

# Faculty of Science and Technology

# **MASTER'S THESIS**

Study program/ Specialization:	Spring semester, 2014	
Environmental Technology/Water Science	Open Access	
and Technology		
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Thesis title:		
Chemical Precipitation and Treatment Contr	ol Parameters in Wastewater Treatment	
Credits (ECTS): 30		
Key words:		
Wastewater treatment, ferric chloride,	Pages: 57	
coagulation, flocculation, chemical		
precipitation, total suspended solids, pH,	+ enclosure: 2	
alkalinity.		
	Stavanger, 30 <sup>th</sup> June 2014	

# Acknowledgements

Thanks to my advisors Roald Kommedal and Leif Ydstebø for the guidance and support during this project.

To Gon, Tomi and my family, for the encouragement, the patience, and for believing in me.

To LP, and the m-roomers.

#### **Abstract**

The requirements for discharges from urban wastewater treatment plants are for  $BOD_5$  at 20 °C a maximum of 25 mg/l  $O_2$ ; for COD a maximum of 125 mg/l  $O_2$ ; and for Total Suspended Solids the maximum concentration allowed is 35 mg/l. To meet these requirements, and to treat the volume of water reaching treatment plants, it is common use to implement a chemical unit process.

The use of chemicals is to increase particle size by means of coagulation and as a consequence the performance of physical unit processes downstream is improved. The removal of suspended solids is thereby enhanced along with the removal of associated pollutants. The second purpose of using chemicals is to precipitate soluble materials, aiding on their removal downstream.

Ferric chloride is one of the most common coagulants used in wastewater treatment; one of its characteristics is its multivalence, which attracts strongly to colloidal particles. Also, it is relatively insoluble, assuring a high degree of removal.

Coagulation is the process whereby destabilization of a given suspension or solution is effected. The function of coagulation is to overcome the factors that promote the stability of a given system.

Flocculation is the process whereby destabilized particles, or particles formed as a result of destabilization, are induced to come together, make contact, and thereby form large(r) agglomerates that can be removed by gravitational sedimentation.

Observations were made at the SNJ Wastewater Treatment Plant that the optimum pH and ferric chloride dose change during the day due to changes in the composition of the wastewater. The aim of the project is to investigate the cause of these observations in order to further understand which parameters affect the precipitation process and to improve the dosing of ferric chloride in wastewater treatment.

A series of jar tests were performed on 6 different dates, under diverse weather conditions. Alkalinity, pH, and total suspended solids were determined and analyzed with relation to different dosages of ferric chloride as coagulant.

It was found that adding ferric chloride significantly increases the removal of suspended solids, but that excess coagulant is counterproductive since it leads to re-stabilization of the particles. Also, the removal rate of TSS decreases with higher doses of coagulant, which means higher costs for treatment.

Higher alkalinity affects precipitation negatively thus requiring higher ferric chloride dosage. Lower alkalinity produced lower effluent TSS.

When the pH drops significantly, the concentration of solids rises again. Precipitation occurs over a range of pH values, and no exact optimum pH could be determined.

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# **Abbreviations**

**COD:** Chemical oxygen demand

**BOD:** Biological oxygen demand

JKL: Ferric chloride

**TSS:** Total suspended solids

**SNJ:** Sentralrenseanlegg Nord – Jæren Wastewater Treatment Plant

## 1 Introduction

The importance of coagulation and flocculation in water treatment is evident when it is taken into account that it has been practiced since ancient times, with the purpose of facilitating the clarification of water (Baker, 1948).

The water is treated prior to being discharged into the natural environment, and in order to avoid threatening the safety of the living organisms that could be affected by the contents of the wastewater.

Regulations for effluent concentrations and requirements for removal of suspended solids and organic loads in water treatment are getting stricter nowadays. According to the Urban Waste Water Directive by the Council of the European Union, the requirements for discharges from urban wastewater treatment plants are: for  $BOD_5$  at  $20~^{\circ}C$  a maximum of  $25~\text{mg/l}~O_2$ ; for COD a maximum of  $125~\text{mg/l}~O_2$ ; and for Total Suspended Solids the maximum concentration allowed is 35~mg/l. Alternatively, the requirements are presented in percentages of reduction in relation to the load of the influent: for BOD being minimum 70-90%, for COD~75% and for TSS a minimum of 90% reduction (EU Council Directive, 1991).

To meet these requirements, and to be able to treat the volume of water reaching treatment plants, a broad array of technologies are available.

The objective of the adoption of any of these technologies may be enhancing plant capacity or capability, improvement of efficiency, and/or decreasing the costs of the treatment itself. These technologies may include biological systems, tertiary technologies, clarifier improvements and chemical treatment (Daigger and Buttz, 1998).

It is common practice to use chemicals to enhance primary treatment or to relieve downstream processes in order to remove particulate material by sedimentation through coagulation and flocculation processes. This practice has

several advantages such as reduced capital costs and space requirements, effective treatment for excess flows during storm events, removal of toxic metals, and efficient removal of phosphorus (Bratby, 2006).

The use of chemicals usually has two purposes. One is to increase particle size by means of coagulation and as a consequence the performance of physical unit processes downstream is improved. The removal of suspended solids is thereby enhanced along with the removal of associated pollutants. The second purpose of using chemicals is to bring materials out of solution, or precipitate soluble materials, aiding on their removal downstream by physical separation unit processes like clarifiers or filters (Daigger and Buttz, 1998).

Both natural and synthetic compounds can be used to accomplish coagulation. The natural ones include starch and some metal salts like iron and aluminum salts. The synthetic compounds include cationic, anionic, and nonionic polymers, which are quite efficient but they have the disadvantage of being more costly usually than the natural compounds (Droste, 1997).

The main chemicals used in wastewater treatment are aluminum sulphate  $[Al_2(SO_4)_3]$ , known more commonly as Alum, and iron salts such as ferric sulphate  $[Fe(SO_4)_3]$  or ferric chloride  $(FeCl_3)$  (Faust and Aly, 1998).

These cations possess characteristics that make them attractive for particle removal in wastewater treatment. One of these characteristics is that they are multivalent, which attracts them strongly to colloidal particles. Also, they are relatively insoluble, and this guarantees a high degree of removal (Droste, 1997).

The removal efficiency when using chemical precipitation depends on the amount of chemicals used, mixing times, and the caution and attention practiced when monitoring and controlling the process (Tchobanoglous et al., 2003).

There are three sequential steps in the process of coagulation as it happens in wastewater treatment: the formation of coagulant, particle destabilization and

inter-particle collisions. The first two take place in under rapid-mixing conditions, while the third step takes place in flocculation tanks (Pontius, 1990).

In general, without the addition of coagulants it is possible to remove by gravitational sedimentation 50 to 70% of the TSS, 25 to 40% of the BOD, and 25 to 75% of the bacteria. While using chemicals the removal ascends to 80 to 90% of the TSS including some colloidal particles, 50 to 80% of the BOD, and 80 to 90% of the bacteria (Tchobanoglous et al., 2003). Table 1 shows the characteristic contents of domestic wastewater in milligrams per liter.

Using coagulation as a way of aggregating particles is important for the removal of many health-related pollutants. Many contaminants that pose a threat to human health are associated with solid particles like some toxic metals. Other contaminants are particles themselves, for example pathogenic organisms (Pontius, 1990).

#### 1.1 Definitions

The following are generally accepted definitions, according to Bratby:

- Coagulation is the process whereby destabilization of a given suspension or solution is effected. That is, the function of coagulation is to overcome the factors that promote the stability of a given system.
- Flocculation is the process whereby destabilized particles, or particles formed as a result of destabilization, are induced to come together, make contact, and thereby form large(r) agglomerates (Bratby, 2006).

There are two types of flocculation depending on the size of the particles implicated:

- Perikinetic flocculation, or microflocculation is the aggregation of particles as a result of collisions between them under the influence of Brownian motion (Stevenson, 1997). This type applies to particles in the size range from 0.001 to about 1  $\mu$ m (Tchobanoglous et al., 2003). Perikinetic flocculation slows down rapidly as the average size of the flocs increases. Orthokinetic flocculation then takes over perikinetik flocculation (Stevenson, 1997).
- Orthokinetic flocculation, or macroflocculation is the aggregation of particles larger than 1  $\mu m$ . It is a result of either induced velocity gradients or differential settling. In the case of induced velocity gradients, particles that move faster will overtake slower-moving particles and if they collide they will be fixed together creating a larger particle that is easier to settle. In the case of aggregation by differential settling the bigger particles overtake smaller ones during gravitational settling (Tchobanoglous et al., 2003).

#### 1.2 Wastewater characteristics

The particles found in the wastewater vary broadly in origin, size and concentration. They generally originate from land runoff, domestic and industrial discharges, vegetation decomposition, and mineral erosion.

According to O'Melia and Amirtharajah (1990) "particles size may vary by several orders of magnitude, from a few tens of nanometers (e.g. viruses) to a few hundred micrometers (e.g. zooplankton)".

Coagulation, sedimentation and filtration processes can remove all this particulate matter, if they are properly carried out and controlled.

Table 1 Typical raw domestic wastewater characteristics (Bratby, 2006).

	Value (mg/l)
Total Suspended Solids (TSS)	240
Total COD	500
Particulate COD	312
Colloidal COD	83
Soluble COD	105
Total BOD	245
Particulate BOD	130
Colloidal BOD	52
Soluble BOD	63
Total nitrogen	40
Particulate nitrogen	8
Soluble nitrogen (including ammonia)	32
Total phosphorus	10
Particulate phosphorus	5
Soluble phosphorus	5

All the components present in wastewater are in the form of suspended, colloidal and dissolved organic and inorganic matter (Bratby, 2006).

Suspended particles are generally larger than 1.0  $\mu m$  and are easily removed by sedimentation, while colloidal particles range in sizes about 0.01 to 1  $\mu m$ , and it takes an extended amount of time for them to settle. Therefore, coagulants and flocculants are used in order to facilitate sedimentation by gravity (Tchobanoglous et al., 2003).

Both hydrophilic and hydrophobic colloidal particles are found in wastewater, but the bulk of inorganic and organic matter in the water is of this last kind. Some examples of hydrophilic particles include soap, synthetic detergents and blood serum. Hydrophilic colloids are not as easy to remove as hydrophobic colloids, and to remove them by coagulation requires typically 10 to 20 times the amount of coagulant used in conventional water treatment (Hammer and Hammer, 2001).

Examples of hydrophobic particles are clays, microorganisms, metal oxides, i.e., practically every solid particle found in wastewater (Pontius, 1990).

Typically, wastewater is alkaline. The hydroxides, carbonates and bicarbonates present in it come most commonly from elements like potassium, calcium, magnesium, sodium and ammonia, and others like silicates and phosphates. These are present in groundwater, the water supply, domestic products, etc. (Tchobanoglous et al., 2003).

# 1.3 The electrical double layer

Colloidal dispersions have a distinctive characteristic, which is the large area-to-volume ratio of the particles that constitute them. The physical properties of the colloidal dispersion system are largely determined by the properties of the surface at the interface between the dispersed phase and the dispersion medium. These surface properties include adsorption and electric double layer effects. The interactions between particles, and between particles and dispersion medium, are most influenced by merely the material contained in a single molecular layer of the interface (Shaw, 1980).

The theory of the electric double layer considers the distribution of ions in the vicinity of the surface of the particles and therefore with the magnitude of the electric potentials that occur near the charged surface (Shaw, 1980).

"Forces acting at interfaces are composed of extensions of forces acting within the two phases. One side of the interface assumes a net electrostatic charge, either positive or negative, and an equivalent number of counter-ions of opposite charge form a counter layer in the aqueous phase" (Stumm and Morgan, 1981). According to Faust and Aly (1998), counter-ions may have originated from the particle itself, or by preferential adsorption from solution.

The fact that the particles in wastewater carry a surface charge, gives rise to forces of attraction and repulsion that distribute the ions around the particles. This added up to the effects of Brownian motion, results in what is known as the electrical double layer (Bratby, 2006).

"The electric double layer can be regarded generally as consisting of two regions: an inner region which may include adsorbed ions, and a diffuse region in which ions are distributed according to the influence of electrical forces and random thermal motion" (Shaw, 1980).

The inner layer is compact and most likely contains water molecules and adsorbed (hydrated) ions (Bratby, 2006).

Counter-ions in the solution adsorb to the surface of the particles and are held there by means of electrostatic and van der Waals forces of attraction which are strong enough to overcome the effects of thermal agitation. This layer is known as the Stern layer (Tchobanoglous et al., 2003).

Beyond the fixed inner layer is a diffuse layer of ions that are scattered depending on the influence of electrical forces and thermal motion. Brownian motion overcomes in part the electrostatic attractions and causes the diffusion of the double layer into the bulk solution (Faust and Aly, 1998).

Figure 1-1 shows a representation of a diffuse electric double layer. This corresponds to the simplest quantitative treatment of the diffuse layer by Gouy and Chapman.

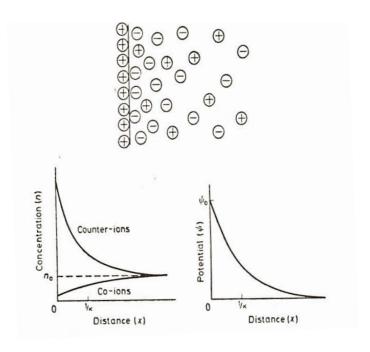


Figure 1-1 Schematic representation of the diffuse double layer (Shaw, 1980)

Stern proposed a model in 1924 in which the two parts of the double layer are separated by a plane called the Stern plane. This plane is situated at about a hydrated ion radius from the surface. He also considered in his model the possibility of specific ion adsorption.

Specifically adsorbed ions are attached, though not permanently, to the surface by electrostatic and/or van der Waals forces that are strong enough to overcome thermal agitation. In the direction of the surface these ions may be dehydrated. Specifically adsorbed ions have centers that are found between the surface and the Stern plane (Shaw, 1980).

In both the fixed and diffuse layers a drop in the potential can be appreciated outwards from the particle to the surroundings (Tchobanoglous et al., 2003). This is represented in figure 1-2 below.

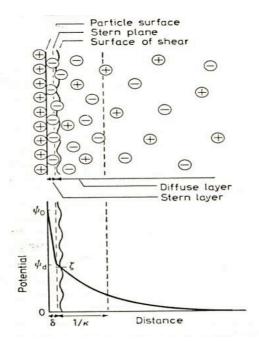


Figure 1-2 Representation of the structure of the electric double layer based on Stern's theory (Shaw, 1980)

The potential changes from  $\Psi_0$  (the surface potential) to  $\Psi_d$  (the Stern potential) in the Stern layer, and decays from  $\Psi_d$  to zero in the diffuse layer.

Using polyvalent counter-ions or surface-active counter-ions can cause a reversal of charge to take place within the Stern layer ( $\Psi_{\theta}$  and  $\Psi_{d}$  with opposite signs). Figure 1-3 is a schematic representation of such situation.

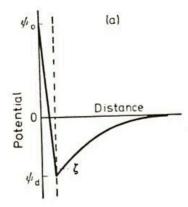


Figure 1-3 Charge reversal situation (Shaw, 1980)

A complete expression for the Stern model of the double layer is:

$$\frac{\in '}{\delta}(\psi_0 - \psi_d) + \frac{\sigma_m}{1 + \frac{N_A}{n_0 V_m} exp[\frac{ze\psi_{d+\emptyset}}{kT}]} - (8n_0 \in kT)^{1/2} sinh \frac{ze\psi_d}{2kT} = 0$$

Where  $\Psi_d$  is the Stern potential and  $\Psi_0$  the surface potential.  $\subseteq$  ' is permittivity of Stern layer with  $\delta$  thickness.

 $\sigma_m$  is the surface charge density corresponding to a monolayer of counter-ions,  $N_A$  is Avogadro's constant and  $V_m$  is the molar volume of the solvent. The adsorption energy is divided between electrical ( $ze\psi_d$ ) and van der Waals ( $\emptyset$ ) terms.  $n_0$  is the bulk concentration of ionic species (Shaw, 1980).

The model proposed by Stern is a good foundation for interpreting most experimental observations related to double layer phenomena (Shaw, 1980).

# 1.4 Stability of colloids

Colloids are stable in aqueous systems. The capacity of colloids to retain a dispersed state and remain as separate entities is known as *stability*. This stability is a result of interfacial forces, which are a consequence of both the presence of a surface charge at the interface between the particle and the liquid, and the hydration of surface layers of the colloid.

The size of colloids (0.01 to 1  $\mu$ m) prevents the attractive forces between particles to overcome the repelling forces that arise from the electrical charge. The influence of interfacial phenomena is more important than the influence of gravity when it comes to colloids (Bratby, 2006).

In the case of hydrophilic colloids, the attraction that they particles have for water molecules is what makes them stable, rather than the minor charge that they may possess (Hammer and Hammer, 2001). "Particle-solvent affinity promotes stability mainly by mechanical means, which can be considered in terms of the positive desolvation free energy change which accompanies particle aggregation" (Shaw, 1980).

Hydrophobic particles, on the other hand, are stable by means of the electrical charge they possess (Hammer and Hammer, 2001). Figure 1-4 is a schematic of the forces acting on hydrophobic colloids.

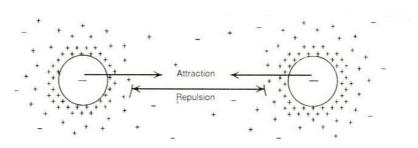


Figure 1-4 Forces on hydrophobic colloids in stable suspension (Hammer and Hammer, 2001)

In wastewater, colloids characteristically have a net negative surface charge. This results from the ionization of surface acidic functional groups and ion adsorption. A colloid that has a negative surface charge attracts counter-ions from the surrounding water, hence developing a diffuse double layer, which yields repulsion forces between the particles and the colloidal suspension is stabilized. Furthermore, the water bound to the surface of the particle hinders inter-particle contact (Maximova and Dahl, 2006).

The negative charge of colloids was reported in 1929 from an early study of chemical coagulation (Christman, 1929).

#### 1.4.1 The Deryagin-Landau and Verwey-Overbeek theory

Deryaguin and Landau (Deryagin and Landau, 1941) and Verwey and Overbeek (Verwey et al., 1948) developed a theory to describe particle-particle interactions. The stability of colloids is treated in terms of the energy changes

that take place when particles come close together. The theory, best known as DLVO theory, includes approximations of the repulsion energy that results from the overlapping of electric double layers and the attraction London-van der Waals energy in terms of the distance between particles. The addition of these energies presents the total interaction energy in terms of inter-particle distance. Figure 1-5 illustrates the total energy curves that are possible. V(1) shows a repulsive energy maximum and V(2) shows a situation where repulsion does not overcome van der Waals attraction at any distance between particles.

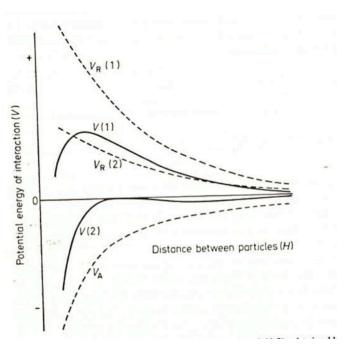


Figure 1-5 Total interaction energy curves V1 and V2 resulting from the addition of  $V_A$ , attraction curve, and different repulsion curves  $V_R(1)$  and  $V_R(2)$  (Shaw, 1980)

#### 1.5 Particle destabilization

The conversion of particulate, colloidal or dissolved material from a stable state into an unstable state is called *destabilization*.

Colloids coagulate when the electrostatic repulsion and the effect of the ordered water structure around the particles is reduced sufficiently to permit particles to

come close together enough for van der Waals forces to predominate over the repulsion forces.

There are several ways to accomplish bringing the particles close enough to each other: reduction of the surface charge; reduction of the zone of influence of the surface charge; and reduction of the number of adsorbed water molecules or extent of zone of ordered water structure (Bratby, 2006).

In water, coagulants act as added counter-ions, which compress the diffuse layer of particles, and thus the energy barrier for particle collision is lowered (Maximova and Dahl, 2006).

There are adsorption phenomena at the particle surface that may have different effects on the charge of the particle, such as augmentation of the charge, or reversal of the charge (in the case of adsorption of counter ions) (Bratby, 2006). If the concentration of ions in the solution is increased, the repulsion between particles will not be as significant since the double layer is being compressed. Nevertheless, there is only a limited range of electrolyte concentration at which destabilization will occur, this is because in the presence of excess of indifferent electrolytes charge reversal may occur, promoting re-stabilization of the particles.

According to Faust and Aly (1998), the mechanism described as compression of the double layer is one of the four mechanisms involved in destabilization of particles.

Further mechanisms are:

#### • Adsorption and charge neutralization

Electrolytes interact with the particle by being adsorbed to its surface thus reducing or neutralizing the surface charge.

• Entrapment in a precipitate

The coagulant precipitates fast, and there is floc formation followed by orthokinetic flocculation.

Adsorption for interparticle bridging

Polymeric ions or molecules adsorb to the surface of particles and create a "bridge" between neighboring particles that allows them to stick together, promoting sedimentation by gravity given the increase in size and weight. Besides inducing aggregation by a bridging mechanism, the adsorption of polymers on the surfaces will promote stability through increased particle-solvent affinity and by an entropic mechanism (Shaw, 1980).

The mechanism that will predominate depends on two factors:

- (1) The nature of the colloidal dispersion, the prevalence of hydrophobic or hydrophilic particles; the surface nature of the colloid; and the intensity of the surface charge
- (2) If the coagulant added is charged, the intensity of the charge; the adsorptive capacity of the species; and the ability to form bridges between adjoining particles (Bratby, 2006).

#### 1.6 Treatment with metal coagulants

Metal coagulants such as those based in aluminum and iron are effective, readily available, and relatively inexpensive. Hence the wide use of them as chemical enhancers in wastewater treatment plants.

In the specific case of the use of metal salts as coagulants, the mechanisms of destabilization are:

 Surface charge reduction, as a result of indifferent electrolytes and adsorption of coagulant species. Adsorption and charge neutralization involves the adsorption of mononuclear and polynuclear metal hydrolysis

- species on the colloidal particles found in wastewater. It should be noted that it is also possible to get charge reversal with metal salts, as described with the addition of counter-ions (Tchobanoglous et al., 2003).
- Bridging mechanism, also as a result of adsorption at the surface of the particle. Metal coagulants tend to polymerize during hydrolysis reactions, as hydrolysis increases, higher polynuclear species form, and they adsorb to particles forming bridges between adjacent particles (Bratby, 2006).
- Precipitate enmeshment, under suitable conditions of concentration of coagulant and pH, metal coagulants form metal-hydroxide precipitates, and they enmesh particulate material, enhancing sedimentation by sweep action (Bratby, 2006). If a sufficient concentration of metal salt is added, large amounts of metal hydroxide floc will form. Following macroflocculation, large floc particles will be formed that will settle readily, sweeping through the water and enmeshing particles. In most wastewater applications, the sweep floc mode of operation is used most commonly where particles are to be removed by sedimentation (Tchobanoglous et al., 2003).

Table 2 gives a general overview of the four mechanisms involved in destabilization with metal coagulants.

 $\begin{tabular}{ll} Table~2~Characteristics~of~destabilization~mechanisms~with~metal~coagulants.~Adapted~from~Bratby~(2006) \end{tabular}$ 

	Influence of indica	ted parameter accor	ding to mechanism	
Parameter	Physical double	Adsorption	Bridging	Precipitation
	layer	destabilization	Diluging	recipitation
Electrostatic	Predominant	Important	Subordinate	Subordinate
interactions		•		
Chemical	.,			May occur but not
interactions and	Absent	Important	Predominant	essential for
adsorption  Zeta potential for				removal
optimum	Near zero	Not necessarily	Usually not zero	Not necessarily
destabilization	iveal Zelo	zero	Ostally Hot Zero	zero
acombinization		Restabilization		
Addition of excess coagulant	No detrimental effect	usually accompanied by charge reversal; may be blurred by precipitation	Restabilization due to complete surface coverage	No detrimental effect
Fraction of surface coverage (θ) for optimum floc formation	Negligible	0 < θ < 1	0 < θ < 1	Unimportant
Relationship	Optimum dosage		Stoichiometry	Optimum dosage
between optimum	virtually	Stoichiometry	between dosage	virtually
coagulant dosage	independent of	possible but does	and particle	independent of
and particle	colloid	not always occur	concentration	colloid
concentration	concentration		Flocs of 3-	concentration
Physical properties of flocs produced	Dense, high shear strength but poor filterability in cake filtration	Flocs of widely varying shear strength and density	dimensional structure; low shear strength, but excellent filterability in cake filtration	Flocs of widely varying shear strength and density

Destabilization with the use of metal coagulants is not brought about by any particular mechanism, but rather by a combination of several of them.

According to Bratby (2006): at relatively high colloid concentrations, the predominant mechanism is probably due to ionic strength effects, or reduction of the double layer. At lower colloid concentrations, it is more likely that metal hydroxide precipitates are formed. Destabilization in this case arises from a sweep mechanism of colloid enmeshment by precipitates.

There are at least two other factors influencing destabilization besides coagulant concentration, and they are the concentration of colloids in the suspension and the pH existing during destabilization.

The organic treatment capacity of the downstream biological treatment facility may be increased as a result of the use of metal salts. There will also be production of inert chemical solids, and the mass of sludge generated in the liquid process will be increased (Daigger and Buttz, 1998).

"Metal salts addition also will increase alkalinity consumption by the treatment liquid process. Either sufficient alkalinity must be present in the influent wastewater to offset this consumption, or supplemental alkalinity must be added to avoid loss of process buffering capacity and uncontrolled declines in the process effluent pH" (Daigger and Buttz, 1998).

#### 1.6.1 Ferric chloride

Ferric (+3) iron compounds are used in chemical precipitation. Ferric iron can accomplish both coagulation of particulate matter and precipitation of phosphorus (Daigger and Buttz, 1998). Ferric chloride is one of the most commonly used chemicals for coagulation (Tchobanoglous et al., 2003).

Adding the metal salts in primary treatment units will result in improved removal of suspended solids,  $BOD_5$ , and phosphorus. Enhanced suspended solids removal occurs as a result of the coagulation reaction that occurs when ferric iron reacts with the alkalinity present in the wastewater, due to the formation of a metal hydroxide (Daigger and Buttz, 1998).

Insoluble ferric hydroxides are formed as a result of the hydrolysis of ferric salts and the reaction with the carbonates in the water. However, the reason for charge neutralization and aggregation of colloids is not the insoluble ferric hydroxides. When ferric salts are used as coagulants, the ions of the coagulant hydrolyse within a short time and form short-lived water soluble ferric hydroxides that convey a positive charge. These are ultimately the main species responsible for the charge neutralization and the resulting aggregation (Licsko, 1997).

The reaction is illustrated as follows:

$$M^{+3} + 3HCO^{-3} - M(OH)_3 + 3CO_2$$

When ferric chloride is added to water, the following reactions occur:

$$2FeCl_3 + 3Ca(HCO_3)_2 \leftarrow \rightarrow 2Fe(OH)_3 + 3CaCl_2 + 6CO_2$$

If lime is added to increase the natural alkalinity of the wastewater, the following reaction is assumed to take place:

$$2FeCl_3 + 3Ca(OH)_2 \leftarrow \rightarrow 2Fe(OH)_3 + 3CaCl_2$$

Ferric salts dissociate to form hydrated reaction products as soon as they are added to a solution. The metal ions form coordination compounds with water molecules to give  $Fe(H20)_{6^{3+}}$  (Basolo and Johnson 1964; Beck 1970; Orgel 1970 as cited by Bratby (Bratby, 2006)).

A stepwise substitution of the ligand molecules or ions for the water molecule takes place. The extent of the substitution depends on the concentration of the substituted ligand. For the destabilization of hydrophobic colloids with iron coagulants, the complexes of principal interest are those comprising H<sub>2</sub>O and OH- as ligands. The extent to which OH- ions are bound to the metal complex is dependent primarily on the pH or the concentration of OH- ions in solution. (Bratby, 2006).

Throughout hydrolysis and substitution reactions, many polymeric species are formed, and as the charge of the metal species decreases, the extent of polymerization becomes more pronounced.

The coagulation process is time dependent. If the objective is to aggregate colloids with mono- and polynuclear species, then rapid and intense initial mixing of the metal salt and the wastewater is important.

"The coordination reactions in which metal cations participate in aqueous solutions are exchange reactions with the coordinated water molecules exchanged for some preferred ligands" (Stumm and Morgan, 1981).

In an aqueous system that comprises several colloidal contaminants of inorganic and organic nature, the overall reaction with iron salts involve competing reactions of hydroxide and other organic or inorganic ligands for complexation with free metal ions and their hydrolysis products. The ways in which the pollutants are removed depend on numerous factors such as the speciation of hydrolysis products, the presence and the reactivity of constituents in complexation with Fe(III) species, the kinetics of hydrolysis and of the reactions between the coagulant and other ligands, and the rates of mass transport among these constituents (Shin et al., 2008).

# 1.7 Sentralrenseanlegg Nord Jæren (SNJ) - IVAR

Following is a general description of the "Sentralrenseanlegg Nord – Jæren (SNJ)" wastewater treatment plant adapted from their web page (IVAR).

Sentralrenseanlegg Nord – Jæren (SNJ)is a wastewater treatment plant with an integrated chemical unit. It is located in Mekjarvik in the Randaberg Municipality, about ten kilometers north of Stavanger. The plant receives and treats water coming from the municipalities of Randaberg, Stavanger, Sola, Sandnes and Gjesdal. It is the largest and most advanced treatment plant in the region. The water to be treated is collected and brought to a main line system that has a total of 35 kilometers from Sandnes to Mekjarvik.

The water contains both wastewater (sewage) and surface water (rain and surface water). Therefore, there are large variations of water flow into the plant depending on rain/dry season.

The feed tunnel has a diameter of 3.5 meters and is 8 kilometers long. It has a volume of 77,000 m 3 and acts as a storage reservoir during rainfall periods.

The effluent of the plant is discharged to Håsteinfjorden through a 4 km long tunnel. The discharge point is located at 1.6 km from shore and has a depth of 80 meters.

SNJ is designed for 240,000 population equivalents (PE) or loading per capita per day.

The wastewater is first pumped into the plant, and is pretreated through screens, to remove coarse materials, followed by a sand and grit removal unit. At this point ferric chloride is added to begin the coagulation process of colloidal particles.

Next, the water is directed towards the sedimentation basins, which are preceded by flocculation chambers where paddles allow slow mixing for the flocs

to grow. After flocculation the water goes into the sedimentation tanks where the flocs sink to the bottom by means of its own weight. The purified water is discharged from the surface of sedimentation basins to the tunnel that goes into Håsteinfjorden.

The entire plant is built with two separate and parallel lines so that it is possible to conduct experiments or carry out maintenance without disruption to operations.

#### 1.7.1 Observations

Observations were made at the wastewater treatment plant that the optimum pH and ferric chloride dose change during the day due to changes in the composition of the wastewater.

Traditionally, the addition of ferric chloride is to achieve one selected pH value, but observations at the wastewater treatment plant has shown that the optimum pH changes during the day because of variations in the wastewater composition. During the morning when the wastewater is most dilute (from the night) it is possible to meet the target effluent TSS of 20 – 30 mg/l by adding ferric chloride to a pH of about 6.4-6.5. In the evening, when the wastewater is more concentrated, ferric chloride must be added to reach a pH about 6.0-6.2 in order to meet the target effluent TSS (Ydstebø, 2014).

### 1.8 Objective

The main objective of the thesis is to study the effect of different parameters such as pH, alkalinity and TSS on chemical precipitation.

Based on the observations made at the wastewater treatment plant, the aim of the project is to investigate the cause of these observations in order to further understand which parameters affect the precipitation process and to improve the dosing of ferric chloride in wastewater treatment.

A series of jar tests will be performed on samples of wastewater from the SNJ treatment plant on 6 different dates, under diverse weather conditions.

Alkalinity, pH, and total suspended solids are the parameters that will be determined and analyzed with relation to different dosages of ferric chloride as coagulant.

#### 2 Materials and Methods

In wastewater treatment, the design and operation of chemical precipitation processes has to be based on empirical laboratory tests because of the heterogeneous nature of the wastewater, and the stoichiometric complexity of trivalent metal precipitation chemistry.

"The lowest dose of chemicals and pH that produce the desired flocs and clarity represents the optimum. This optimum is then used as the dose in the actual operation of the plant" (Sincero and Sincero, 2003).

The jar test is used to assess the efficiency of the coagulation and flocculation process. It is a testing procedure that will allow the evaluation of the optimal conditions for the process, which depends on many different variables.

Some of these variables are type and dosage of coagulant, final pH, type and dosage of other chemical aids, intensity and duration of mixing (both rapid and slow), type of mixing device, etc. (Bratby, 2006).

A jar test comprises different phases:

- Rapid mixing for a short period of time (normally between 30 and 60 seconds), in which the coagulant is added to the wastewater. During this stage destabilization of particles takes place.
- Slow mixing for 10 minutes. This is when the particles come together and form flocs, which will enmesh small suspended particles, increasing the size of the flocs.
- Sedimentation, no mixing. In this phase the flocs are allowed to settle by gravitation. The clarified water that remains on the top represents the effluent.

Rapid mixing is important so a uniform dispersion of the chemical is allowed and the opportunity of particle-to-particle contact is increased. Following gentle and prolonged mixing sticks the microscopic coagulated particles into larger flocs.

These flocs then are able to aggregate with suspended matter, and settle by gravity when they reach sufficient size and weight (Maximova and Dahl, 2006).

### 2.1 Alkalinity

In wastewater treatment, alkalinity analyses are used for process control and interpretation.

Alkalinity is the ability of water to neutralize acid, or to absorb hydrogen ions without significant pH change (Loewenthal et al., 1989).

In wastewater, this parameter results from the hydroxides  $[OH^-]$ , carbonates  $[CO_3^{2-}]$ , and bicarbonates  $[HCO_3^-]$  of elements like calcium, magnesium, sodium, potassium and ammonia. Typically, wastewater is alkaline. The concentration of alkalinity is significant when it comes to treatment if chemical and biological processes are to be applied (Tchobanoglous et al., 2003).

Alkalinity is mainly bicarbonate, and at pH 4.5 all bicarbonate has been neutralized. When acid is added to the water, most of the hydrogen ions from the acid combine with the carbonate ions present in the water to form bicarbonates. As further additions of acid are made, all carbonate radicals are converted to bicarbonates. Below pH 4.5 the addition of hydrogen ions reduce the bicarbonates to carbonic acid (Hammer and Hammer, 2001).

# 2.2 Total Suspended Solids (TSS)

Analyzing solids contents is essential in process control in wastewater treatment and for evaluating observance of effluent discharge limitations by regulatory organisms.

The term "suspended solids" refers to the portion of solids that are retained by a filter of 2.0  $\mu$ m or smaller nominal pore size under specified conditions (Clesceri et al., 1998).

# 2.3 pH

The range of pH in which most biological life can exist is typically 6 to 9, which is rather narrow. Hence the concentration of hydrogen ions in both natural waters and wastewaters is an important quality parameter (Tchobanoglous et al., 2003). If the pH in the wastewater is too low, it can interfere with the biological treatment downstream. Furthermore, the natural waters at the discharge point may be altered and the biological life affected negatively.

The permitted pH range for the effluent discharge into the environment usually varies from 6.5 to 8.5 (Tchobanoglous et al., 2003).

#### 2.4 Materials

- Volumetric flask (1,000 mL)
- Analytical balance
- Coagulant: FeCl<sub>3</sub> Kemira Pix 318 (Appendix B) (referred to herein as "JKL")
- Jar tester with six paddles capable of variable speeds from 0 to 140 rpm,
   ISCO AMF/6
- Beakers (1,000 mL)
- Syringe for sampling
- Sample flasks (50 mL)
- Clock
- pH-meter WTW Multi 340i; WTW SenTix 41 pH probe; TetraCon 325 conductivity cell.
- Glass microfiber filters, VWR 696 particle retention: 1.5 μm
- Filtering device
- Pipette, volumetric
- Burette, volumetric 25 ml, subdivision 0.05 ml
- HCL 0.07246 M
- Magnetic mixer
- Drying oven, for operation at 103 to 105 °C

Automatic sampler, Liquistation CSF48 Endress & Hauser

Wastewater samples were collected from the wastewater treatment plant "Sentralrenseanlegg Nord-Jæren – IVAR" located in Mekjarvik, Randaberg.

All samples were taken from the inlet water, after the screens and before the sand and grit removal unit.

The laboratory experiments were carried out in Universitetet i Stavanger premises on the same day that the "morning" samples were taken.

The first laboratory was done with the assistance of Leif Ydstebø as training for the following experiments, and it was held on the 24<sup>th</sup> of January 2014.

The subsequent experiments were carried out during March 2014, on the  $5^{th}$ ,  $12^{th}$ ,  $17^{th}$ ,  $19^{th}$  and  $21^{st}$ .

The samples that were taken in the morning (referred to herein as "morning water") were acquired manually by Leif Ydstebø.

The samples acquired in the evening (referred to herein as "evening water") were provided by an automatic sampler over the course of three hours (20:00 – 23:00 hrs on each date), and were taken on the evening before the laboratory experiments. The wastewater was kept refrigerated in order to keep it stable before being analyzed.

# 2.5 Procedure

The laboratory experiments were based on the procedures described in Standard Methods (Clesceri et al., 1998); and on a recommendation from Kemira (Ydstebø, 2014).

Each laboratory exercise comprised a jar test in which morning and evening water were treated with different dosages of ferric chloride. Both treated and raw wastewaters were analyzed for alkalinity, TSS, and pH. Conductivity was measured only on the untreated wastewater.

#### 2.5.1 Jar test

- Three beakers were filled with 1000 mL of homogenous morning water and three with evening water.
- The mixer was started at maximum speed (140 rpm) and the different dosages of ferric chloride were added using a pipette.
- Rapid mixing was allowed for 30 seconds.
- Next slow mixing at 40 rpm for 10 minutes.
- Observation of any changes of the wastewater in the jars (destabilization, formation of primary particles, coagulation and flocculation).
- The paddles were removed from the beakers and the water was left to settle quiescently for 10 minutes. After sedimentation, samples were taken of the clear phase (below the surface) using a syringe. The samples were then analyzed for alkalinity and TSS was determined.
- pH was measured before the test and during the slow mixing phase. The pH-meter was calibrated using standard buffers of pH 4.00 and 7.00.

#### 2.5.2 TSS determination

- Glass microfiber filters were dried in an oven at 105 °C overnight, then weighed using an analytical balance.
- The volume of the samples taken varied according to the expected TSS concentration.
- The samples were mixed thoroughly and filtered through 1.5  $\mu m$  glass microfiber filters prewashed with distilled water.
- The filters were then allowed to dry in the oven at 105 °C overnight.
- The dried filters were weighed.

## 2.5.3 Alkalinity

- Hydrochloric acid 0.07246 M was added to the burette.
- Settled wastewater samples of 100 ml were placed on a magnetic stirrer for the entire duration of the titration procedure.
- Samples were titrated with 1-2 ml of HCl until a 4.5 pH was reached,
   making smaller additions of acid as the desired pH was approached.

## 3 Results and Discussion

The results from the laboratory experiments reflect accordance to expectation and theory.

However, there are some interesting differences between "morning water" and "evening water", and some results in particular that shall be commented and discussed in this section.

In Appendix A, a table containing the results obtained in all the experiments can be found. It includes all the results on the different parameters measured: pH, conductivity, suspended solids concentration, suspended solids removal, alkalinity and alkalinity consumption, and the JKL dosages used in each of the experiments.

Conductivity was measured just as control and merely to document the levels in the raw wastewater. It is a parameter not used in process control at the treatment plant in Mekjarvik.

## 3.1 Coagulant dose and weather conditions

"Morning water" samples represent the water that reached the plant during the night, when the activity in the industry/households is lowest; therefore the suspended solids load is expected to be lower than that of the "evening water".

The ferric chloride dosages were chosen depending on if the water was "evening" or "morning", adding more coagulant to the evening water, since it is the one carrying more suspended solids.

Another reason for choosing the coagulant dose was based on the weather conditions before the samples were taken, adding lower dosages when it had been raining and higher when it had been dry weather; again grounding the decision on the expected concentration of particulates in the wastewater.

The weather conditions varied during the experiments. It was possible to analyze the wastewater in both dry weather and under rain conditions.

The weather had been dry when the experiments on the samples of the  $24^{th}$  of January and the  $5^{th}$  of March were carried out. The values of suspended solids in the evening raw wastewater were higher than the morning ones, as expected. Morning waters contained 139.10 mg/l and 198 mg/l on the  $24^{th}$  of January and  $5^{th}$  of March respectively; evening waters presented concentrations of 232 mg/l and 215 mg/l on the same dates.

On the 17<sup>th</sup>, 19<sup>th</sup>, and 21<sup>st</sup> of March it had been raining in the area, therefore the water was more dilute. The values of suspended solids in the raw wastewater of the morning water were 57 mg/l, 61.25 mg/l and 59.33 mg/l respectively. The evening water concentrations were 85.33 mg/l, 93 mg/l and 115 mg/l on the mentioned dates.

The ferric chloride dosages were reduced by 30% on March 17<sup>th</sup> and by 50% on the 19<sup>th</sup> and 21<sup>st</sup>. This last further reduction of the coagulant dose was due to the fact that on the 17<sup>th</sup> there was a high removal of suspended solids, the final concentrations ranging between 5.00 mg/l and 8.57 mg/l in the morning water, well below the effluent requirements. In the evening water, the end concentrations ranged between 4.00 mg/l and 36.40 mg/l. The latter result suggests that the coagulant addition was too high and hence it allowed for the ferric chloride to be reduced even more in the subsequent experiments with similar weather conditions.

March 12<sup>th</sup> was exceptional. The morning wastewater appeared to be more concentrated than the evening water at first sight. Nevertheless, the jar test was carried out as usual, the morning water receiving less FeCl<sub>3</sub> than the evening water. The results reflected that this assumption was correct: the morning water contained 282 mg/l of suspended solids, while the evening water contained 120.80 mg/l. After the experiment it was known that due to maintenance activities being carried out at the treatment plant, the tunnel that carries the wastewater had been full for a certain amount of time and that allowed some

settling to take place, therefore the evening water was more dilute. And the morning water on the 12<sup>th</sup> of March was more concentrated because the tunnel had been emptied and the water left contained all the particulate material that had settled before. Furthermore, 282 mg/l was the highest concentration of suspended solids found throughout all the experiments.

## 3.2 Sources of errors and variability

All the samples were analyzed immediately after sedimentation to avoid microbial action or loss or gain of CO<sub>2</sub> or other gases. Loss of CO<sub>2</sub> will result in conversion of bicarbonate to carbonate.

In general the total suspended solids (herein referred to as TSS) method is not complex, but care must be taken when carrying it out and attention to detail must be paid. It is of particular importance the volume of the sample that is filtered: increasing the size of the samples taken would result in a more pronounced difference in the weight of the filters before and after passing the samples. Nevertheless, each beaker contained only one liter of water, and samples had to be taken from these for both TSS and alkalinity determination. Hence, in the cases in which the suspended solids appeared to have been thoroughly removed by the ferric chloride it was not possible to filter as much water as it would have been desirable in order to obtain a more pronounced weight difference.

The residue left on the filters and then dried in the oven at 103-105 °C may retain water of crystallization as well as some mechanically occluded water. The loss of any organic matter by volatilization is usually insignificant at this temperature (Clesceri et al., 1998).

Alkalinity could not be determined on March  $5^{th}$  and March  $21^{st}$  due to lack of equipment at the time of the laboratory experiments.

When titrating for alkalinity determination, care must be taken to avoid a slow response that could be caused by waste matter coating the pH probe (Clesceri et al., 1998). In order to allow the electrode come to equilibrium, brief pauses between acid additions were done, and the probe cleaned regularly.

Sampling and sample handling tends to generate more uncertainties than the titration method itself, which is more precise (Clesceri et al., 1998).

In order to accurately assess the optimum coagulant dosage, as well as the relationship with other parameters to provide the best performance of the water treatment process, other analyses should be performed in parallel, for example turbidity analysis. Unfortunately, during these experiments it was not possible since the turbidity meter in the laboratory was not in conditions of being used.

Furthermore, a way to increase the accuracy of the results is to carry out all experiments in duplicate or triplicate, which could not be done because of lack of equipment and/or human resources.

### 3.3 Final TSS vs. Ferric Chloride Dose

As mentioned before, the values of suspended solids concentration in the raw wastewater varied both depending on the weather conditions and the time of day when the samples were taken.

The final values of suspended solids concentration after addition of coagulant can be seen in Figures 3-1 – 3-3.

There are two points that are above the 35 mg/l concentration requirement for the effluent, and they both correspond to data obtained on the 24<sup>th</sup> of January. The difference in these results in the final value of TSS with all the other results (which are below the effluent concentration requirements) is in the initial

alkalinity contents of the water. On this date, the alkalinity was above 3 mmol/l, which was the highest value as appreciated in Figures 3-13 and 3-14.

The results indicate that higher alkalinity reduce the TSS removal, which may result from a higher pH during the reaction or affecting the chemical reaction itself.

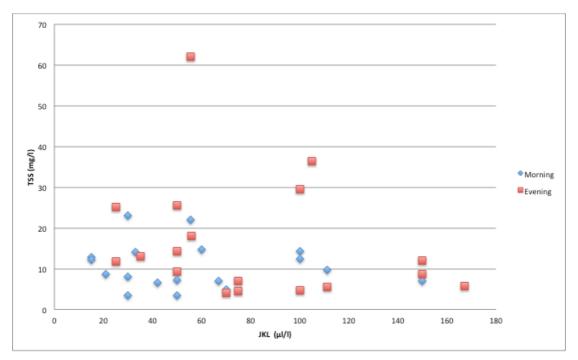


Figure 3-1 The relationship between TSS and JKL

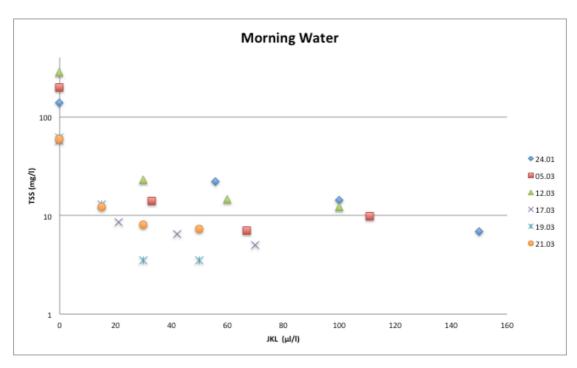


Figure 3-2 The relationship between TSS and JKL in the jar tests on morning water.

From Figure 3-3, it is possible to observe the effect that excessive amount of coagulant can have in the concentration of particulates in wastewater. On March  $5^{th}$ ,  $12^{th}$  and  $17^{th}$  the highest addition of ferric chloride resulted in an increase of suspended solids in relation to the preceding dose. Figure 3-4 shows these observations. This picture corresponds to the laboratory done on  $12^{th}$  March, evening water. The 50  $\mu$ l/l dose removed 78% of the TSS, the 100  $\mu$ l/l dose removed 96% and the dose of 150  $\mu$ l/l removed 92% of the particulates.

At 92 and 96% removal the TSS is very low, so the error in the TSS analysis could also influence these results.

It is particularly noticeable on the  $17^{th}$  of March, the sample that had the highest coagulant dose (evening water,  $105~\mu l/l$ ) was observed to be very turbid and yellow/orange, suggesting the dose was too high and the particles had actually started to stabilize again in the suspension.

On these three dates, the pH after the addition of the highest dose of coagulant dropped significantly: to 3.72 on the  $5^{th}$  of March; 3.73 on the  $12^{th}$  of March; and 3.31 on the  $17^{th}$  of March.

In general, and from Figures 3-1 and 3-5, it is possible to observe how the water is clearified more and more with the addition of higher doses of the chemical. But on this particular case the water looked quite turbid (Figure 3-6).

The initial value of suspended solids was 85.3 mg/l in the evening raw water. The removal was 85% for a dose of 35  $\mu$ l/l and 95% corresponding to a dose of 70  $\mu$ l/l of ferric chloride. The 105  $\mu$ l/l dose only reduced the suspended solids contents by 57%, supporting the initial observations made.

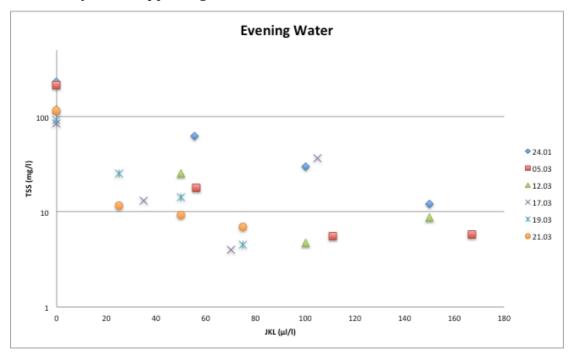


Figure 3-3 The relationship between TSS and JKL in the jar tests on evening water.



Figure 3-4 Evening water on the 12th of March with doses of 50, 100 and 150 microliters of JKL



Figure 3-5 Evening water on the 19th of March with doses of 25, 50 and 75 microliters of JKL



Figure 3-6 Evening water on the 17th of March with doses of 35, 70 and 105 microliters of JKL

In the laboratory under ideal conditions, the ferric chloride dosages that prove to reduce the TSS contents in the wastewater are approximately doubled in full-scale plant operations in order to reduce the TSS in the same proportion.

This is mainly because in full-scale the conditions are not ideal. The initial mixing of ferric chloride is slower and the flow in the settling tanks is not ideal (Ydstebø, 2014).

### 3.4 TSS Removal vs. Ferric Chloride Dose

The figures below (Figs. 3-7 and 3-8) show the relationship between the TSS that were removed in each test and the ferric chloride dosage. It appears that the removal of solids is independent of the ferric chloride addition. This suggests that some of the tests may have had an excess of coagulant, since the removal does not improve significantly with higher dosages of coagulant.

Furthermore, in Figures 3-9 – 3-11, which represent the removal of TSS in milligrams per microlitre of JKL added, it can be appreciated that the slope smoothens with increasing JKL addition. The removal rate of suspended solids is more pronounced between the first two additions of coagulant in each experiment than between the second and third additions. This indicates that the removal of the last percentages of TSS are the most costly and there will be a breaking point at which further TSS removal will not be economical.

The highest removal of TSS per  $\mu$ l JKL was 8.63, on the morning water of the 12<sup>th</sup> of March, with a JKL dose of 30  $\mu$ l/l. This is interesting since it was the water that presented the highest initial concentration of suspended solids, and the JKL dosage is the lowest that was tested on that day.

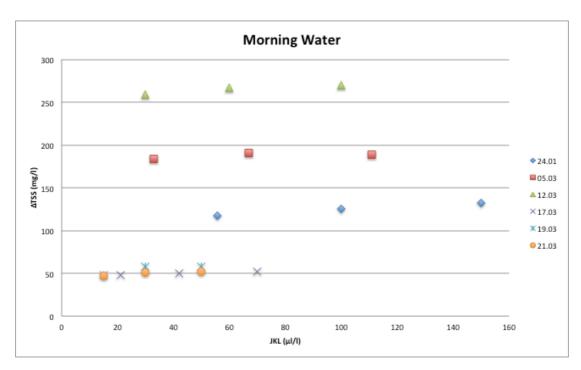


Figure 3-7 Relationship between TSS removal and JKL on morning water

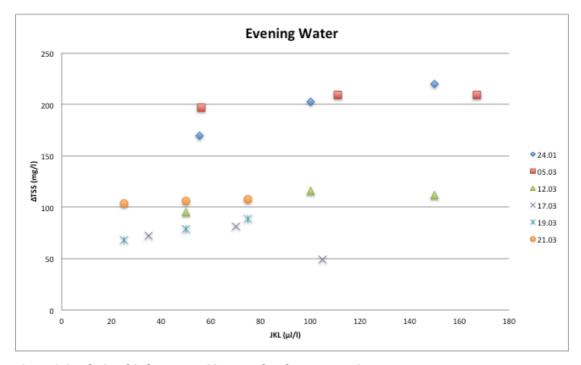


Figure 3-8 Relationship between TSS removal and JKL on evening water  $\,$ 

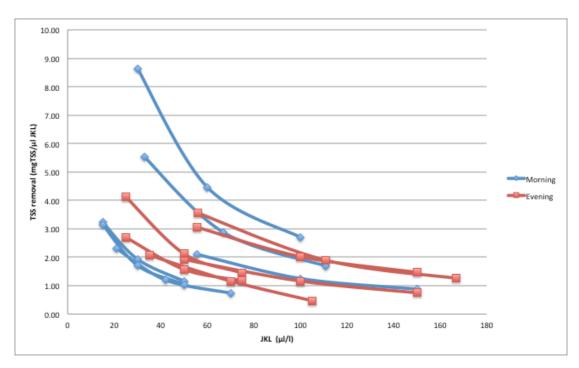


Figure 3-9 TSS removal per microliter JKL added

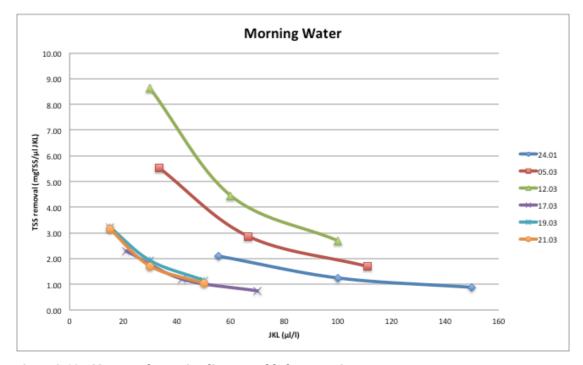


Figure 3-10 TSS removal per microliter JKL added on morning water  $\,$ 

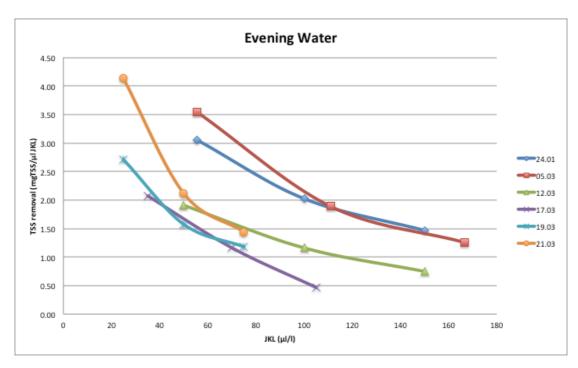


Figure 3-11 TSS removal per microliter JKL added for evening water

## 3.5 pH vs. Ferric Chloride Dose

From Figure 3-12, it is obvious that pH is reduced by JKL addition, as expected based on theory: the drop in pH is caused by the fact that the hydrolyzed ferric iron is acting as a weak acid in water. The buffer capacity of the water can only tolerate this acid-producing reaction for as long as there is alkalinity present. An increase in the dosage of JKL leads to a further reduction of the pH.

The pH dropped drastically to 4.00 or below with doses of 100  $\mu$ l/l JKL or more, except on January 24<sup>th</sup>. The alkalinity on this date was the highest of all: 3.08 mmol/l and 3.80 mmol/l for morning and evening water respectively. The alkalinity then was not completely consumed by the addition of the coagulant in doses of 100  $\mu$ l/l JKL or more, keeping the pH around 6.00, which is the optimum pH for the treatment process.

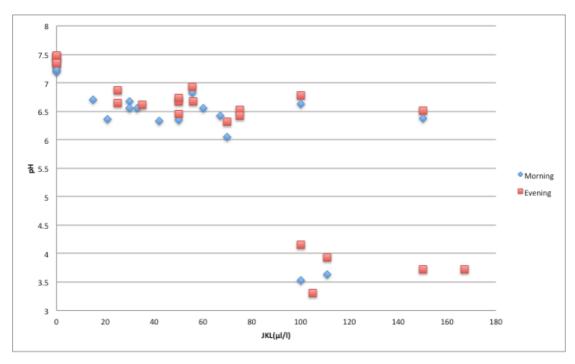


Figure 3-12 Relationship between pH and JKL dose

## 3.6 Alkalinity vs. Ferric Chloride dose

As seen in Figure 3-13, the alkalinity decreases proportionally with the addition of ferric chloride in all the experiments, again as a result of the acidic characteristics of the coagulant, which consumes the alkalinity present in the water.

To follow on this, the Figure 3-15 showing TSS against alkalinity indicates that as alkalinity is consumed, the final concentrations of TSS are lower. Therefore, it could be alleged that since more coagulant means less alkalinity; and from the graph, that less alkalinity means lower end concentration of TSS, that adding more ferric chloride would be desirable for treatment. This has been proven to not be entirely accurate in the previous analyses of the relationships between the studied parameters.

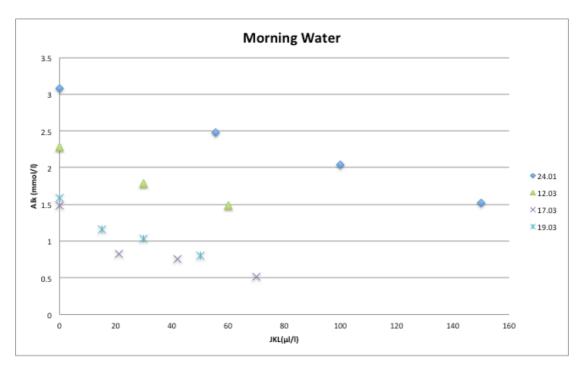


Figure 3-13 Alkalinity and JKL dose on morning water

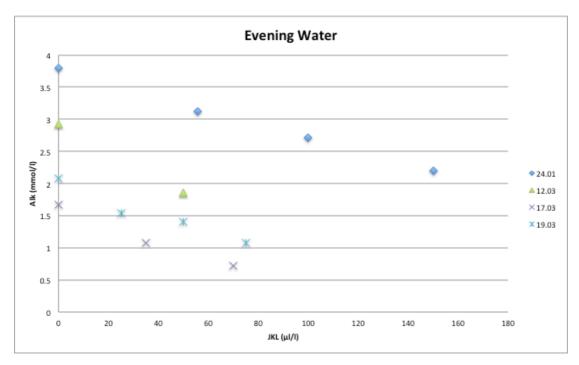


Figure 3-14 Alkalinity and JKL dose on evening water

## 3.7 TSS vs. Alkalinity

Figure 3-15 shows the relationship between the final concentrations of TSS and the end values of alkalinity for morning and evening water.

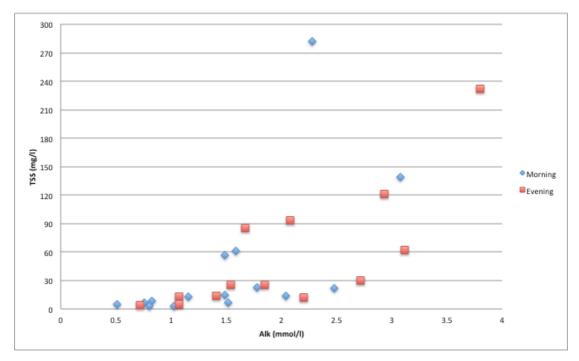


Figure 3-15 Relationship between final TSS and alkalinity

## 3.8 TSS vs pH

As mentioned before, the optimum pH for removal of TSS is around 6.00. When the pH drops below this value, eventually the concentration of suspended solids will start to go up again. This can be clearly seen on Figure 3-16 below.

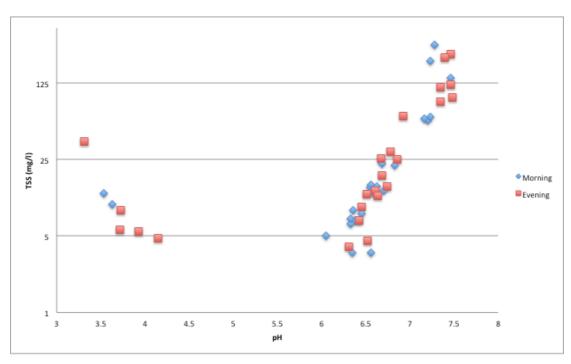


Figure 3-16 Relationship between TSS and pH

## 4 Conclusions

Adding ferric chloride as a coagulant to wastewater significantly increases the removal of suspended solids. However, excess coagulant is counterproductive since it leads to re-stabilization of the particles. Furthermore, the removal rate of TSS decreases with higher doses of JKL, which means higher costs for treatment.

The results indicate that higher alkalinity affects precipitation negatively; so high alkalinity requires higher ferric chloride dosage. This is corresponding to the observations at the plant. Lower alkalinity produced lower effluent TSS.

The alkalinity is proportionally reduced with increasing additions of ferric chloride.

The pH is reduced with increasing dosages of coagulant. When the pH drops significantly, the concentration of solids rises again. It was observed that precipitation occurs over a range of pH values, and no exact optimum pH could be determined for this wastewater.

## 5 Future Research

It was seen that lower alkalinity produced lower effluent TSS, and further studies of this should be to alter the alkalinity by adding acid or base to the wastewater before adding ferric chloride. This could indicate if it is only alkalinity that is affecting the precipitation process or if other parameters are involved. Such tests could also contribute to explain the exact mechanism of the chemical reactions involved.

Since no exact optimum pH could be determined for this wastewater, it is still necessary for further studies to be carried out in order to determine how to control the ferric chloride dosage based on pH.

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Appendix

# Appendix A

Date	Time	JKL (μl/l)	рН	Conductivity (mS/cm)	TSS (mg/l)	ΔTSS (mg/l)	Removal %	TSS removal (mgSS/μl JKL)	Alk (mmol/l)	ΔAlk (mmol/l
24.01		0	7.46	2.12	139.10	-	0.00	-	3.08	-
	Morning	55.6	6.83	-	22.00	117.10	84.18	2.11	2.48	0.60
		100	6.63	-	14.30	124.80	89.72	1.25	2.04	1.04
		150	6.38	-	6.90	132.20	95.04	0.88	1.52	1.56
		0	7.46	1.62	232.00	-	0.00	-	3.8	-
	Evening	55.6	6.92	-	62.10	169.90	73.23	3.06	3.12	0.68
		100	6.78	-	29.60	202.40	87.24	2.02	2.72	1.08
		150	6.51	-	12.00	220.00	94.83	1.47	2.2	1.60
05.03	Morning	0	7.23	5.47	198.00	-	0.00	-	-	-
		33	6.55	-	14.00	184.00	92.93	5.52	-	-
		67	6.42	_	7.00	191.00	96.46	2.87	_	_
		111	3.63	_	9.75	188.25	95.08	1.69	_	_
		0	7.39	3.06	215.00	-	0.00	-	-	-
	Evening	56	6.68	-	18.00	197.00	91.63	3.55	_	_
		111	3.93	_	5.50	209.50	97.44	1.89	_	_
		167	3.72	_	5.75	209.25	97.33	1.26	_	_
	Morning	0	7.28	1.25	282.00	-	0.00	-	2.28	
		30	6.68	1.25	23.00	259.00	91.84	8.63	1.78	0.51
		60	6.56	-	14.67	267.33	94.80	4.46	1.49	0.80
		100	3.53	-	12.33	269.67	95.63	2.70	NA	-
12.03		0	7.46	1.13	120.80	-	0.00	-	2.93	-
				1.15						1.00
	Evening	50	6.67		25.50	95.30	78.89	1.91	1.85	1.09
		100	4.15	-	4.75	116.05	96.07	1.16	NA	-
		150	3.73	-	8.67	112.13	92.83	0.75	NA	-
		0	7.20	3.01	57.00	-	0.00	-	1.49	0.55
	Morning	21	6.36	-	8.57	48.43	84.96	2.31	0.83	0.65
	_	42	6.33	-	6.50	50.50	88.60	1.20	0.76	0.72
17.03		70	6.05	-	5.00	52.00	91.23	0.74	0.51	0.98
		0	7.35	1.07	85.33	-	0.00	-	1.67	-
	Evening	35	6.61	-	13.00	72.33	84.77	2.07	1.07	0.60
		70	6.31	-	4.00	81.33	95.31	1.16	0.72	0.94
		105	3.31	-	36.40	48.93	57.34	0.47	NA	-
		0	7.23	1.89	61.25	-	0.00	-	1.59	-
19.03	Morning	15	6.70	-	12.86	48.39	79.01	3.23	1.16	0.43
		30	6.56	-	3.50	57.75	94.29	1.93	1.03	0.57
		50	6.35	-	3.50	57.75	94.29	1.16	0.80	0.80
	Evening	0	7.48	1.36	93.00		0.00	-	2.08	
		25	6.86	-	25.20	67.80	72.90	2.71	1.54	0.54
		50	6.74	-	14.29	78.71	84.64	1.57	1.41	0.67
		75	6.52	-	4.50	88.50	95.16	1.18	1.07	1.01
21.03	Morning	0	7.16	2.30	59.33	-	0.00	-	-	-
		15	6.59	-	12.29	47.05	79.29	3.14	-	-
		30	6.45	_	8.00	51.33	86.52	1.71	-	-
		50	6.33	_	7.25	52.08	87.78	1.04	_	_
		0	7.35	3.29	115.00	02.00	0.00	-	-	-
		25	6.64	-	11.72	103.28	89.81	4.13	_	_
	Evening									
	Evening	50	6.45	_	9.25	105.75	91.96	2.12	_	

## **Kemira PIX-318**

Kemira PIX-318, jernkloridsulfat, er et flytende fellingsmiddel for vannresning og inneholder aktive 3-verdige jernforbindelser. PIX-318 egner seg for avløpsvanns- rensing, overflate- og grunnvannsrensing og slamkondisjonering i de fleste renseprosesser. PIX-318 er effektiv ved bekjempelse av hydrogensulfid.

### Kjemisk data

Jern Fe <sup>3+</sup>	$11,6 \pm 0,3$	%
pH	<1,0	
Tetthet	$1,50 \pm 0,03$	g/cm <sup>3</sup>
Fri syre	<20	g/kg PIX-318
Sulfat (SO <sub>4</sub> 2-)	<230	g/kg PIX-318
Klorid (CI)	<100	g/kg PIX-318
Uløst stoff	<0,05	%
Krystallisasjonstemp	0°C	
Aktiv stoff (Me)	ca 2,1	mol/kg (3,1 mol/l)

#### Sporstoff Typiske analyseverdier <1,00 mg/kg PIX-318 <0,05 mg/kg PIX-318 <20,00 mg/kg PIX-318 Bly (Pb) Kadmium (Cd) Kobolt (Co) <1,00 mg/kg PIX-318 <5,00 mg/kg PIX-318 <0,05 mg/kg PIX-318 Kobber (Cu) Krom (Cr) Kvikksølv (Hg) <40,00 mg/kg PIX-318 <70,00 mg/kg PIX-318 Nikkel (Ni)

### Dosering

Dosering av PIX-318 skjer med pumper i korrosjonsbeskyttet utførelse. Rørledninger og ventiler skal være utført i plast eller gummiert stål. PIX-318doseres uten fortynning direkte fra lagertank.

**Godkjenning**PIX-318 er godkjent av SNT som fellingsmiddel ved drikkevannsrensing.

### Kvalitet og miljø

Kemira Chemicals er sertifisert iht ISO9001/PR2 og 14001.

### Omregningstabell for dosering

ml PIX- 318/m³	g PIX- 318/m <sup>3</sup>	g Fe /m³
20 40 60 80 100 120 140 160 180 200 300 400 500	29,8 59,6 89,4 110,2 149,0 174,8 208,6 238,4 268,2 298,0 447,0 596,0 745,0	3,46 6,91 10,37 13,83 17,28 20,74 24,20 27,65 31,11 34,57 51,85 69,14 86,42
1	l	1

### Håndtering

Beskyttelsesbriller skal benyttes ved åpen håndtering av PIX-318.

Personlig verneutstyr benyttes ved behov.

Lagertanker og beholdere skal merkes:

### FTSENDE VÆSKE **JERNKLORIDSULFAT**

### Lagring

PIX-318 bør ikke lagres mer enn 12 måneder. Lagertank bør utføres i glassfiberarmert polyester eller gummiert ståltank. Lagertank bør inspiseres og rengjøres 1 gang per år.

### Vernetiltak

PIX-318 er svakt etsende. Kroppsdeler som kommer i kontakt med væsken skal skylles med rikelig mengder

vann. Øynene skylles godt med øyen-skyllevann fra spyleflaske i minst 5 minutter. Ved varig irritasjon i øynene eller på huden bør lege kontaktes.

 $\stackrel{-}{\text{Ved søl bør det spyles med vann }} og$ nøytraliseres med kalk eller kalkstensmel.

KCAS

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