l.



**Figure 11.10.** The figure gives the quality of the effluent obtained by precipitation with lignosulphonic acid (lower curve) and glucose-tri-sulfate (upper curve) on brewery waste water. Optimum dosage of chemicals according to Fig. 11.9 is presumed.

The temperature influences the solubility of magnesium-ammonium-phosphate and of proteins. The solubility decreases for both with increasing temperature, but it is hardly possible to regulate the temperature to obtain better conditions for the precipitation.

The settling rate is also dependent on the temperature, too. Various expressions have been suggested to describe this relationship:

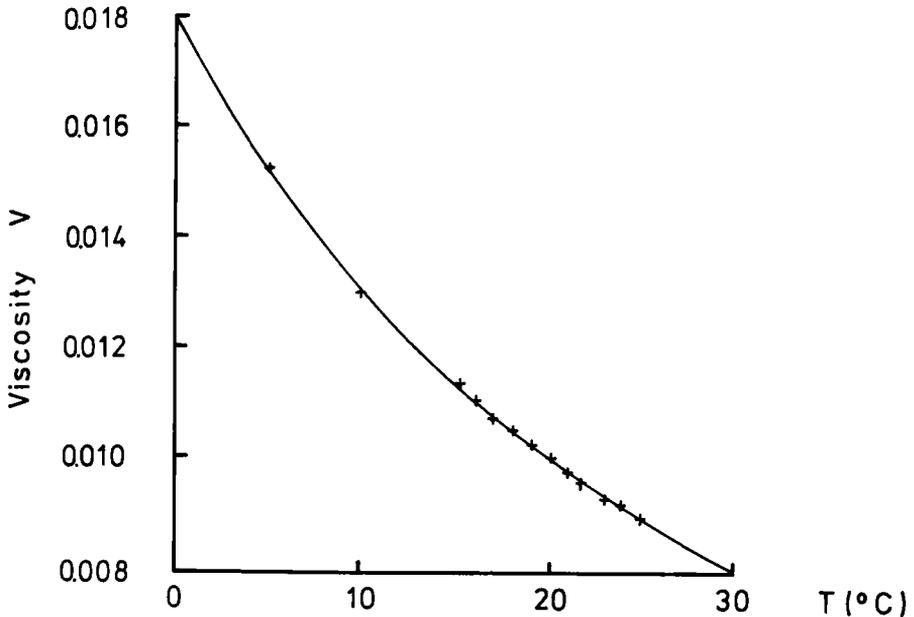
$$V_{S,T} = V_{S,Tr} \cdot \sqrt{(T/Tr)} \quad (11.35)$$

where  $V_{S,T}$  is the settling rate at the absolute temperature  $T$ , and  $V_{S,Tr}$  is the settling rate at the absolute reference temperature  $Tr$ .

Tetra Tech (1980) uses:

$$fs(T) = \frac{157.5}{0.069T^2 - 5.3T + 177.6} \quad (11.36)$$

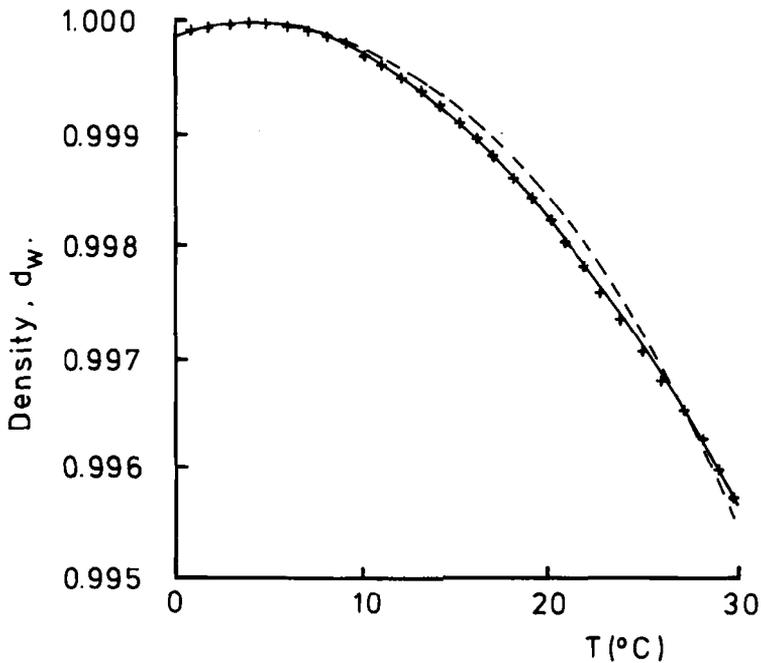
where T = temperature in °C and fs(T) is a temperature adjustment function.



**Figure 11.11.** Viscosity,  $v$ , plotted versus temperature. A regression analysis will show the following relationship:  $\mu_w = 0.178 / (1 + 0.0337 \cdot T + 0.00022 \cdot T^2)$

Straskraba and Gnauck (1985) suggest another method for considering the influence of temperature on the settling rate. They use the known relations between viscosity and density of water on the one hand and the temperature on the other; see Figs 11.11 and 11.12.

These relations have been used in the construction of a diagram giving the settling rate versus the temperature, as it is known that the sedimentation rate,  $U$ , is proportional to  $da - dw / \mu_w$ . The larger  $da$ , the more strongly pronounced is the temperature dependence.  $da$  is the density of the particles,  $dw$  the density of water and  $\mu_w$  is the viscosity of water.



**Figure 11.12** Density of water,  $d_w$ , plotted versus temperature. A regression analysis will show the following relationship:  $d_w = 0.999879 + 6.02602 \cdot 10^{-5} \cdot T^3$ .

### 11.3. Design of Plants for Precipitation of Nitrogen Compounds

As mentioned in Section 11.1, the application of precipitation requires a three-step plant. **Addition of chemicals** is the first step. It requires some sort of automatic dosage equipment, where the amount of chemicals added to the waste water is determined by either pH, the flow or another parameter, that is feasible to measure and relates to the quality of the influent.

The **design of the flocculation tank** can be based on a first order process.

The number of particles/ volume, N, is transformed into the volume of particles per unit volume of suspension:

$$R = \frac{\pi d^3}{6} N \quad (11.37)$$

where R = the volume of colloidal particles per unit volume of suspension.

Substitution of equation (11.37) into equation (11.19) gives:

$$\frac{dN}{dt} = -4 \frac{h}{\pi} \bar{G} \cdot R \cdot N \quad (11.38)$$

- a first order reaction.

Integration of this equation for the boundary conditions  $N = N_0$  at  $t = 0$  yields:

$$\ln \frac{N}{N_0} = \frac{-4hR \cdot \bar{G} \cdot t}{\pi} \quad (11.39)$$

These considerations allow us to apply the equations for a complete mixed flow reactor in combination with an equation for a *first order reaction*.

A complete mixed flow (CMF) reactor is generally designed on the basis of the following equation; see Fig.11.13:

$$\frac{VdC_1}{dt} = Q \cdot C_0 - QC_1 + V \cdot r(C_1) \quad (11.40)$$

where  $r(C_1)$  = the reaction rate.

For steady state conditions, provided the reaction is a first order reaction, we have:

$$Q \cdot C_0 - QC_1 - k \cdot C_1 \cdot V = 0 \quad (11.41)$$

where k = the reaction coefficient.

Dividing this equation by  $Q \cdot C_1$ , gives:

$$\frac{C_0}{C_1} - 1 - k * t_m = 0 \quad (11.42)$$

where  $t_m = V/Q$ , the mean residence time in the complete mixed flow reactor.

The equation can also be written as:

$$\frac{C_1}{C_0} = \frac{1}{1 + k * t_m} \quad (11.43)$$

or

$$t_m = \frac{1}{k} \left( \frac{C_0}{C} - 1 \right) \quad (11.44)$$

However, there are advantages in applying a number of reactors in series. Let us consider  $m$  first order CMF-reactors each with volume,  $V$ . A mass balance identical to the one used for equation (11.43) gives for the second tank:

$$\frac{C_2}{C_1} = \frac{1}{1 + k * t_m} \quad (11.45)$$

where  $C_2$  = the effluent concentration from tank 2.

The effluent concentration from reactor 2 can also be expressed in terms of inflow concentration of the first reactor by multiplying equations (11.43) and (11.45):

$$\frac{C_2}{C_0} = \left( \frac{1}{1 + k * t_m} \right)^2 \quad (11.46)$$

In a similar way, the effluent concentration,  $C_m$ , from the last reactor in a series of first order CMF-reactors may be expressed in terms of the concentration of the inflow to the very first reactor:

$$\frac{C_m}{C_0} = \left( \frac{1}{1 + k * t_m} \right)^m \quad (11.47)$$

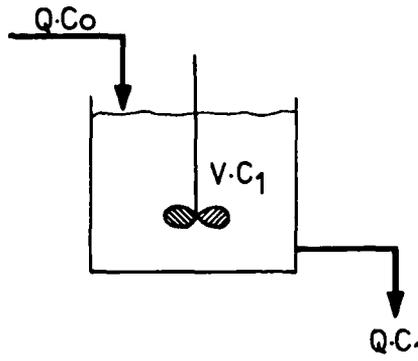
The total detention time required to achieve a given reaction will therefore

be:

$$mt_m = \frac{m}{k} \left( \left( \frac{C_0}{C_m} \right)^{1/m} - 1 \right) \quad (11.48)$$

If this consideration is used for the flocculation unit the following equation can be set up:

$$mt_m = \frac{\pi * m}{4\pi GR} \left( \left( \frac{N_0}{N_m} \right)^{1/m} - 1 \right) \quad (11.49)$$



**Figure 11.13.** Complete mixed flow reactor. Flow rate  $Q$ , volume of tank  $V$ , concentration in tank  $C_1$ , and the input concentration is  $C_0$ .

The third step is the separation of the suspended matter and the clear water phase. Several possibilities are available for this step, as mentioned in Section 11.1. Centrifugation and filtration are, however, rarely used due to their high costs for the great amount of waste water which must be treated in most cases. The design of these two operations is therefore not included, while settling and flotation will be covered in this section.

Suspended solid in waste water cannot usually be described as discrete particles. If any of the interacting particles have characteristics that might cause agglomeration, growth of individual particles to larger size is a natural consequence. Hence, the greater the tank depth, the greater is the opportunity for contact among particles and so sedimentation depends on the depth as well as on the properties of the fluid and the particles.

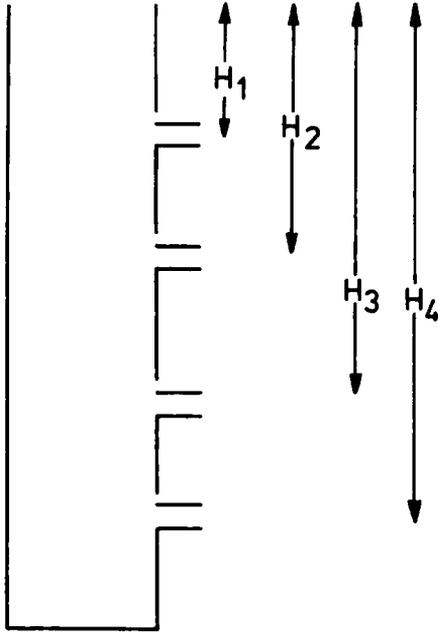
At present there is no satisfactory formulation for predicting the effect of flocculation on the settling rate. Thus flocculent settling requires extensive testing to define the characteristics of the waste water in this respect.

Evaluation of the **sedimentation** characteristics of flocculent settling can be accomplished by placing a quantity of the waste water in a column similar to the one shown in Fig. 11.14. The diameter of the column must be sufficient to ensure that the edge effect is almost eliminated. The suspension is settled and the concentration of the particles is determined from samples withdrawn at the different sampling points. The fraction of the particles removed at each step is used to construct lines showing equal fraction or equal percentage removal, as illustrated in Fig. 11.15. The lines are named iso-concentration lines; the per cent maximum settling path for the indicated per cent removal.

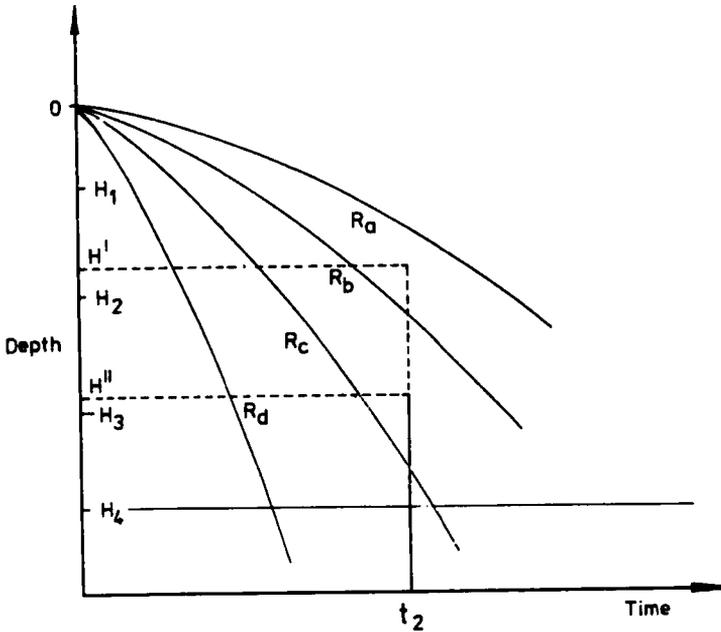
If the tank has an overflow of  $v_1 = H_4 / t_2$ , (see Fig. 11.15) all particles having a settling velocity  $\geq v_1$  will be removed from the tank and particles with a velocity  $v < v_1$  will be removed in proportion to  $v / v_1$ . The figure shows that the remaining solid between  $R_a$  and  $R_b$  has settled with an average velocity of  $v = H' / t_2$ , and the solid between  $R_c$  and  $R_d$  has settled with an average velocity of  $H'' / t_2$ . An approximation for the total overall removal,  $R$ , by the chosen overflow is given by:

$$R = R_c + H'' (R_b - R_c) / t_2 v_1 + H''' (R_a - R_b) / t_2 v_1 \quad (11.50)$$

This approximation can be improved by adding more terms and decreasing the interval between the iso-concentration lines.

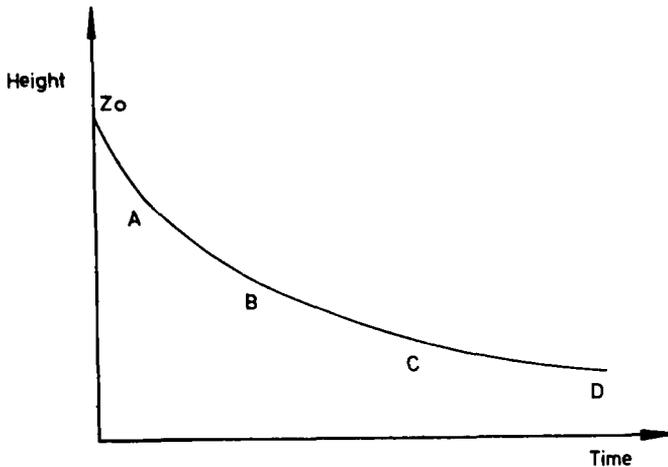


**Figure 11.14.** Column with four sampling points for settling tests.

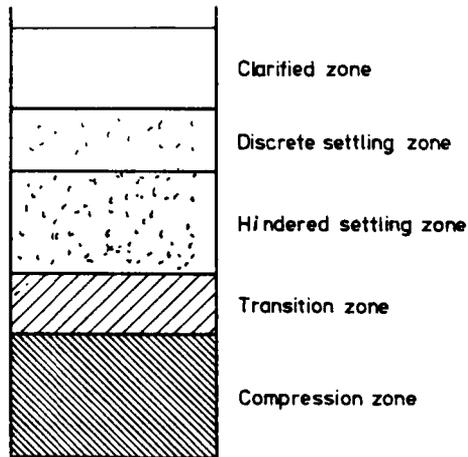


**Figure 11.15.** The results of a settling test illustrated with iso-concentration lines.

**Zone settling** of flocculated chemicals suspension occurs when the concentration of solids exceeds approximately 0.5 g/l. The particles form a mass, which settles as blanket with a distinct interface between the settling sludge and the clarified effluent. The interface can be observed in a batch settling test. Initially all the suspension is at a uniform concentration and the height of the interface as  $Z_0$ ; see Fig. 11.16, which shows the height of the interface plotted versus time. In the region A-B, settling is hindered, but proceeds at a constant rate. The region B-C shows a transition into the compression zone, represented by C-D. The zones are further illustrated in Fig. 11.17.



**Figure 11.16.** Height of interface in zone settling as function of the time.



**Figure 11.17.** Illustration of the zones in zone settling.

It is possible to design a continuous clarifier based on the batch test. Two areas must be calculated; A1, the area required for clarification, and A2, the area required for thickening. A1 can be calculated from:

$$A1 = Q / v_s \tag{11.51}$$

where  $v_s$  is the velocity for hindered settling and Q is the rate of flow through the tank. To find A2 it is necessary to find the relationship between settling rate and the concentration of the sludge. The tangent is drawn at different points of the settling curve and the slope of the tangent indicates the settling rate, v; see Fig. 11.18. The corresponding concentration in the sludge is calculated from the following equation:

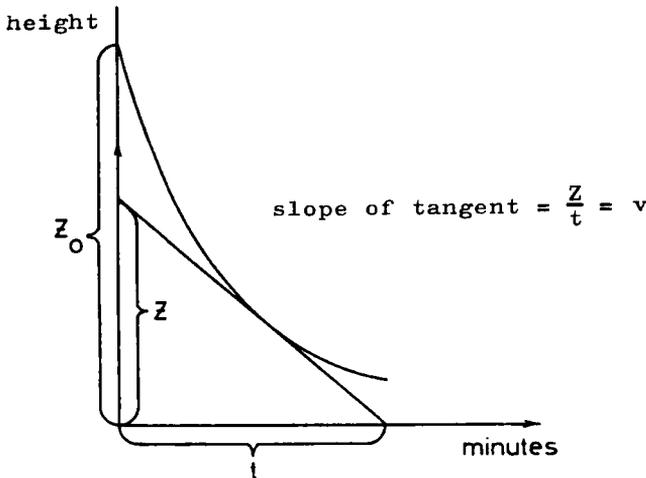
$$C = C_0 \cdot Z_0 / Z \tag{11.52}$$

where  $C_0$  is the slurry concentration at the start of the settling,  $Z_0$  is the total height of the clarifier and  $Z$  is shown in Fig. 11.18. By this equation it is possible to calculate  $C$ , the concentration of suspended solid in the sludge layer, as a function of the settling rate. It is now possible to calculate  $W_s$ , defined as the weight of solid in sludge produced per minute per  $m^2$ :

$$W_s = v / (1/C - 1/C_s) \quad (11.53)$$

where  $C_s$  is the required concentration of suspended solid in the layer.  $W_s$  is calculated for values of  $C$ , and the minimum value is used to determine the area necessary for thickening. The area per  $m^3/h$ ,  $A$ , is found by dividing the sludge concentration  $C_0$  by  $W_s$ , where  $C_0$  is defined above. It means that:

$$A = C_0 / W_s \quad (11.54)$$



**Figure 11.18.** Sedimentation curve.  $Z_0$  is total height. Slope of tangent (0 settling rate) is found as  $Z/t$ .

It is frequently possible to improve the performance in an existing settling tank by making modifications based on the results of a dispersion test. The addition of stream-deflecting baffles, inflow dividing mechanism and velocity dispersion feed wells may decrease short circuiting and increase efficiency.

Fig. 11.19 illustrates the principle of tube settlers. The design incorporates the use of very small diameter tubes in an attempt to apply the shallow depth principle as suggested by Camp (1946).

Flow through tubes with a diameter of 5-10 cm offers optimum hydraulic conditions and maximum hydraulic stability. Culp et al. (1968) have reported excellent results using tube settlers with a retention time of less than 10 minutes. The retention time can be calculated according to the following equation:

$$YA = v_s \left( \frac{L}{S} \cos \beta + 1 \right) \quad (11.55)$$

where

$$YA = \frac{Q}{A} = \frac{\text{flow rate}}{\text{area of tube settler}}$$

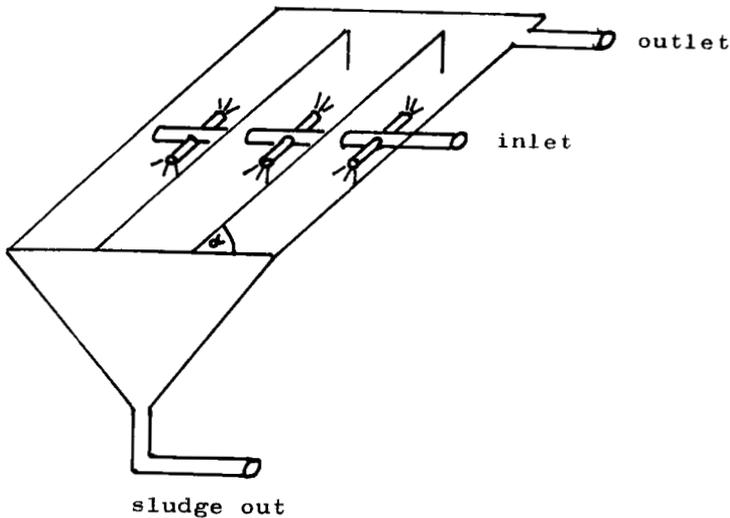
- L = length of tube
- S = distance between the tubes (the diameter of the tubes)
- $\beta$  = the angle of the tube to the horizontal (see Fig. 11.19)
- $v_s$  = direct settling rate

As can be seen from this equation,  $Q/A$  will increase as  $\beta$  decreases. It should therefore be an advantage to place the tubes as near as possible to horizontal. However, the horizontal settler is not self-cleaning and must be back-washed. Therefore, the steeply inclined  $60^\circ$  tube settler is more commonly used. Continuous gravity draining of settled solid might be achieved from tubes inclined at angles between  $45$  and  $60^\circ$ .

The clarifier may be designed as a rectangular or circular tank, and may utilize either center or peripheral feed. The tank can be designed for center sludge withdrawal or for withdrawal over the entire tank bottom.

It is very difficult to design a full-scale sedimentation tank based on settling experiments, as presented above. Several important factors influencing particle behavior in a full-scale operation are neglected in such experiments. Tanks are

subject to eddies, currents, wind action, resuspension of sludge, etc. A full-scale clarifier will therefore show a slightly reduced efficiency compared to settling experiments, but this can be considered by incorporating a safety factor. The choice of an acceptable safety factor requires experience. The practical factor might vary from 1.5 when the tank is very small, baffled and protected from wind, to 3.0 in the case of a large tank, unbaffled and unprotected from wind. Even with the use of the safety factor, however, perfect performance should not be expected.



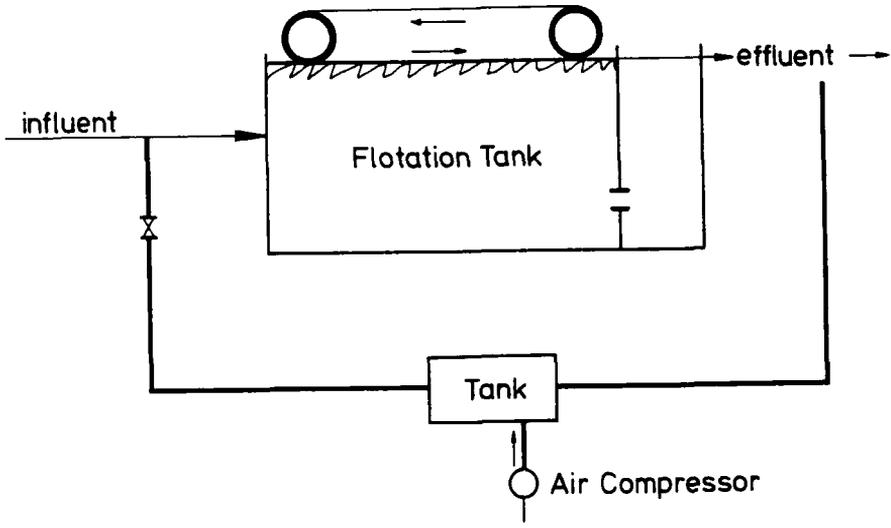
**Figure 11.19.** Steeply inclined tube settler.

**Flotation** is used to remove suspended solid from waste water and to concentrate sludge. Thus flotation offers an alternative to sedimentation, especially when the waste water contains fat and oils.

Either a portion of the waste water or the clarified effluent is pressurized at 3-6 atm. When the pressurized water is returned to normal atmospheric pressure in a flotation unit, air bubbles are created. The air bubbles attach themselves to particles and the air-solute mixture rises to the surface, where it can be skimmed off, while the clarified liquid is removed from the bottom of the flotation tank.

Fig. 11.20 shows a flotation system with partial recirculation of the effluent. Generally it is necessary to estimate the flotation characteristics of the waste water by use of a laboratory flotation cell:

1. The rise of the sludge interface must be measured as a function of time.
2. The retention time must be varied and the corresponding saturation of pressurized water determined.
3. The effluent quality must be determined as a function of the air/solids ratio, Based on such results it is possible to scale up appropriately.



**Figure 11.20.** Flotation unit.

#### 11.4. Application of Nitrogen Removal by Precipitation

Nitrogen removal by precipitation of magnesium-ammonium-phosphate has not yet found a full scale application, but it cannot be excluded that the process will be used in the nearest future for industrial waste water of the right composition to allow an economical removal of phosphorus and nitrogen at the same time.

Schulze-Rettmer (1991) has examined the process in details and finds that it is an attractive method to use for nitrogen removal, from a technical as well as from an economic's point of view. He calculates that the removal of 1 kg ammonium- N by precipitation as magnesium-ammonium-phosphate, using magnesium oxide and phosphoric acid as chemicals, will cost about 5 U.S. Dollars. The costs are

reduced if the waste water contains significant quantities of phosphate and magnesium. The cost of chemicals is estimated to be 70% of the total costs. This implies that a reduction of the ammonia concentration in municipal waste water from 40 mg ammonium-N / l to 5 mg ammonium- N / l will cost about 25 U.S. cents / m<sup>3</sup>, which is comparable to nitrification and denitrification. The value of the magnesium ammonium phosphate produced by this process can be estimated as 12 U.S. cents / kg, considering the purity of the product, compared with 25 U.S. cents / kg for the usually applied technical quality. The conclusion from this review of the process by Schulze-Rettmer is that the precipitation of ammonium-N as magnesium-ammonium-phosphate is economically feasible and should be considered as a serious alternative to other nitrogen removal processes.

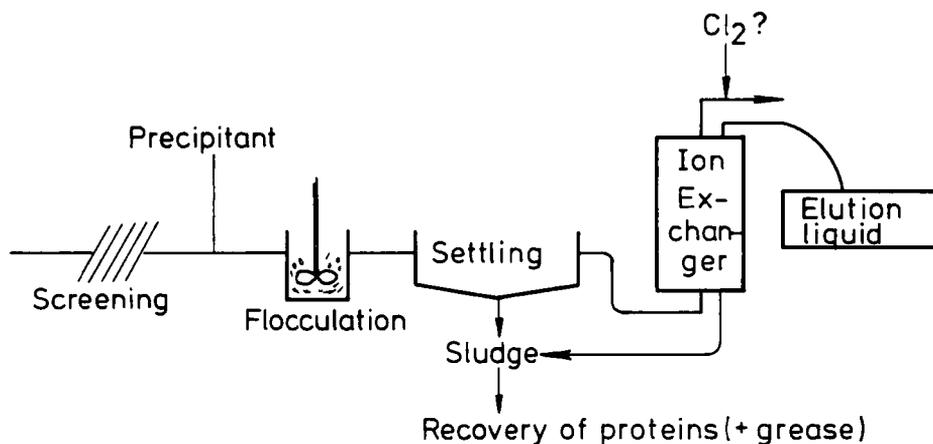
Precipitations of proteins have, however, been widely used. A discharge fee for waste water related to the concentrations of pollutants has been introduced in many countries, i.e. the fee is found on basis of BOD<sub>5</sub>, COD, phosphorus and/or nitrogen concentrations in the effluent. This has provoked many industries and in particular food industries to introduce a waste water treatment, which is able to reduce the concentrations of BOD<sub>5</sub>, COD, phosphorus and / or nitrogen to the level of municipal waste water. The industries are thereby able to reduce their discharge costs considerable. It can be shown that the costs of the treatment including depreciation and interest of the treatment plant often are much lower than the discharge costs, which makes it profitable for the industries to introduce treatment of the effluent.

Recovery of proteins gained by precipitation of industrial waste water is, unfortunately, only accomplished in few industries. Some industries deliver free of charge the protein-rich sludge to meat-bone-meal factories, where the sludge is treated as other waste, which is the raw material for the production. As it is expected that dumping of any solid waste product will be more and more limited in the future, the use of the sludge from treatment of food processing waste water for production of animal feed will probably become more and more attractive. The general development seems clear for industrial waste water: from no treatment, to treatment due to high discharge fees and finally to recirculation and recovery of waste products.

Figure 11.21 is a flow diagram of the combination of chemical precipitation and ion exchange used in the treatment of waste water from the food industry

(Jørgensen, 1971, 1973, 1976 and 1978). This process allows recovery of fat, grease and proteins. Table 11.2 gives the analytical data obtained when this process was used on waste water from herring filleting after centrifugation of the raw waste water to recover fish oil. Table 11.3 gives the analyses of this process for waste water from an abattoir. For comparison Table 11.13 includes the results obtained by using a biological plastic filter.

It can be concluded from these results that the application of chemical precipitation to waste water from the food processing industry is advantageous to use to reduce the pollution to or almost to the level of municipal waste water. The process is able to reduce the nitrogen concentration of these types of waste water considerably and can therefore be considered as an attractive method for the removal of nitrogen, although the method is most often selected because of its over-all effect of BOD-5, COD, P and N-reduction. The method is simultaneously a practical method for recovery of proteins and it is expected that this feature of the process will become increasingly important in the coming years.



**Figure 11.21** Recovery of proteins (+ grease).

**Table 11.2.****Analytical data of waste water from herring filleting**

	Raw waste water	After cen- trifuga- tion 1. step	After chem. precipi- tation 2. step	After Cel- lulose ion- exchanger 3. step
BOD5 (mg/l)	11000	5800	2000	1100
N (mg/l)	180	162	60	23
Susp. matter (mg/l)	400	170	40	2
KMnO <sub>4</sub> (mg/l)	8000	4000	1200	600

**Table 11.3****Analysis of waste water from an abattoir (mg/l)**

	Raw water	After biolo- gical plastic filter	After chem. precipitation (glucose sul- fate is used)	After chem. precipitation and ion ex- change
BOD5	1500	400	600	50
KMnO <sub>4</sub>	950	350	460	60
Total N	140	42	85	15
HN <sub>3</sub> -N	20	15	18	2
NO <sub>3</sub> --N	4	5	4	1
P	45	38	39	1.5