Coagulation and flocculation

coagulant dosing

a raw water feed
b stirring mechanism
c blending space
d floc blanket
e clear water exit
f floc exit

humic acid
(- charge)

$Fe(OH)^{2+}$
(+ charge)

+   →   →

Contents

This handout is based on *Drinking Water, Principles and Practices* by de Moel et al.

1. Introduction

In surface water there are three types of compounds that must be removed for the production of drinking water. These can be subdivided into:
- suspended solids
- colloidal solids
- dissolved (organic) solids.

Suspended solids have a diameter larger than 10^{-6} m, colloidal solids between 10^{-9} and 10^{-6} m and dissolved solids smaller than 10^{-9} m.

Particles with a diameter larger than 10^{-5} m, and a specific density larger than 2,000 kg/m^3 will settle in water. Smaller particles will also settle, but more slowly.
In Table 1 the settling time of particles with a density of 2,650 kg/m^3 (e.g., sand) is given.
To remove particles that are smaller than 10^{-5} m, these must be made larger or heavier.

To express the concentration of suspended, colloidal and dissolved organic compounds in water, sum parameters are used, such as total suspended solids concentration (dry weight), turbidity, natural organic matter (expressed in TOC/DOC) and color.
The suspended solids concentration and turbidity (Figure 1) are caused by small particles (order of magnitude 0.1 - 10 µm) that are negatively charged and repulse each other, thus remaining stable in suspension. In tropical countries, with heavy rain storms high concentrations of suspended solids can occur and rivers can even become "mud f

Figure 1 - Turbidity in surface water

Figure 2 - Rivers in the tropics sometimes have high suspended solids contents

flows" (Figure 2).

Color (Figure 3) is caused by humic substances (order of magnitude 0.01 µm). The charge of humic substances (and thus the removal) is dependent upon the pH of the water.

In Table 2 the water quality data from the surface water of several rivers in the Netherlands and in tropical countries are given. The high values of organic matter and color in the Drentsche are caused by peat-containing soils (with high organic matter content).

With coagulation-flocculation, suspended solids, turbidity and color-causing substances are removed from surface water by destabilization of the particles, adsorption of the dissolved compounds and formation of settleable flocs through the dosage of coagulants and (gentle) stirring.

Table 1 - Settling time of particles with a density of 2,650 kg/m^3

Diameter (m)	Types of particles	Settling time over 30 cm
10^{-2}	gravel	0.3 sec
10^{-3}	coarse sand	3 sec
10^{-4}	fine sand	38 sec
10^{-5}	silt	33 min
10^{-6}	bacteria	35 hours
10^{-7}	clay	230 days
10^{-8}	colloids	63 years

Figure 3 - Color in water

2. Coagulation

2.1 Theory

Coagulation consists of the destabilization of the negatively charged particles in the water through the dosing of a coagulant. By destabilization, the particles become neutral and are able to aggregate in flocs.

Coagulants

The coagulants consist of positively charged salts that are not harmless to health.

In the Netherlands, iron chloride ($FeCl_3$) is frequently used as a coagulant., Alternatively, aluminum sulfate ($Al_2(SO_4)_3$) can be applied.

Iron chloride is easy to dissolve in water and its solubility product (Ksp) is 27.9 $mol^4 \cdot l^{-4}$. Consequently, 162 mg $FeCl_3$ can be dissolved in one liter of water, resulting in 55.8 mg/l Fe^{3+} and 106.5 mg/l Cl^-.

Fe^{3+}- and OH^- ions, present in the water, precipitate into $Fe(OH)_3$ flocs, because the solubility product of iron hydroxide is low. Since Ksp $Fe(OH)_3$ = 1 • 10^{-38} $mol^4 \cdot l^{-4}$, only $7.8 \cdot 10^{-10}$ mol/l Fe^{3+} can be present in dissolved form in water.

In addition to iron hydroxide the following hydrolysis products of Fe^{3+} are also formed: $Fe(OH)^{2+}$, $Fe(OH)^{2+}$, $Fe(OH)^{4-}$.
In Table 3 the solubility constants of different reactions are given. Considering such table and some calculation, Figure 4 can be constructed.
When the pH of water is known, the amount of hydrolysis product in a volume of water can be determined. With a pH of 4.6, 10^{-7} mol/m^3 Fe^{3+}, 10^{-4} mol/m^3 $FeOH^{2+}$ and 10^{-4} mol/m^3 $FeOH^{2+}$ are present.
The pH and the predominant hydrolysis product influence the predominant coagulation mechanisms.

As a result of the dosing of iron chloride, OH^- ions are removed and the pH will decrease.
The magnitude of the pH drop depends on the buffering capacity of the water. The higher the buffering capacity, the smaller the pH drop is. When the pH drop is too large, pH can be increased by dosing a base, such as caustic soda.

Aluminum sulfate (alumn) is also easy to dissolve in water and Al^{3+} and SO_4^{2-} ions will be formed. $Al(OH)_3$ has a low solubility product and precipitates. In the same way as iron chloride, different hydrolyses products are formed and, after calculating the solubility products, Figure 5 can be drawn.

Table 2 - Water quality data of several rivers

River	Suspended solids (mg/l)	Turbidity (NTK)	Color (mg Pt/l)	DOC (mg/l)
Rhine	9 - 53	5.5 - 22.5	9 - 17	3.1 - 6
Meuse	4 - 31	2.2 - 27	10 - 22	3.4 - 5.4
Biesbosch reservoirs	1.5 - 9	0.9 - 5.6	6 - 12	3.2 - 4.0
IJsselmeer	4 - 115	2.5 - 4.0	10 - 30	5 - 13.3
Drentsche Aa	2 - 20	3.4 - 39	10 - 100	4.8 - 14.9
Tropical river	10,000	5,000	1,000	500
Drinking water	< 0.05	< 0.1	< 20	1

Iron hydrolyses reactions			K_S
$Fe(OH)_3$	$\leftrightarrow$	$Fe^{3+} + 3OH^-$	$1 \cdot 10^{-38}$
$Fe^{3+} + 2H_2O$	$\leftrightarrow$	$Fe(OH)^{2+} + H_3O^+$	$6.8 \cdot 10^{-3}$
$Fe(OH)^{2+} + H_3O^+$	$\leftrightarrow$	$Fe(OH)_2^+ + H_3O^+$	$2.6 \cdot 10^{-5}$
$2Fe^{3+} + 4H_2O$	$\leftrightarrow$	$Fe_2(OH)_2^{4+} + 2H_3O^+$	$1.4 \cdot 10^{-3}$
$Fe(OH)_3 + OH^-$	$\leftrightarrow$	$Fe(OH)_4^-$	$1.0 \cdot 10^{-5}$

Coagulation mechanisms

The process of coagulation can occur through three different mechanisms:
- electrostatic coagulation
- adsorptive coagulation
- precipitation coagulation.

Electrostatic coagulation

In electrostatic coagulation, positively charged ions approach the negatively charged colloids. In the diffusive layer around the colloid, the positively charged ions accumulate, destabilizing the colloid.

In Figure 6 the mechanism of electrostatic coagulation is represented.
In the left part of the Figure the negatively charged colloids are shown. After dosing coagulant (right part of the Figure), the exterior of the colloidal particle is destabilized and can collide with other particles forming removable flocs.

Electrostatic coagulation occurs after dosing 0.025 mol/m³ of trivalent ions. These concentrations are large and not found in surface water treatment and thus electrostatic coagulation does not play an important role in water treatment.
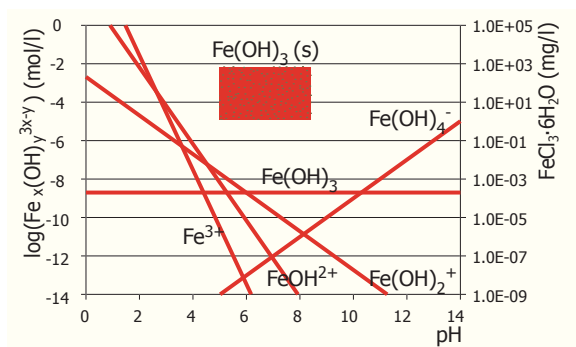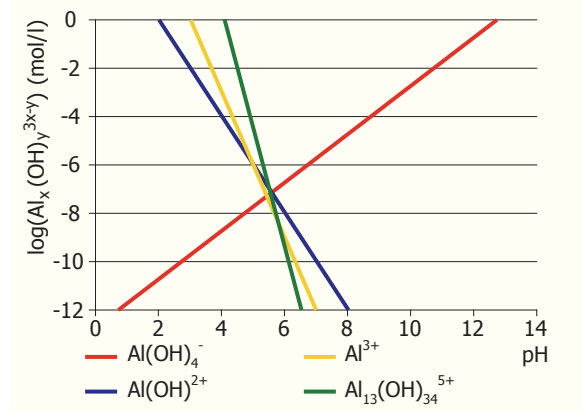

Figure 4 - Forms of iron hydrolyses products

Figure 5 - Forms of aluminum hydrolyses products

Adsorptive coagulation

In adsorptive coagulation, particles are adsorbed to the positively charged hydrolysis products $FeOH^{2+}$ and $FeOH^{2+}$. These products mainly occur at low pH (Figure 4).

Adsorptive coagulation is a rapid process. Within one second, positively charged hydrolyses products are formed and are adsorbed to the negatively charged solids (Figure 7). This is the main mechanism for the removal of organic matter.
Characteristics of adsorptive coagulation are that dosing is proportional to the removal of organic matter and that re-stabilization can occur after an overdose of coagulant. Then the solids will be positively charged and repulsion of the particles will take place.

Precipitation coagulation

In precipitation coagulation, or sweep coagulation, colloids are incorporated into the neutral (iron) hydroxide flocs (Figure 8). This mechanism occurs mainly in waters with low suspended solids concentration (10 mg/l).
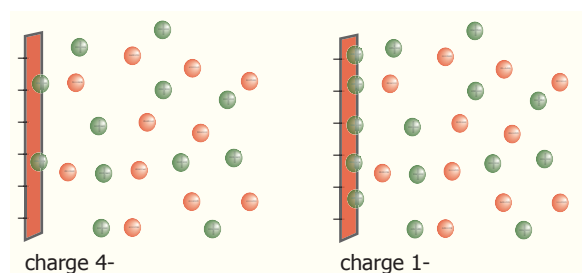

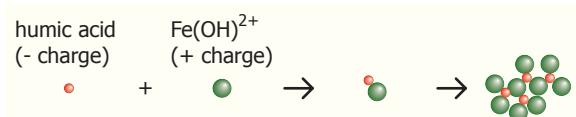*Figure 6 - Mechanism of electrostatic coagulation*

humic acid   Fe(OH)$^{2+}$
(- charge)   (+ charge)

Figure 7 - Mechanism of adsorptive coagulation

2.2 Practice

Jar test

The interactions between the solids in the water and the coagulants are complex and the removal mechanisms, which occur in parallel, are dependent on many different characteristics of the raw water, such as temperature, salinity, pH, solids and concentration.

Therefore, before designing a full-scale coagulation-flocculation treatment, the so-called "jar tests" are used to simulate the destabilization and floc formation processes.

The jar test apparatus consists of 6 jars filled with the water to be treated (Figure 9). A certain dose of coagulant is added to each jar and submitted to rapid mixing, followed by slow stirring and a settling phase. After settling, the water turbidity (or DOC concentration) is measured.

By modifying the process conditions (dosage, pH, flocculation time, settling time, stirring energy for mixing and/or flocculation), the optimal conditions can be determined.

In Figure 10 and 11 the results of a jar test experiment of Biesbosch water is shown. Biesbosch water originates from the river Meuse and is collected in reservoirs. Due to the long retention times (about 6 months) in the reservoirs, the suspended solids concentration of Biesbosch water is low, about 5 mg/l.

$$Fe^{3+} + H_2O \xrightarrow{< 1 \text{ sec}} Fe(OH)^{n+} \xrightarrow{1-7 \text{ sec}} Fe(OH)_3\text{-floc}$$

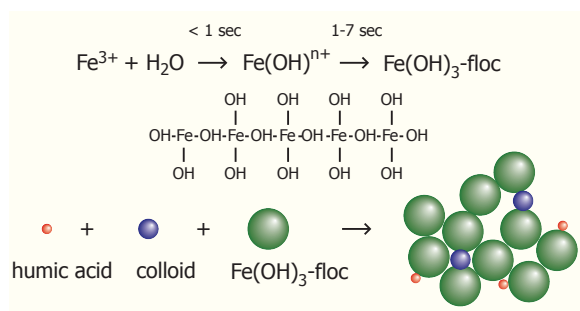humic acid   colloid   Fe(OH)$_3$-floc

Figure 8 - Mechanism of precipitation coagulation

Figure 9 - Jar test apparatus

From Figure 10 it can be observed that turbidity decreases with an increased coagulant dosing. The lowest turbidity was attained when about 12 mg/l iron chloride was dosed. With a higher dosage the turbidity did not increase and thus re-stabilization did not occur.

In Figure 12 a coagulant dose of 12 mg/l and a varying pH is represented. The turbidity increased with a decreasing pH (pH<7).

The predominant coagulation mechanism of Biesbosch water is therefore precipitation or sweep coagulation.

In the province of Zeeland in the Netherlands, the drinking water is produced from polder water. Polder water has a high content of organic matter (like humic acids).

Figure 13 shows the results for jar test experiments in which the coagulant dose was varied with pH. At a pH between 6 and 7 the lowest turbidity was found. At higher pH the turbidity was higher.
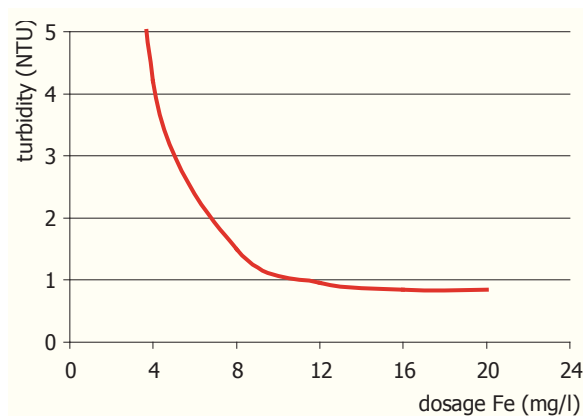
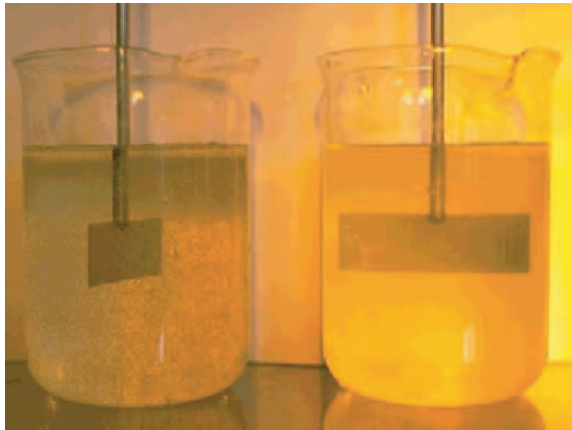Figure 10 - Results of jar test experiment with varying coagulant dosing

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Figure 11 - Influence of coagulant dose (left: high dose, right: low dose)

Figure 13 - Results of jar test experiment of "polder water" with varying pH

The prevailing mechanism is thus, adsorptive coagulation.

An evident difference between mechanisms is encountered during the coagulation of water from the Rhine, when this is abstracted directly from the river at Nieuwegein (WRK I-II) or from the IJsselmeer lake, at Andijk (WRK III) (Figure 14)

The river water has a higher turbidity than the lake water; the lake water has a higher organic matter content than the river water due to algae blooms in summer.

During coagulation of lake water, re-stabilization can occur and the prevailing mechanism is therefore adsorptive coagulation.

However, re-stabilization is not detected in the co-agulated river water and, therefore, the prevailing mechanism is precipitation or sweep coagulation.

Mixing

Rapid mixing after (or during) coagulant dosing is an important design parameter. The coagulant must be uniformly mixed with the raw water. In case mixing is poor, local under- and overdosing occurs, resulting in a poor performance of the process.

The parameter expressing mixing intensity is called the velocity gradient or G-value.

The velocity gradient is defined as follows:

$$G_c = \sqrt{\frac{P}{\mu \cdot V}}$$

in which:

G_c	=	velocity gradient for rapid mixing	(s-1)
P	=	dissipated power	(W)
μ	=	dynamic water viscosity	(N•s/m²)
V	=	volume of mixing tank	(m³)

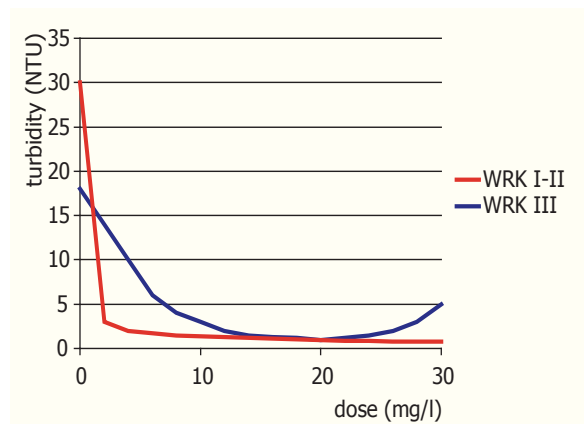*Figure 12 - Results of jar test experiment with varying pH*
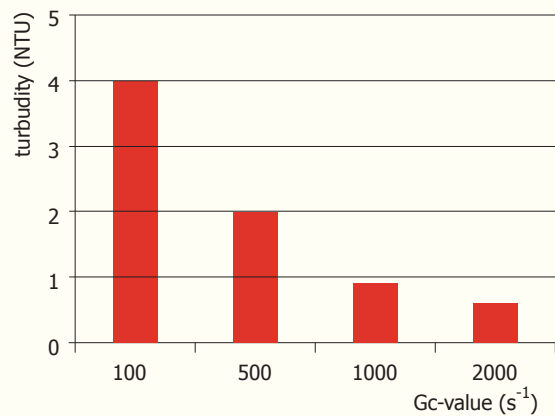

Figure 14 - Coagulation of Rhine water

Figure 15 - Rest turbidity at different G_c-values

The influence of the velocity gradient can be determined by jar test experiments (Figure 15).
When the velocity gradient is low (less intensive mixing), the residual turbidity will be higher than in situations where the velocity gradient is high.
In practice, the recommended G-value for rapid mixing is at least 1500 s-1.

Two different mixing systems can be applied:
- mechanical mixing
- static mixing

In the first system, mechanical mixers (Figure 16) dissipate the power in the raw water, while in the second system gravity forces cause the mixing effect. Here, the dissipated power is a consequence of the head loss over the mixing tank:

$$P = \rho \cdot g \cdot Q \cdot \Delta H$$

in which:

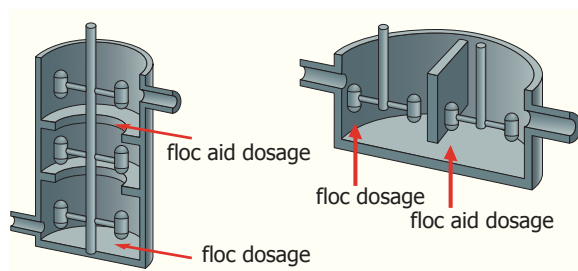|		
ρ	= density of water	(kg/m^3)
g	= gravity constant	(m/s^2)
Q	= flow	(m^3/s)
ΔH	= head loss over mixing tank	(m)

Figure 16 - Mechanical mixers

The equation for the velocity gradient for static mixers can be written as:

$$G_c = \sqrt{\frac{\rho \cdot g \cdot \Delta H}{\mu \cdot \tau_c}}$$

where:

τ_c = residence time in the mixing zone   (s)

The most frequently applied static mixer is the cascade (Figure 17). Water falls over a weir into a receiving body. In the turbulent space that is caused by the falling water, the coagulant is dosed.

3. Flocculation

3.1 Theory

Flocculation consists of collision of destabilized particles or pin-flocs (obtained by coagulation) to form settleable flocs.

The collision of particles can take place under natural circumstances (perikinetic floc formation) or by dissipation of mixing energy (orthokinetic floc formation).
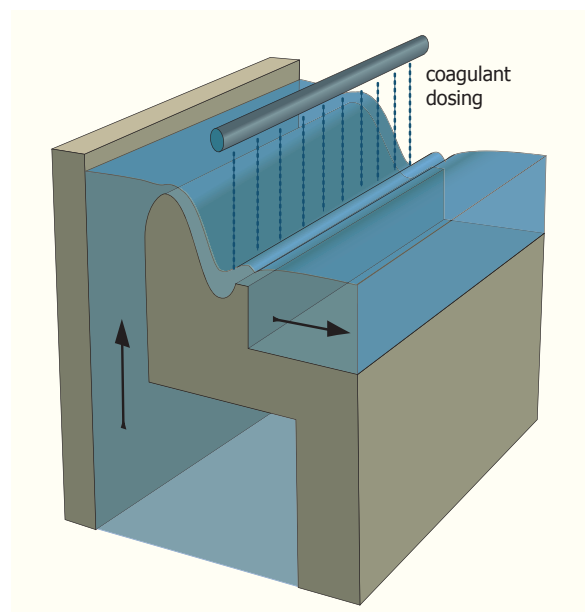

Figure 17 - Cascade mixer

Perikinetic floc formation

During perikinetic floc formation, particles collide as a result of Brownian motion. Von Smoluchowski described the decrease in the total number of spherical particles as a function of time with the following equation:

$$-\frac{dn}{dt} = \alpha \cdot \frac{4 \cdot k \cdot T}{3 \cdot \mu} \cdot n^2$$

where:

n = total number of particles per unit water volume (m^{-3})
α = collision efficiency (-)
K = Boltzmann constant (J•K^{-1})
T = absolute temperature (K)

Not every collision will result in attachment and therefore the collision efficiency is incorporated into the equation.

From experiments it can be concluded that perikinetic floc formation is only relevant for the collision of very small particles.

Orthokinetic floc formation

By mixing, the collision frequency of the particles is artificially increased. The decrease in the total number of particles as a function of time is described by the following equation:

$$-\frac{dn}{dt} = \frac{4}{3} \cdot \alpha \cdot n_1 \cdot n_2 \cdot R^3 \cdot G_v$$

where:

Gv = velocity gradient for floc formation (s^{-1})
R = collision radius (m)
n1 = number of particles with diameter d1 (-)
n_2 = number of particles with diameter d$_2$ (-)

The collision radius is defined by 0.5•(d1+d$_2$). Assuming that all particles have the same diameter, the equation can be rewritten as:

$$-\frac{dn}{dt} = \frac{4 \cdot \alpha \cdot n^2 \cdot d^3 \cdot G_v}{3}$$

For spherical particles the volumetric concentration is described as:

$$c_v = \frac{1}{6} \cdot \pi \cdot n \cdot d^3$$

Deriving n•d^3 and substituting it:

$$-\frac{dn}{dt} = \frac{8 \cdot \alpha \cdot n \cdot c_v \cdot G_v}{dt}$$

resulting in a solution for plug flow:

$$\frac{n}{n_o} = e^{-k_a \cdot c_v \cdot G_v \cdot t}$$

and for completely mixed systems:

$$\frac{n}{n_o} = \frac{1}{1 + k_a \cdot c_v \cdot G_v \cdot t}$$

With these equations it can be calculated that orthokinetic floc formation of particles with a diameter of 1 µm only takes place when velocity gradients higher than 10 s^{-1} are applied. Otherwise, perikinetic floc formation is predominant.

3.2 Practice

To design a flocculation installation, the following parameters must be considered:
- residence time, T
- residence time distribution
- velocity gradient for floc formation, Gv

Residence time

The residence time for floc formation is determined through jar test experiments. The applied time varies between 500 and 3600 sec, being on average about 20-30 minutes.

Residence time distribution

When water flows through a tank, the residence time of every droplet is different. For some droplets the residence time is longer and for others shorter than the average, negatively influencing the floc

formation process.

In order to approach a plug flow, where every droplet has the same residence time, criteria are developed for the design of a flocculation chamber:
- The ratio between the length and width of a tank must be at least equal to 3.
- The mixers, that take care of the dispersion of energy and collision of the particles, must be in line with the flow direction (Figure 18).

There are two types of flocculation systems that fulfill the requirements mentioned above:
- horizontal, long and narrow (Figure 19 right).
- vertical, deep and narrow chambers (Figure 19 left).

Velocity gradient for floc formation
After coagulation the colloids and humic acids are destabilized and incorporated in many small particles or pinflocs in the water. The Mechanical mixers used in flocculation dissipate energy in the water (Figure 20), to promote the collision of the neutral particles and the formation of flocs.

The degree of energy dissipation is expressed, like for coagulation, by the velocity gradient.

The velocity gradient for floc formation is expressed in the parameter Gv and is defined by:

flow parallel to stirring axis: no short circuit flow

flow perpendicular to stirring axis: short circuit flow

if flow speed = 0.03 m/s, tip speed = 1 m/s
then water speed -0.97 to 1.03 m/s

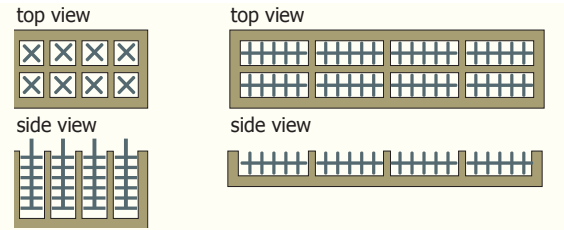Figure 18 - Mixers in line and perpendicular to the flow direction of the water

Figure 19 - Plug flow mixing systems for floc formation, mixer in line with water flow

$$G_v = \sqrt{\frac{P}{\mu \cdot V}}$$

The energy dissipation from the mixers can be calculated with the following equation:

$$P = \rho_w \cdot \pi^3 \cdot (1 - k_2)^3 \cdot N^3 \cdot \sum (c_d \cdot L_{blade} \cdot (r_u^4 - r_i^4))$$

in which:

k_2	=	constant ≈ 0.25	(-)
N	=	rotation speed	(rpm)
Cd	=	constant ≈ 1.50	(-)
Lblade	=	length of mixer blade	(m)
ru	=	distance from exterior of mixing blade to axis	(m)
ri	=	distance from interior of mixing blade to axis	(m)

According to the formula for the energy dissipation from the mixer, the rotation speed is the only operation parameter. The other parameters are already determined during the design process.

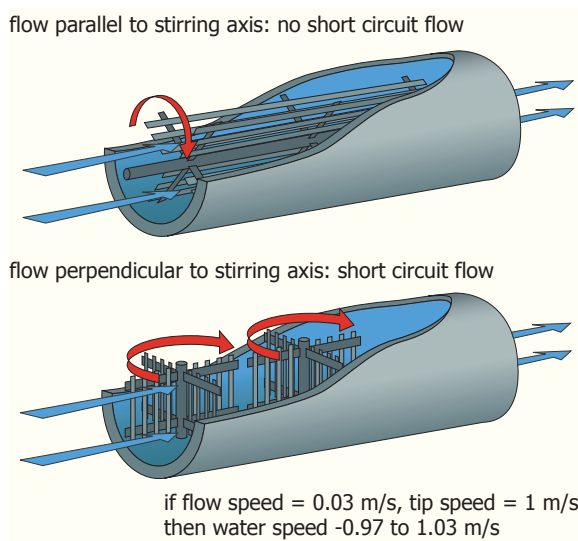The velocity gradient in operation can thus be calculated by:
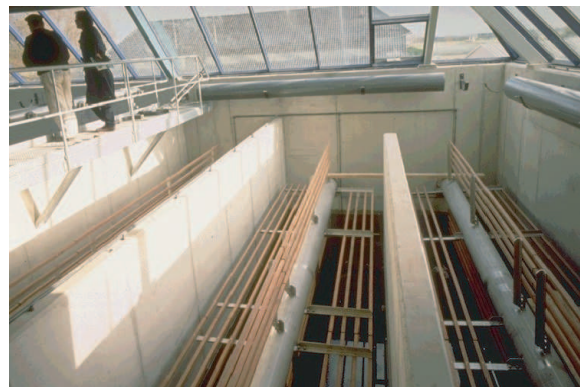

Figure 20 - Mixing device
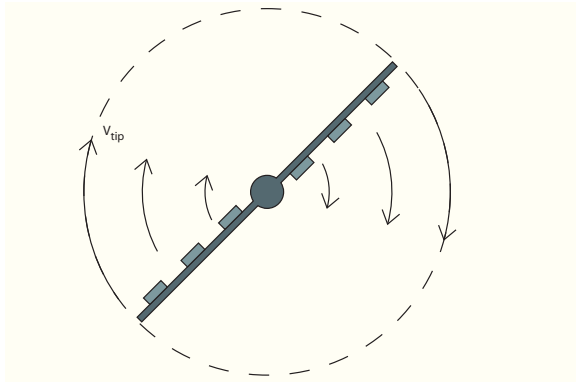
Figure 21 - Tip velocity

$$G_v = const. \cdot \sqrt{N^3}$$

The velocity of the mixing blade in the flocculation chamber depends on the radius and the rotation speed of the mixer. The velocity is greatest at the tip of the mixing blade, being called the tip velocity (Figure 21) and can be calculated by:

$$v_{tip} = 2 \cdot \pi \cdot r \cdot N$$

The higher the rotation speed, the higher the tip velocity. When the tip velocity is higher than 1 m/s, formed flocs are broken up.
When the rotation speed of a mixer is known, the maximum radius of a mixing blade can be determined. A rotation speed of 4 rotations per minute e.g. allows for a maximum radius of 2.4 meters.

To increase the collision frequency of the neutral particles of pin flocs formed during coagulation, a high mixing intensity must be applied. The small particles collide and larger particles are formed, but in the meantime, the risk of floc break-up increases as a result of fluid shear.
Therefore, the flocculation chamber is divided into several compartments (Figure 22 and 23) with decreasing velocity gradients (Figure 24).
In the first compartment the velocity gradient is high (about 100 s^{-1}) and in the last compartment the velocity gradient is low (about 5 s^{-1}). The optimal operation of the mixers must be determined empirically (in jar test experiments).
The flow opening between the compartments must be large enough to avoid local energy dissipation,
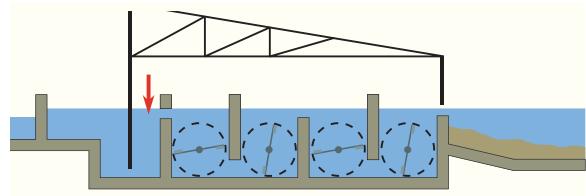

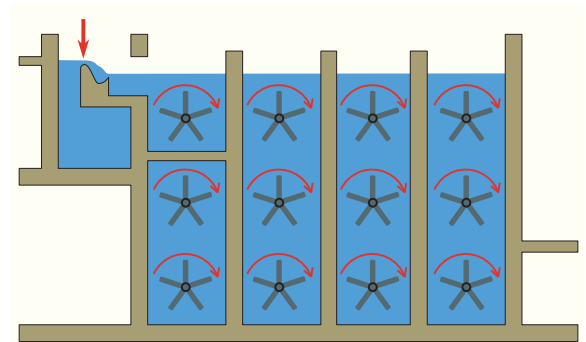Figure 22 - Floc formation installation WRK I/II

Figure 23 - Floc formation installation WRK III, division in different compartments
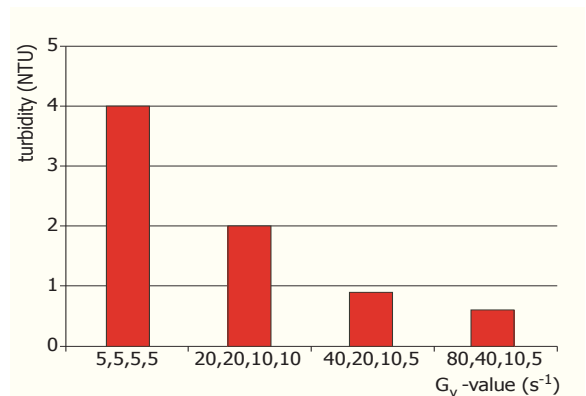

Figure 24 - Influence of G_V-value on floc formation in different compartments

as in the case of hydraulic flocculation (Figure 25).

Figure 25 - Hydraulic floc formation