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**INTENSIFICATION OF OPERATION OF INCLINED PLATE SETTLER AT
FERTILIZER PLANT**

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TIIVISTELMÄ

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Lannoitetehtaan lamelliselkeyttimen toiminnan tehostaminen

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Keywords: wastewater treatment processes, inclined plate settler, sedimentation, chemical precipitation, flocculation

Lannoitetehtaan prosessivedet sisältävät typpiyhdisteitä, kuten ammoniumia ja nitraattia, suurina pitoisuksina. Prosessivesissä on myös fosforia ja fluoria, jotka ovat peräisin lannoitteiden valmistuksessa käytettävästä fosforihaposta ja raakafosfaatista. Fosfori ja typpi ovat vesistöjen rehevöitymistä aiheuttavat pääraavinteet.

Lannoitetehtaan prosessivedet kiertävät suljetussa kierrossa. Prosessivettä käytetään kaasunpesurijärjestelmässä lannoiterektoilelta ja rakeistusrummuihelta tulevien kaasujen pesuun sekä lannoiteprosessin jäähdytysvetenä neuralointireaktoreilla. Kiintoaineet erotetaan prosessivesistä lamelliselkeytimessä painovoimaisesti laskeuttamalla. Nykytilanteessa lamelliselkeytin ei toimi tyydyttäväällä tavalla.

Tutkimuksen tavoitteena oli lamelliselkeyttimen toiminnan tehostaminen ja siten kiintoaineen erotustehokkuuden parantaminen esim. koagulaatio- ja/tai flokkulaatioprosessien kautta. Lisäksi tutkittiin liuonneiden aineksien, erityisesti typen, fosforin ja fluorin, poistamista prosessivesistä kemiallisella saostuksella.

Fosfori- ja fluoripitoisuudet pienentivät merkittävästi kemiallisella saostuksella. Vuotuiset kemikaalikustannukset olivat lähes kahdeksan kertaa pienemmät kuin aiemmissa tutkimuksissa esitetyt. Typpiyhdisteet sen sijaan ovat hyvin vesiliukoisia, ja niiden poistaminen saostamalla on hankala. Mahdollisia tekniikoita typpiyhdisteiden poistamiseen ovat adsorptio, ioninvaihto ja käänteisosmoosi. Laskeutumisnopeudet pH-säädetyillä ja flokatuilla prosessivesillä olivat riittävät lamelliselkeyttimen toiminnan kannalta. Jatkotutkimuksissa olisi hyödyllistä mallintaa virtausominaisuudet lamelliselkeytimessä sekä selvittää erilaisten adsorbenttien, ioninvaihtohartsien ja kalvojen soveltuvuutta typpiyhdisteiden poistamiseen laboratoriokokeiden avulla.

ABSTRACT

Lappeenranta University of Technology
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Intensification of Operation of Inclined Plate Settler at Fertilizer Plant

Master's thesis

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108 pages, 41 figures, 18 tables, and 4 appendices.

Examiners: Professor Ilkka Turunen

M.Sc. (Tech.) Johanna Heikkinen

Keywords: wastewater treatment processes, inclined plate settler, sedimentation, chemical precipitation, flocculation

Fertilizer plant's process waters contain high concentrations of nitrogen compounds, such as ammonium and nitrate. Phosphorus and fluorine, which originate from phosphoric acid and rock phosphate (apatite) used in fertilizer production, are also present. Phosphorus and nitrogen are the primary nutrients causing eutrophication of surface waters.

At fertilizer plant process waters are held in closed internal circulation. In a scrubber system process waters are used for washing exhaust gases from fertilizer reactors and dry gases from granulation drums as well as for cooling down the fertilizer slurry in neutralization reactor. Solids in process waters are separated in an inclined plate settler by gravitational sedimentation. However, the operation of inclined plate settler has been inadequate.

The aim of this thesis was to intensify the operation of inclined plate settler and thus the solids separation e.g. through coagulation and/or flocculation process. Chemical precipitation was studied to reduce the amount of dissolved species in process waters. Specific interest was in precipitation of nitrogen, phosphorus, and fluorine containing specimens.

Amounts of phosphorus and fluorine were reduced significantly by chemical precipitation. When compared to earlier studies, annual chemical costs were almost eight times lower. Instead, nitrogen compounds are readily dissolved in water, thus being difficult to remove by precipitation. Possible alternative techniques for nitrogen removal are adsorption, ion exchange, and reverse osmosis. Settling velocities of pH adjusted and flocculated process waters were sufficient for the operation of inclined plate settler. Design principles of inclined plate settler are also presented. In continuation studies, flow conditions in inclined plate settler should be modelled with computational fluid dynamics and suitability of adsorbents, ion exchange resins, and membranes should be studied in laboratory scale tests.

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Kuopio, March 2015

Jarkko Hukkamäki

“No amount of experimentation can ever prove me right; a single experiment can
prove me wrong.”

— *Albert Einstein*

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NOMENCLATURE

θ	inclination angle from horizontal plane	[deg]
ω	angular velocity	[radians/s]
a	acceleration	[cm/s ²]
A_p	projected surface area of single plate	[m ²]
A_{tp}	total projected surface area	[m ²]
A_{tot}	total surface area	[m ²]
d	perpendicular distance between the plates	[m]
$HLR(cs)$	hydraulic loading rate based on plate cross section	[m/h]
$HLR(hp)$	hydraulic loading rate based on projected area	[m/h]
L	length of plate	[m]
m	mass of a particle	[g]
m/m	mass/mass % (mass of solute/mass of total solution)	[%]
m/v	mass/volume % (mass of solute/volume of total solution)	[%]
n	integer (in this context 0, 1, or 2)	[-]
n	number of inclined plates	[-]
ppm	parts per million	[-]
Q	influent flow	[m ³ /h]
$Q(plate)$	flow per cell between plates	[m ³ /h]
t	settling time	[s]
u	vertical fluid velocity	[m/h]
\vec{v}_P	advection velocity (vector)	[m/h]
\vec{v}_R	vector sum (vector)	[m/h]
\vec{v}_s	fall velocity of particle (vector)	[m/h]
v	fluid velocity	[m/h]
v_o	overflow velocity	[m/h]
v_{ov}	overflow velocity based on total surface area	[m/h]
v_P	mean velocity within plate cell	[m/h]

v_s	settling velocity of free-falling particles	[m/h]
v_{sx}	settling velocity component in the x direction	[m/h]
v_{sy}	settling velocity component in the y direction	[m/h]
w	width of single plate	[m]
$w(plate)$	width of plate assembly	[m]
x	radial distance from rotation axis to particle	[cm]

ABBREVIATIONS

AN	ammonium nitrate
CFD	computational fluid dynamics
DADMAC	diallyldimethylammoniumchloride
DLVO	Derjaguin–Landau–Verwey–Overbeek (theory)
EDL	electrical double layer
HLR	hydraulic loading rate
ICP-OES	inductively coupled plasma – optical emission spectrometry
IFDC	International Fertilizer Development Center
LBM	lattice Boltzmann method
MAP	magnesium ammonium phosphate (struvite)
MF	microfiltration
NF	nanofiltration
PA	polyamine
PAM	polyacrylamide
PNK	Ponder–Nakamura–Kuroda (theory)
RCF	relative centrifugal force
RO	reverse osmosis (hyperfiltration)
SOR	surface overflow rate
TOC	total organic carbon
TOPS	technical and operating standard
UF	ultrafiltration
UNIDO	United Nations Industrial Development Organization
WEF	Water Environment Federation

1 INTRODUCTION

Phosphorus and nitrogen are the primary nutrients when considering eutrophication of surface waters. Although, nitrogen (N_2) is the major component of the Earth's atmosphere and essential component for all living things, excessive concentrations of certain nitrogen species in atmosphere as well as in terrestrial and aquatic environments can lead to significant environmental problems. In chemical compounds nitrogen can exist in seven different oxidation states. Except for N_2 (oxidation state 0), nitrogen compounds in all oxidation states are of environmental concern. From the environmental point of view, the most significant phosphorus compounds are inorganic in nature, such as phosphates or their dehydrated forms, usually referred to as polyphosphates or condensed phosphates [1a].

Fluorine is present in surface and groundwater as an almost completely dissociated fluoride ion (F^-). Fluoride occurrence and concentrations in water resources (surface water and groundwater), depends on several contributing factors, such as pH, total dissolved solids, alkalinity, hardness, as well as geochemical composition of aquifers [2]. In many countries worldwide, elevated fluoride concentrations results from fluorine polluted waste water discharges. Although, fluoride can at an optimum level control the dental caries, excessive amounts can cause severe health problems [1b].

Fertilizer plant at Yara's Siilinjärvi site produces different NPK, NP, and NK products with varying concentrations of nitrogen (N), phosphorous (P), and potassium (K) for markets in Finland as well as for international markets. Production capacity of fertilizers is 500 000 t/a [3]. In addition technical ammonium nitrate solutions are produced with a capacity of 85 000 t/a [3]. At Siilinjärvi site, fertilizers are produced by a mixed acid process. Circulation of process waters in a scrubber system and granulation in granulation drums are characteristics for this process.

Process waters of fertilizer plant have high concentration of nitrogen compounds, such as ammonium and nitrate. Process waters also contain phosphorus and fluorine

which originate from phosphoric acid and rock phosphate (apatite) used in fertilizer production. Concentrations of phosphorus and fluorine are low when compared to concentrations of nitrogen compounds. All process waters are held in closed internal circulation. Due to high nutrient concentrations, the chemical water treatment plant cannot process these waters.

At fertilizer plant, exhaust gases from dissolution reactors and neutralization reactors as well as dry gases from granulation drums are washed in a specific scrubber system, in which process waters are circulated. After scrubbing, all gases are directed to the exhaust stack. Process waters are also used to cool down the fertilizer slurry in neutralization reactor due to the exothermic neutralization reaction between ammonia and acids. Process waters with high concentration of dissolved species or nearly saturated are not able to wash the exhaust gases properly. This will probably have its effect on periodic difficulties to control the emissions into the air. Emissions are primarily controlled by adjusting the pH of the scrubbers. Process waters enriched by nutrients are diluted with raw water, which will increase the amount of process waters and thus have a negative influence on water balance.

Solids in process waters are separated in an inclined plate settler by gravitational sedimentation. However, solids separation by plate settler has been inadequate. The underflow slurry of plate settler device is fed back to the neutralization reactor.

As discussed above, two major challenges in process water treatment are (1) decreasing the concentration of dissolved species and (2) enhancing the solids separation. The aim of this thesis is to intensify the operation, i.e. solids settling by gravity, of inclined plate settler at fertilizer plant. This can be carried out through coagulation and/or flocculation process. In order to reduce the amount of dissolved species in process waters, the suitability of chemical precipitation is examined. The specific interest is in chemical precipitation of nitrogen, phosphorus, and fluorine containing specimens. The target of the chemical precipitation is to decrease the fluorine concentration in process waters to the level of <700 mg/L and reduce the concentrations of ammonium and nitrate by 30 %.

In addition to sedimentation and precipitation, the focus is also on other possible water treatment processes. Applicability of those processes and possible devices will be evaluated. Special attention is paid to inclined plate settler, its operation, and design principles.

2 WASTEWATER TREATMENT PROCESSES

Wastewater treatment is a combination of physical, chemical, and biological processes. Treatment methods where physical forces predominate are known as physical unit operations. Typical physical unit operations are for example screening, mixing, flocculation, sedimentation, flotation, filtration, and membrane separation [4, 5]. The four types of membrane separation processes are [6]:

- Microfiltration (removes colloids and bacteria)
- Ultrafiltration (removes viruses)
- Nanofiltration (removes large molecular weight organic molecules and some ions)
- Hyperfiltration, more commonly called reverse osmosis (removes molecules and ions)

Wastewater treatment methods in which removal of contaminants is brought about by the addition of chemicals or by other chemical reactions are known as chemical unit processes. Most common examples of chemical unit processes used in wastewater treatment are coagulation, precipitation, gas transfer, adsorption, ion exchange, and electrodialysis [4, 5].

In biological unit processes the removal of contaminants is brought about by biological activity. Primarily, biological treatment is used to remove the biodegradable organic substances, colloidal or dissolved in nature, from wastewater. Biological treatment is also used for nitrogen removal in wastewater [5]. Examples of biological unit processes are activated sludge process, trickling filtration, and sludge digestion.

Suspended solids are the most visible of all impurities in wastewater and may be inorganic or organic in nature. Coarse suspended solids are not a serious problem in wastewater treatment and can be removed readily by e.g. filtration and sedimentation. Instead, submicron particles will not settle to any significant extent and a suitable membrane filtration or agglomeration–sedimentation is needed for separation [7]. Wastewaters also contain dissolved impurities, which can be divided into three groups: inorganic, organic, and gases. For separation of dissolved matter chemical processes or membrane separation processes must be applied. Typical wastewater treatment technologies classified with the size of removable components are listed in Table 1.

Table 1. Methods for separation of wastewater impurities. [7]

	Size fraction of impurity (μm)				
Soluble <0.001	Colloidal 0.001–1.0	Filtrable 1–100	Settleable 100–1 000	Coarse $>1\ 000$	
Methods for separation	Adsorption	Coagulation/ Flocculation	Deep bed filtration	Settling tanks	Coarse screens
	Ion exchange			Medium screens	
			Precipitation	Microfiltration	
	Precipitation			Hydrocyclones	
			Ultrafiltration/ Microfiltration	Flotation	
	Nanofiltration			Fine screens	
	Reverse osmosis			Magnetic separation	
	Distillation/ Evaporation			Centrifugation	
	Air stripping				
	Electrodialysis				

As the focus of this thesis is on performance intensification of fertilizer plant's inclined plate settler and enhancing the chemical precipitation of dissolved fluorine,

phosphorus, and nitrogen, the separation techniques of main interest are sedimentation for solids removal and chemical precipitation for decreasing the dissolved matter. Unfortunately, most nitrogen compounds are readily dissolved in water implying that precipitation cannot be used as an easy solution to the nitrogen removal problem. The most potential alternatives for nitrogen removal are adsorption, ion exchange, and membrane separation techniques [8]. Coagulation–flocculation processes remove mainly the suspended particulates of colloidal dimension as indicated in Table 1 and will be discussed in Chapter 6. Inclined plate settler, its operation and principles of design are described in Chapter 3.

Biological processes for removing nitrogen compounds are not applicable in fertilizer plant's conditions due to restrictions of organic carbon in the process, and therefore they are excluded in this thesis. Specifications for maximum limits of impurities in the fertilizer product are given in Yara's technical and operating standard (TOPS) [9]. Limit for total organic carbon (TOC) is 50 ppm and for copper and chlorine 1 ppm and 10 ppm, respectively. Limit for total heavy metal impurities is 50 ppm. When nitrogen rich fertilizer grades are produced, concentration of ammonium nitrate (AN) is typically >70 %. Organics, copper, and chlorine catalyze decomposition of ammonium nitrate especially at low pH value [10] and thus, for reactor safety, concentrations of those are kept as low as possible.

3 PLATE SETTLER

Modern plate settler technology was first described by Allen Hazen in 1904 when he proposed dividing of sedimentation basin by horizontal plates into two or more compartments. He stated out that the action of the sedimentation basin is dependent on its area and not on its depth and thus one horizontal subdivision would provide two surfaces for receiving the sediment and double the capacity of the basin. In 1936 Thomas R. Camp introduced the term overflow velocity, the idea of partial removal of the particles with settling velocities slower than overflow velocity, and the concept of the ideal basin. The notion of overflow velocity as a key parameter for design of settling basins instead of detention time and tank depth was reinforced on Camp's

1946 paper. The mathematics for partial removal of particles was also extended in that paper. As Hazen, Camp also advocated horizontal plates to add surface area without increasing the horizontal velocity, but had recognized that solids removal was the problem. [11]

The improved performance of the settling basins resulted to the higher rate sludge accumulation. Thus, the focus on tray settling shifted from hydraulics to sludge and the continuous sludge removal. In the late 1950's, a study of variables such as distance between plates, angle of inclination, and inlet and outlet arrangements was started at Chalmers University of Technology (Gothenburg, Sweden). The extensive testing performed by Weijman-Hane showed that an angle of inclination at least 55° is needed for gravitational removal of solids from the plates [12]. Plate settlers came into the market around 1970 under the trade names Lamella Separator (Parkson Corporation) and GEWE Sedimentation System (Purac Corporation) [6]. GEWE plate system is shown in Figure 1. Both companies have the same origin, company named Axel Johnson.

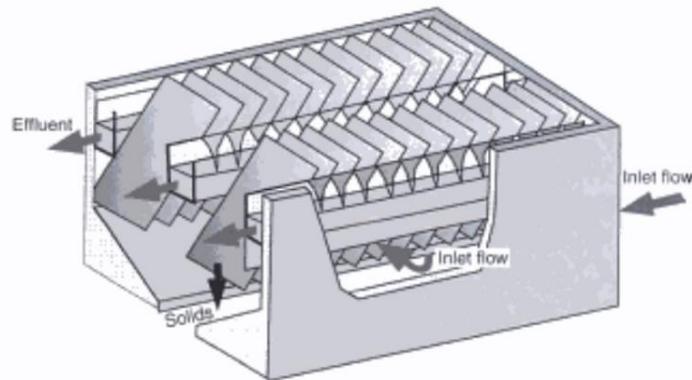


Figure 1. GEWE plate system. [11]

When referring to plate settlers, the terms lamella clarifier, lamella settler, lamella gravity settler, and inclined plate clarifier or settler are used in the literature. To be precise, the term "lamella" is a registered trademark of Parkson Corporation (Fort Lauderdale, USA), although, it is commonly used interchangeably with "plates".

3.1 Settler types

Commercial inclined plate settlers are high-rate sedimentation devices equipped with inclined parallel plates stacked to form channels for gravitational separation. The plates are typically inclined at an angle of 55° from the horizontal. In most cases, the plate spacing varies between 50–100 mm (approximately 2–4 inches). Several types of inclined plate sedimentation systems [13, 14] are commercially available as shown in Figure 2.

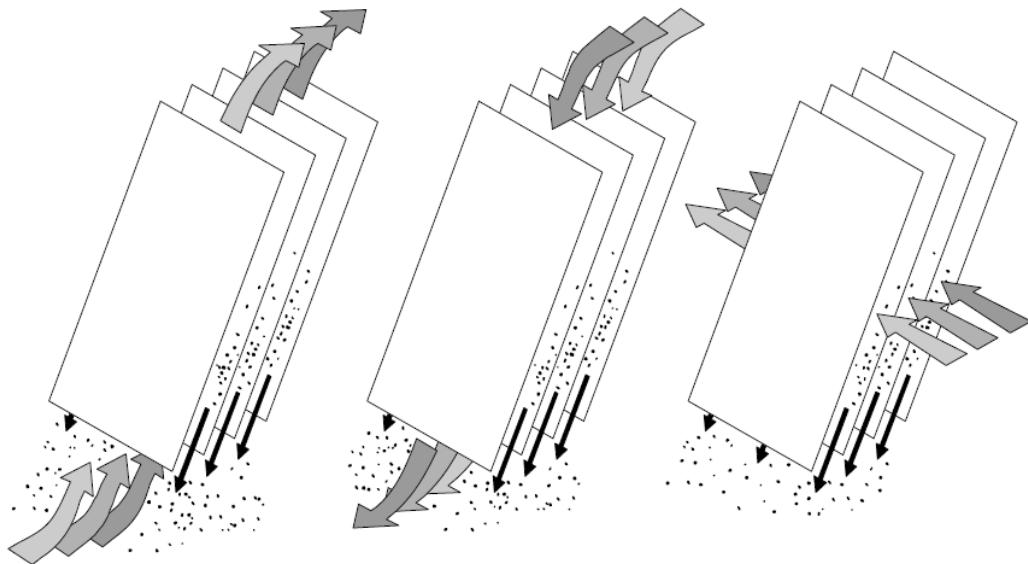


Figure 2. Inclined plate sedimentation systems of (left) counter-flow, (middle) parallel flow, and (right) cross-flow type. [14]

Most inclined plate settlers are of counter-flow type, where the suspension flows in the direction of opposite to that of the settling particles. In the cross-flow configuration the suspension flows horizontally and the sediment passes along the inclined plates in the direction normal to that of the suspension movement. The applications of parallel flow system, where the suspension flows in the same direction (downwards) as the settling particles, are few due to the mixing of the clarified suspension and thickened sediment when leaving the sedimentation area [15]. However, a parallel flow system performs really well as a sludge thickener. The focus of this thesis is on the counter-flow inclined plate sedimentation systems.

3.2 Principle of operation

The main components of the inclined plate settler are the upper tank containing the inclined lamella plates (plate packs) and the lower conical or cylindrical sludge tank. A structural drawing of commercial counter-flow inclined plate settler with different functional zones is presented in Figure 3.

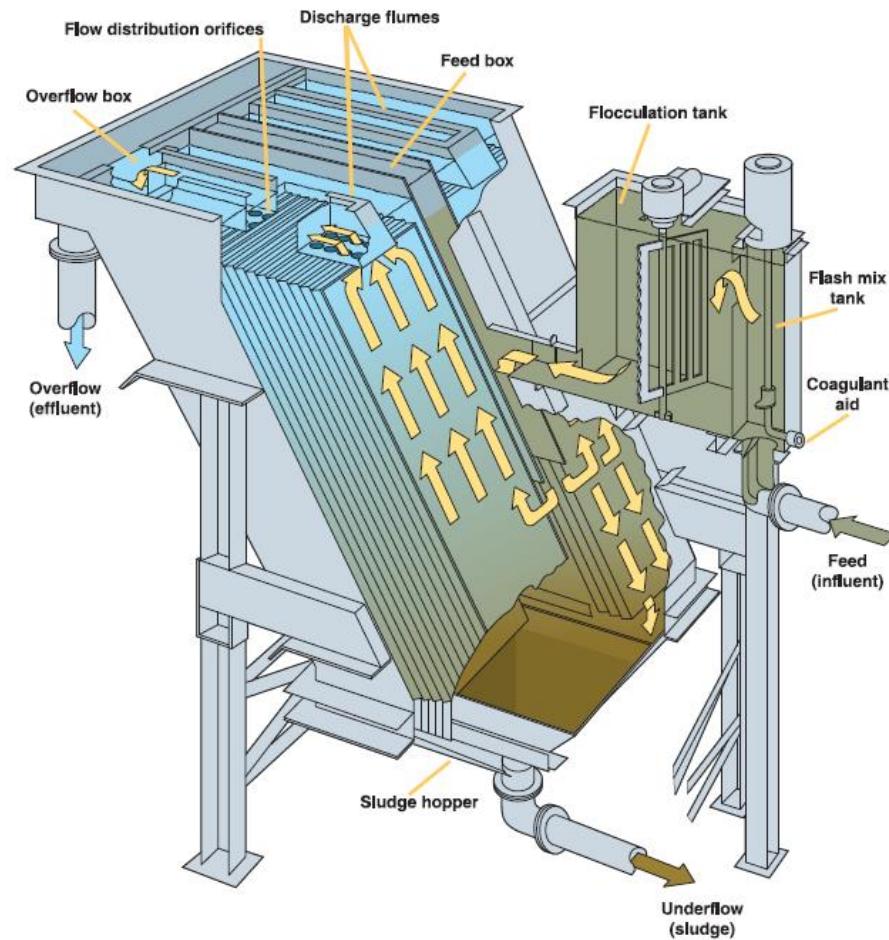


Figure 3. A structural drawing of Lamella® EcoFlow™ inclined plate settler (Parkson Corporation). [16]

The influent enters the inclined plate settler and flows downward through the vertical inlet chamber (feed box) in the center of the unit and passes into each plate gap through side-entry plate slots. Liquid flows upward and the solids settle on inclined, parallel plates and slide down to the sludge hopper at the bottom.

Above each plate pack there is a full-length overflow launder (discharge flume) with flow distribution weirs or orifices to create a slight hydraulic back pressure on the incoming feed stream. This method of feed control ensures equal flow distribution across the plates in order to utilize the full settling area with minimum turbulence at the entry points [16, 17].

Inclined plate settlers perform the same function as conventional sedimentation basins. Sedimentation efficiency of the plate settler is based on the inclined plate design. The effective gravity settling area of the inclined plate design equals each plate's area projected on a horizontal surface. When compared to a conventional clarifier, the available settling area is significantly increased within a given footprint, i.e. the physical area occupied by the unit as presented in Figure 4.

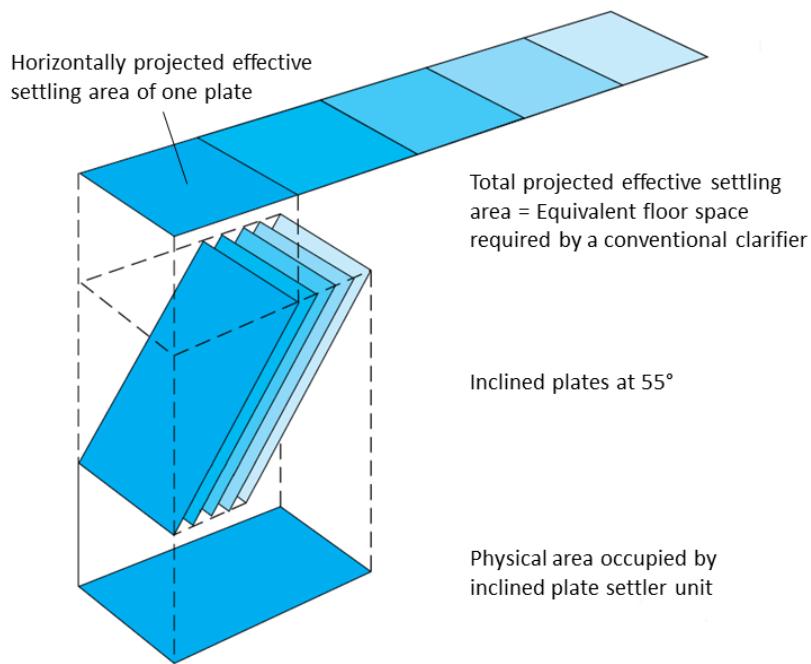


Figure 4. The footprint of the inclined plate settler and a conventional clarifier with equal effective settling areas.

The operating principle of inclined plate settler stems from the well-known Boycott effect. In 1920, A.E. Boycott discovered that the sedimentation of red blood cells under gravitational forces occurred much more rapidly in slightly inclined tubes than

in vertical ones [18]. Boycott effect for enhancing the sediment rate has been explained by analytical model (“PNK theory”) developed by Ponder (1925) and Nakamura and Kuroda (1937) as well as by numerical simulation using the lattice Boltzmann method (LBM) by Xu *et. al.* (2003) [19, 20].

3.3 Particle path

For an inclined plate settler, the particles take paths that are the vector sum of v_s and v_p , i.e., v_R [6].

$$\vec{v}_s + \vec{v}_p = \vec{v}_R \quad (1)$$

where

\vec{v}_s = fall velocity of any particle (m/h),

\vec{v}_p = advection velocity of water flow between plates of settler (m/h), and

\vec{v}_R = vector sum of fall velocity and advection velocity (m/h).

A special case in which v_s is equal to v_o , the overflow velocity, is illustrated in Figure 5.

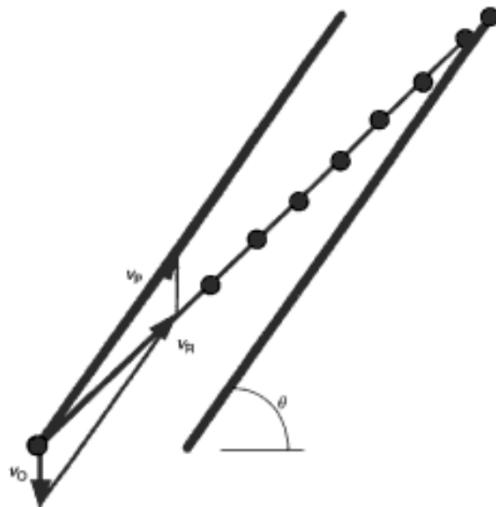


Figure 5. Velocity vectors within plate. [6]

The velocity vector \vec{v}_p is considered as the mean velocity. This is due to the simplifying of the analysis by assuming the velocity profile between the plates to be uniform. Actually, the velocity profile between the plates is parabolic as it occurs in the viscous flow range where $R<1\,000$ [6]. Based on the above assumption, all particles with the fall velocity $v_s \geq v_o$ will strike the lower plate and will be removed from the suspension.

As noted earlier, the sludge removal when operating the horizontal tray settlers proposed by Hazen and Camp was problematic. To remove solids, the settler was drained from water and the sludge was hosed to the drains. Eventually, the sludge removal problem was solved by tilting the trays to sludge slide down by gravity. Sequence for the particle removal from suspension is presented in Figure 6. The movement occurs when the shear resistance of the solids mass is exceeded by the weight component of the sludge mass in the plate direction, i.e. $m(\text{sludge mass})g\cos\theta \geq \text{shear force of sludge mass}$.

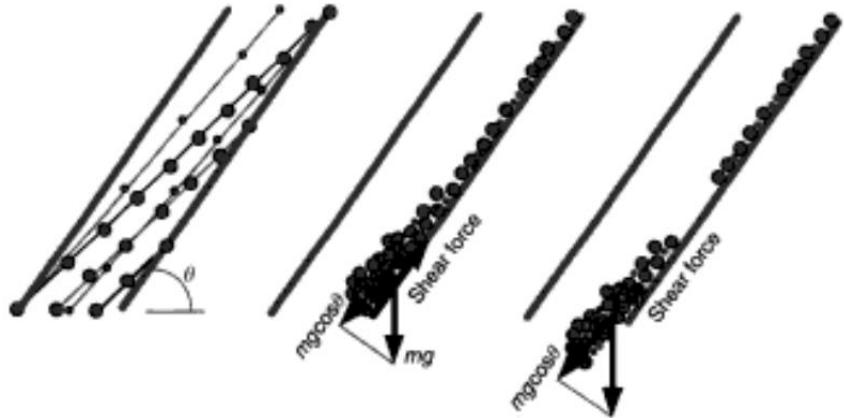


Figure 6. Phases of particle removal by inclined plate settler: (left) paths of two particle sizes with fall velocities depending on the particle size, (middle) accumulation of particles on the lower plate surface, and (right) particle mass weight component exceeding the shear force. [6]

3.4 Surface overflow rate

Design of settling tanks and inclined surface settlers (plate or tube) is governed by a parameter called surface overflow rate (SOR) already proposed by Hazen in 1904 [21]. Let's consider particle trajectories for counter-flow plate settler presented by the vector diagrams in Figure 7. Again, the smallest particles to be removed when at the entrance corner (point **a**) will strike the opposite plate at the exit (point **c**).

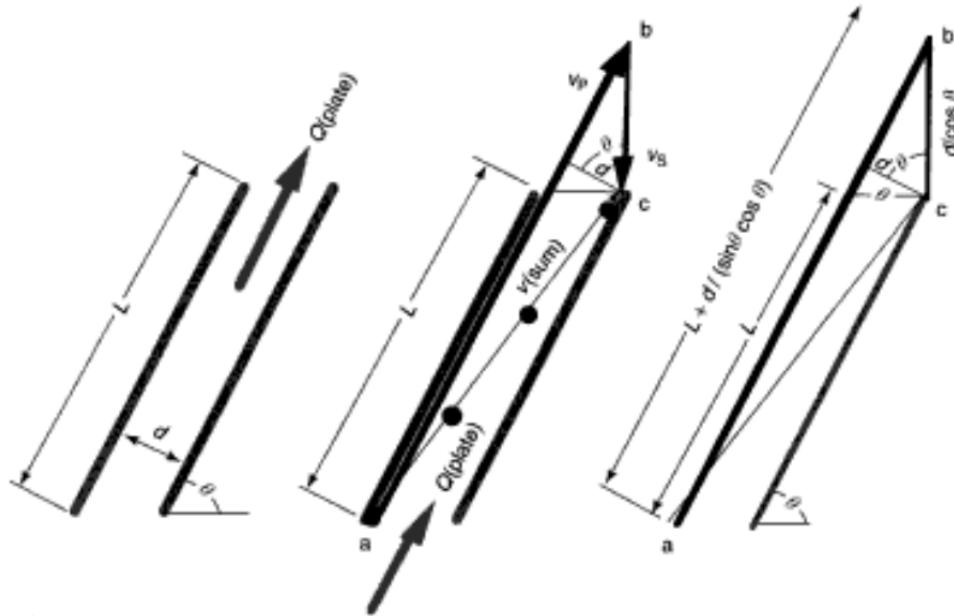


Figure 7. Particle trajectories for counter-flow plate settler: (left) flow direction, (middle) velocity vectors, and (right) geometric similarity. [6]

Mathematical relationship between the velocity vectors and the plate geometry is as follows:

$$\frac{v_o}{v_p} = \frac{d/\cos\theta}{L + d/(\cos\theta \cdot \sin\theta)} \quad (2)$$

where

v_o = fall velocity of smallest particles to be removed completely (m/h),

v_p = mean velocity within plate cell (m/h),

d = distance between the plates (m),

L = length of plate (m), and

θ = angle of plate from horizontal (deg).

Modifying the Equation 2 by placing $\cos\theta$ in the denominator gives:

$$\frac{v_o}{v_p} = \frac{d}{\left(L + \frac{d}{\cos\theta \cdot \sin\theta}\right) \cos\theta} \quad (3)$$

$$\frac{v_o}{v_p} = \frac{d}{\left(L \cdot \cos\theta + \frac{d}{\sin\theta}\right)} \quad (4)$$

Mean velocity within plate cell is determined as flow per unit of cross section area normal to the velocity vector v_p :

$$v_p = \frac{Q(\text{plate})}{w(\text{plate}) \cdot d} \quad (5)$$

where

$Q(\text{plate})$ = flow per cell between plates (m^3/h) and

$w(\text{plate})$ = width of plate assembly (m).

Substituting Equation 5 in Equation 4:

$$v_o = \left(\frac{Q(\text{plate})}{w(\text{plate}) \cdot d} \right) \cdot \frac{d}{\left(L \cdot \cos\theta + \frac{d}{\sin\theta} \right)} \quad (6)$$

$$v_o = \frac{Q(\text{plate})}{\left(L \cdot \cos\theta + \frac{d}{\sin\theta} \right) \cdot w(\text{plate})} \quad (7)$$

The denominator is the effective area for settling. If angle of plate from horizontal θ is 55° , then $d/\sin \theta = 1.22d$, which corresponds with distance of plates of 50 mm to the value of 0.06 m. Relative to the length of plate (typically 2.5–3 m) this is very small and can be neglected from the Equation 7:

$$v_o \approx \frac{Q(\text{plate})}{L \cdot \cos \theta \cdot w(\text{plate})} \quad (8)$$

Now we can see that the effective area of the plate is approximately the projection of its area to the horizontal plane. The surface overflow rate is then:

$$v_o \approx \frac{Q(\text{plate})}{A(\text{projected} - \text{plate-area})} \quad (9)$$

When referring to surface overflow rate the terms e.g. surface loading rate, overflow velocity, overflow rate, lamella velocity, and Hazen velocity are used interchangeably.

3.5 Hydraulic loading rate

Hydraulic loading rate (HLR) is also used for expressing the capacity of a plate settler system. Settling theory, however, relates v_o (SOR) to the removal of particles in a suspension. Occasionally, hydraulic loading rate is used interchangeably with surface overflow rate, although the definitions of the terms differ from each other.

Hydraulic loading rate based on plate cross section and plate area projected on the horizontal plane should be divided. The relationship between hydraulic loading rate and surface overflow rate for counter-flow plate settler is derived in the following.

Surface overflow rate is expressed by the Equation 8. By the definition, hydraulic loading rate based on plate cross section is defined as the flow between two plates per unit of cross sectional area normal to the velocity vector v_p :

$$HLR(cs) = v_p = \frac{Q(plate)}{w(plate) \cdot d} \quad (10)$$

Multiplying the Equation 8 by d/d and rearranging the equations gives:

$$v_o = \frac{Q(plate)}{w(plate) \cdot d} \cdot \frac{d}{L \cdot \cos \theta} \quad (11)$$

$$v_o = HLR(cs) \cdot \frac{d}{L \cdot \cos \theta} \quad (12)$$

Hydraulic loading rate based on projected area is expressed as the flow divided by the area of plates projected on the horizontal plane:

$$HLR(hp) = v_p \sin \theta = \frac{Q(plate)}{w(plate) \cdot d / \sin \theta} \quad (13)$$

3.6 Design principles

The theory for sedimentation tank design was developed by early papers of Hazen *et al.* (1904) and Camp (1945). The most important finding was that suspended solids removal in gravity clarifiers depends only on the surface area and not the tank depth [13]. Knowledge of suspension characteristics and settler hydraulics are the basis for settler design. Theoretical prediction of suspension behavior is not straightforward due to the distribution of particle sizes with varying settling velocities and interparticle forces determining the suspension stability. A settling particle is also subject to hydraulic complexity, e.g. uneven flow patterns, superimposed eddies, and microscale turbulence. Such effects are not predictable except by the computational fluid dynamics (CFD) [6]. Thus, the empirical approach is substantial in settler design.

The basic geometry for calculating the additional area provided by inclined plates with settling definitions is presented in Figure 8.

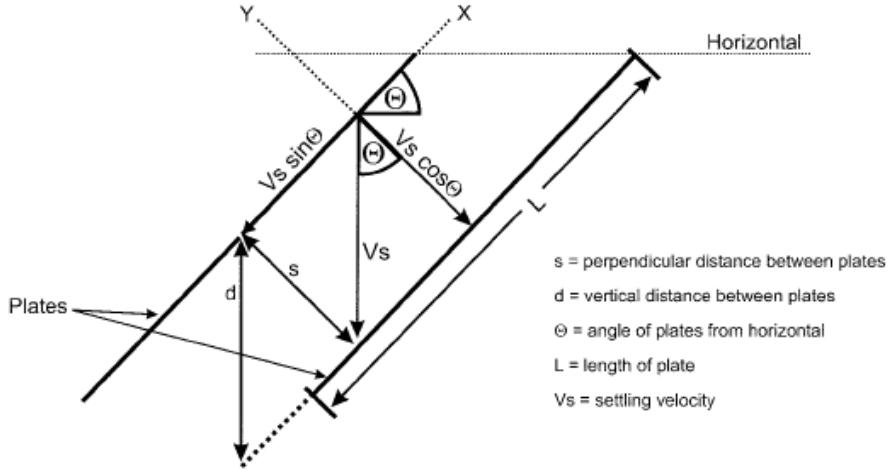


Figure 8. Settling definitions for the inclined plates. [13]

Particle velocity vectors for inclined plate settlers are expressed in the Equations 14–16:

$$v_{sx} = v - v_s \cdot \sin \theta \quad (14)$$

$$v_{sy} = -v_s \cdot \cos \theta \quad (15)$$

$$v = \frac{u}{\sin \theta} \quad (16)$$

where

θ = angle of inclination of plate from horizontal plane (deg),

u = vertical fluid velocity through the inclined plates (m/h),

v = fluid velocity (m/h),

v_s = settling velocity of free-falling particles (m/h),

v_{sx} = settling velocity component in the x direction (m/h), and

v_{sy} = settling velocity component in the y direction (m/h).

Equations for calculation of surface overflow rate as well as projected surface area are as follows:

$$v_o = \frac{Q}{A_{tp}} \quad (17)$$

$$A_p = L \cdot w \cdot \cos \theta \quad (18)$$

$$A_{tp} = n \cdot L \cdot w \cdot \cos \theta \quad (19)$$

where

Q = influent flow (m^3/h),

A_p = projected surface area of single plate (m^2),

A_{tp} = total projected surface area (m^2),

L = length of single plate (m),

w = width of single plate (m), and

n = number of inclined plates.

As stated out earlier, all particles with $v_s \geq v_o$, i.e. settling velocity greater than the overflow velocity, will strike the lower plate and will be removed from the suspension. In Ref. [13] this correlation is defined so that solids separation occurs if the component of the settling velocity in the y direction is greater than the overflow velocity based on the total surface area:

$$-v_{sy} = v_s \cdot \cos \theta \geq v_{ov} \quad (20)$$

$$v_{ov} = \frac{Q}{A_{tot}} \quad (21)$$

$$A_{tot} = n \cdot L \cdot w \quad (22)$$

where

v_{ov} = overflow velocity based on total surface area (m/h) and

A_{tot} = total surface area (m^2).

Definitions are the same. The former compares the vertical settling velocity to the surface overflow rate which is based on horizontally projected plate area, the latter compares settling velocity in the y direction (coordinate axes are presented in Figure 8) to the overflow velocity based on the total plate area in the x direction.

4 SEDIMENTATION

Sedimentation is a unit operation where suspended solid particles are separated from a suspension by gravitational or centrifugal settling [22a]. The main groups of sedimentation technology and their further subdivision into operations and equipment is presented in Figure 9. The terms clarification and thickening of sludge apply to the same unit operation depending on if the process focus is to remove the suspended particles and produce a clear effluent or to increase the concentration of suspended solids in a feed stream, respectively [13, 17, 22a].

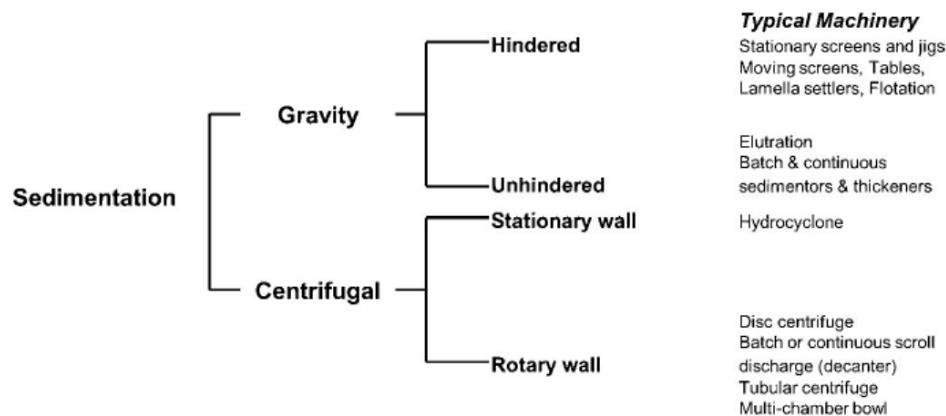


Figure 9. General classification of sedimentation equipment. [22a]

4.1 Gravity sedimentation

In gravity sedimentation a particle suspended in a liquid medium of lesser density sediments down due to the gravitational force. Feed slurry is separated into an underflow of higher solids concentration and an overflow of substantially clear liquid.

Density difference between the solids and the suspending liquid is a necessary prerequisite [22a].

Gravitational settling in a liquid medium is opposed by the forces, buoyancy force and frictional force [23]. The buoyancy force, already noted by Archimedes, is defined as an upward force equivalent to the weight of the displaced fluid. At pressures up to several bars, the buoyancy force in air or other gaseous media can be neglected, but in a liquid medium the buoyancy force is substantial. In addition to the buoyancy force, the settling of a particle through a fluid medium is restricted by the viscosity of the fluid. The frictional force is proportional to the particle velocity and its diameter. In a gas, the frictional force is negligible at low velocities and pressures. At higher velocities the frictional force becomes substantial even in gases. At the end, the frictional force together with the buoyancy force equals to the opposing gravitational force, which means that particle is no further accelerated [23].

Separation efficiency of smaller particles is also limited by the diffusional forces. In diffusion, the net movement of solute or suspended particles from higher concentration regions to lower concentration regions is generated by the random Brownian movement [23]. Generally, the diffusion rate is more pronounced on smaller particles and increases with increasing temperature. Diffusional effects can be diminished by higher centrifugal forces.

In practice, the settling of small to medium size particles under the gravity, is often taking too long time. Gravitational settling may also be hindered by the forces between the particles and/or medium resulting in stable suspension. Thus, coagulation and flocculation agents are often used to enhance gravitational settling. The use of centrifugal settling also provides greater force for disrupting the particle–particle and particle–medium interactions [23]. The theory of gravity sedimentation with mathematical expressions is presented in Refs [22a], [23], and [24].

4.1.1 Sedimentation mechanisms

Sedimentation rates of particles are dependent on particle properties such as size, size distribution, shape, and density [22a]. Particles with diameters of few micrometers settle too slowly for most practical operations. Thus, wherever possible, coagulation and/or flocculation agents are used to form larger agglomerates, called flocs, which will settle out more rapidly. Spherical or near-spherical particles and agglomerates settle considerably more rapidly than plate or needle-like particles of similar weights. Other factors affecting the sedimentation efficiency are the density and viscosity of the surrounding medium [22a].

The concentration of the particulate solids and the state of aggregation of the particles are the main factors determining the behavior of a settling suspension. Their effect on the sedimentation characteristics can be understood by analyzing a fictional batch settling experiment illustrated in Figure 10.

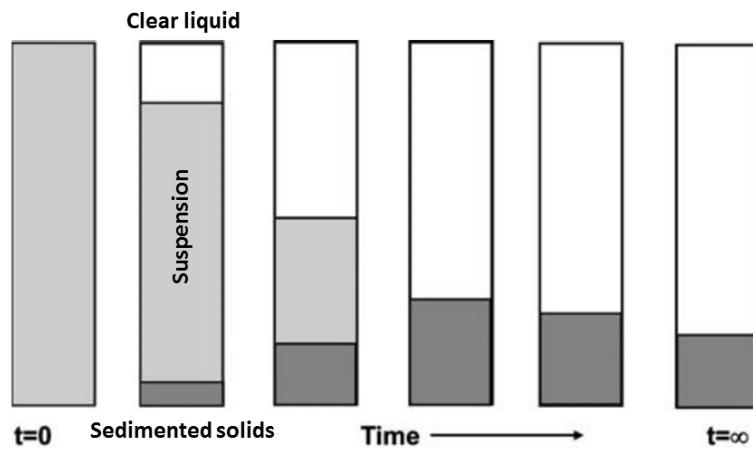


Figure 10. Schematic of a batch settling experiment. [22a]

At starting point, particles are thoroughly mixed in a suspension. In this dilute sedimentation region, solid particles are sufficiently far apart and are generally able to settle freely as discrete particles without cohering other particles. Discrete particle will settle in accordance with Stoke's law [6, 22a, 24]. Cohesion between two

contacting flocculent particles may result in increasing agglomerate size and thus a more rapidly sedimenting particle.

As particle concentration in a fluid increases, the settling rate of each individual particle decreases. This phenomenon is called hindered settling and can be explained by the relative velocity effect of a return flow as well as particle interference by collision and coagulation. It has been observed that at intermediate flocculent particle concentration the settling occurs by channeling. The sizes of the channels are around the same as the particles and they are developed during an induction period in which an increasing quantity of return fluid forces its way through the mass [22a].

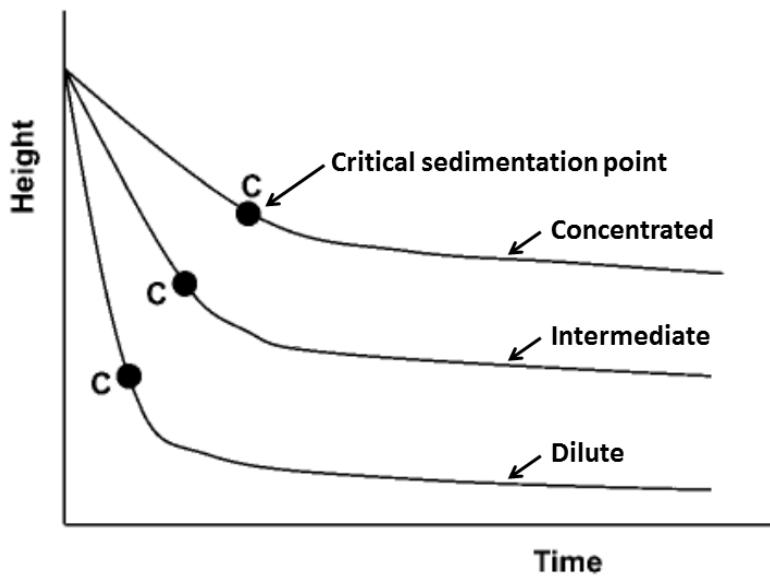


Figure 11. Effect of concentration on sedimentation. [22a]

Particles settle down into a concentrated sludge, until the suspension zone disappears and all the solids are in the sediment. This state is called the critical sedimentation point. The solids–liquid interface follows an approximately linear relationship with time until the critical sedimentation point reached as illustrated in Figure 11. The upward fluid flow in such concentrated suspensions is possible only through the very small voids between the primary particles. Resistance of the touching particles reduces the sedimentation rate to a relatively low compaction rate. In the compression

regime the rate of sedimentation is a function of both the solids concentration and the depth of settled material in the tank [22a]. The compression of sediment continues until the equilibrium between the weight of the flocs and their mechanical strength is achieved. The effects of particle coherence and solids concentration on settling characteristics of a suspension are summarized in Figure 12. It is important to note that although the suspension feed may start in one regime, it may pass through all of the regimes during clarification or thickening.

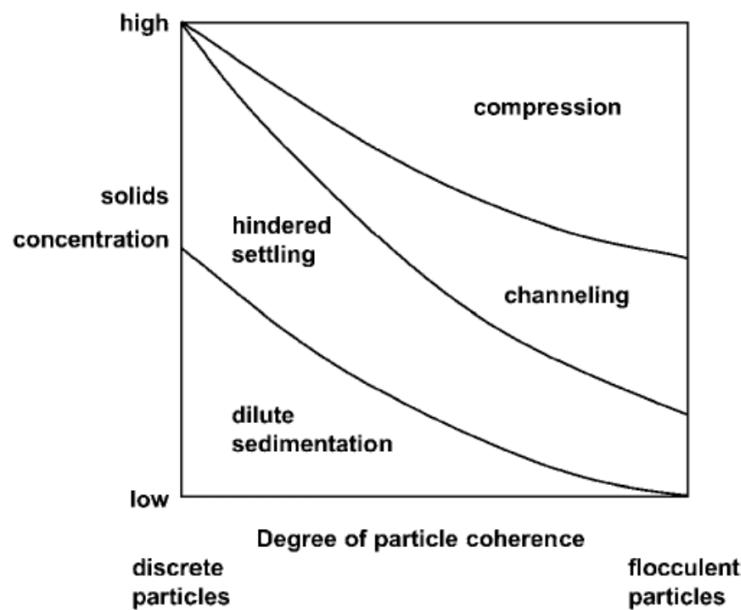


Figure 12. Effect of particle coherence and solids concentration on settling characteristics of a suspension. [22a]

Gentle stirring results to further sludge compacting by breaking up the flocs and permitting encapsulated water to escape. Required stirring in the sedimentation tanks is usually provided by mechanical rakes. Furthermore, it has been observed that stirring also improves the settling efficiency in the hindered settling region [24].

4.1.2 Gravity sedimentation equipment

Two distinct forms of sedimentation equipment are in common usage [22a]. The clarifiers, which are intended to produce a clear overflow, and thickeners, which aim

to produce an underflow that is considerably more concentrated than the feed suspension. Often thickeners produce a clear overflow as well [25]. In inclined plate clarifiers the effective settling area is increased by tilting the plates and assembling those into the stacks parallel to each other. Classification of sedimentation equipment to clarifiers and thickeners is wavering, since most of these devices can operate either clarifiers or thickeners as such or with minor modifications. For example, by modification of sludge collecting systems, the thickening of sludge in clarifiers have been improved.

Sedimentation equipment can be also divided into batch settling tanks and continuous thickeners or clarifiers. Clarifiers are typically rectangular or circular in shape. Conventional circular clarifier/thickener is presented in Figure 13.

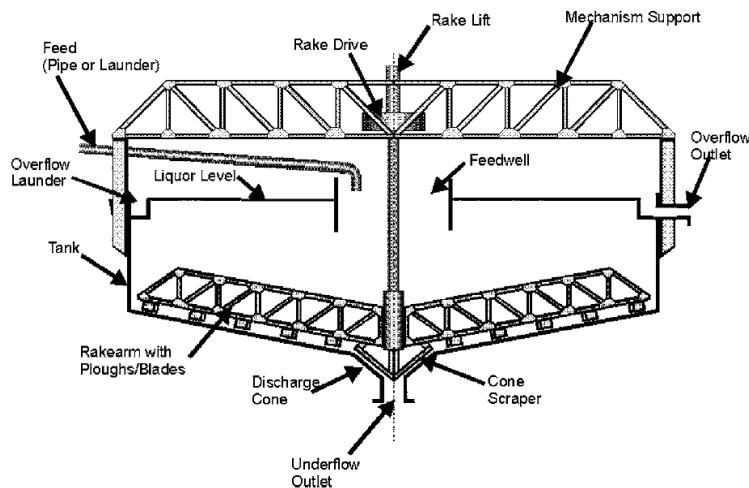


Figure 13. Conventional circular clarifier/thickener. [17]

For sludge removal circular and rectangular clarifiers are usually equipped with rakes (typically also rake lifting system is included) and flights systems, respectively. Most commercial equipment is built for continuous sedimentation with relatively simple settling tanks. Clarifiers are widely utilized in mineral processing and wastewater treatment.

4.2 Centrifugal sedimentation

Centrifugal sedimentation increases the force on particles beyond that provided by gravity, hence extending the sedimentation to finer particle sizes and to normally stable emulsions. Centrifugation equipment is divided into rotating wall (sedimenting centrifuges) and fixed-wall (hydrocyclones) devices [22a].

4.2.1 Sedimentation in centrifugal field

The forces experienced by a particle suspended in a liquid medium are presented in Figure 14. Centrifugal force, F_c , drives particles away from the axis of rotation within the centrifugal plane. The buoyancy and frictional forces, F_b and F_f , respectively, resist the centrifugal force. In general, the effect of Earth's gravity, F_g , can be neglected [23].

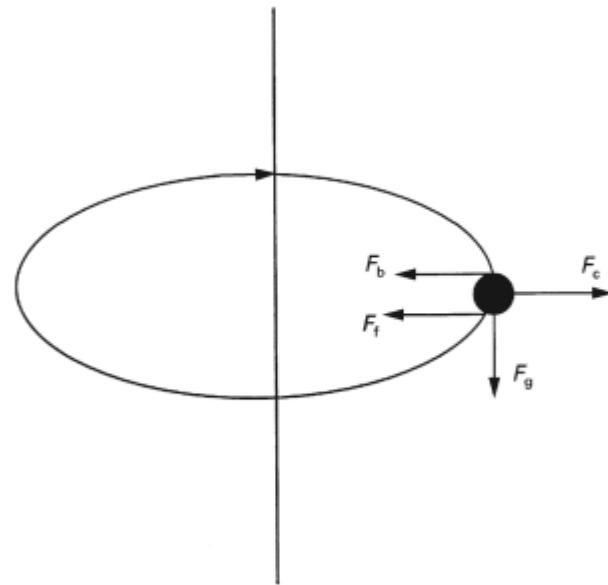


Figure 14. Forces acting on a particle in a centrifugal field. [23]

The centrifugal force acts in the plane, which is described by the circular path and its direction is away from the rotation axis. The centrifugal force is expressed as:

$$F_c = ma = m\omega^2 x \quad (23)$$

where

- m = mass of a particle (g),
- a = acceleration (cm s^{-2})
- ω = angular velocity (radians $\text{s}^{-1} = 2\pi \text{ rpm}/60$), and
- x = radial distance from rotation axis to particle (cm).

According to the Equation 23, the centrifugal force is proportional to the square of the angular velocity and to the radial distance from the rotation axis. The force generated by the centrifugal field is comparable with gravitational force by the concept of relative centrifugal force (RCF):

$$RCF = F_c/F_g = (m\omega^2 x)/(mg) = (\omega^2 x)/g \quad (24)$$

By converting ω to rpm and substituting values for the acceleration by gravity, the Equation 24 can be written in the following form:

$$RCF = 1.119 \cdot 10^{-5} \cdot (\text{rpm})^2 \cdot x \quad (25)$$

The relative centrifugal force is unitless, but it is commonly expressed in the units of g for comparison of the force generated by centrifugal field to the force of gravity [23]. The theory of centrifugal sedimentation with more mathematical expressions is presented in Refs [22a] and [23].

4.2.2 Sedimenting centrifuges

A simple batch bottle centrifuge designed to handle small material batches is common in laboratories. Industrial centrifuges are more complex and available in a variety of sizes and types [22a, 23]. Process centrifuges are divided into batch, continuous, and semi-continuous types.

Tubular centrifuges (presented in Figure 15) are used for liquid–liquid separation and clarification of dilute liquid–solid mixtures containing less than 1 % of solids and fine particles. These devices utilize long tubular bowls rotating around their vertical axis. Feed suspension is introduced at the base of the rotor. The solids are collected at the bowl wall and manually recovered after the rotor capacity is reached. Liquid is discharged continuously. The longer the feed material spends in the bowl, the longer the centrifugal force is allowed to act on the particles, resulting in a progressively clarified cleaned feed stream as it flows up the length of the tubular bowl [22a]. Industrial models are available up to diameters of 1.8 m, throughput rates of 250 m³/h, and forces ranging up to 20 000 g [23].

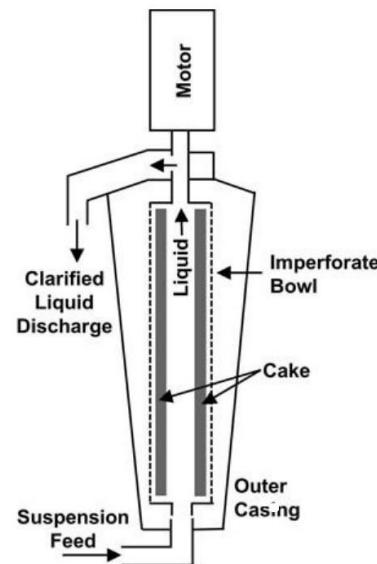


Figure 15. A tubular centrifuge. [22a]

In multi-chamber centrifuges a closed bowl is sub-divided into a number of concentric vertical cylindrical compartments. The suspension flows through the compartments in series. The efficiency of multi-chamber centrifuges is high due to the reduced traveling distance with relation to the collecting surface, but cleaning is more difficult and time consuming than for the tubular type centrifuge. Schematic of multi-chamber centrifuge is illustrated in Figure 16.

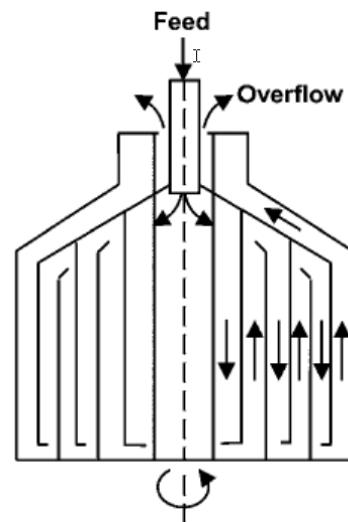


Figure 16. A multi-chamber centrifuge. [22a]

Disc centrifuge is essentially a rotating bowl equipped with a set of conical settling plates of disc mounted at an angle to the axis of rotation. The angle is typically 30–40°. The discs decrease the sedimentation path length and increase the sedimentation surface area, i.e. capacity factor [23]. The basic idea of increasing the settling capacity by the parallel plates is the same as the inclined plate principle in gravity sedimentation. Industrial scale units generate centrifugal forces of 10 000 g and are able to separate solid particles as small as 0.1 µm. In disc centrifuge denser material sediment onto the plates and slide down across the plates before accumulating on the bowl wall. Clarified liquid exists continuously. In addition to centrifugal force and flow rate, the capacity of the disc centrifuge also depends on the number of plates, plate spacing as well as the diameter of the plates. Three types of disc centrifuges divided by the solids handling are available as presented in Figure 17.

Solids retaining disc centrifuges are suitable for liquid–solid and liquid–liquid separations where the solids content is less than 1 % by volume. In some designs, removable baskets are incorporated to ease the solids removal. Solids ejecting disc centrifuges are for processing of feeds with solids content to about 15 % by volume. Solids ejecting disc centrifuge operate the same way as solids retaining disc centrifuge by the exception that solids are intermittently discharged through

peripheral opening [23]. Continuous solids discharge disc centrifuges are used for suspensions with solids content from 5 % to 30 % by volume. Solids are continuously discharged. Industrial units are available up to 200 m³/h throughput capacity, elevated temperature (≤ 200 °C) or pressure (7 bar) capability, and particle removal down to 0.1 µm [23]. Generally disc centrifuges have the best ability to collect fine particles at a high rate [22a].

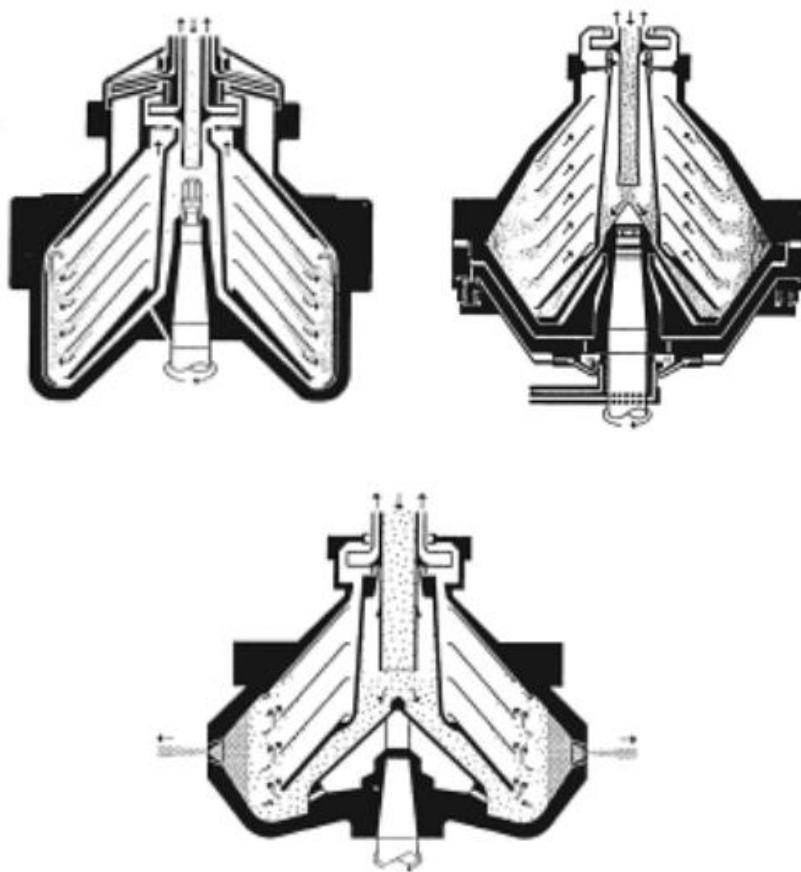


Figure 17. Disc centrifuge configurations: (up left) Solids retaining disc centrifuge, (up right) solids ejecting disc centrifuge, and (bottom) continuous solids discharge disc centrifuge. [23]

Scroll centrifuges or decanters are for continuous processing of large volume feeds. The bowl shape is tubular having length to diameter ratio of 1.5–5.2 and either horizontal or vertical operation is possible. The solids discharge mechanism is usually a helical screw rotating at a slightly slower rate than the rotor. Figure 18 illustrates a

helical screw configuration applied for three phase (liquid–liquid–solid) separation. Solid–liquid and liquid–liquid configurations with cocurrent or countercurrent flow regimes are commercially available [23].

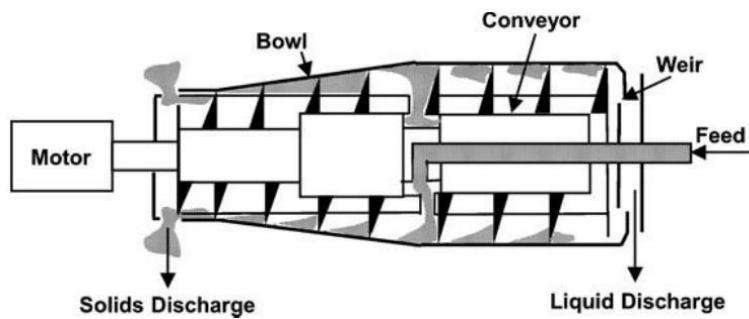


Figure 18. Schematic of a horizontal type scroll centrifuge. [22a]

Compared to disc centrifuges lower centrifugal forces to 5 000 g are generated because of the conveyor and its associated discharge mechanism. However, scroll centrifuges are capable of high throughput up to 300 m³/h and can be used to process feed streams up to 50 % solids by volume [23].

4.2.3 Hydrocyclones

Hydrocyclones operate similarly as the centrifuges, but with much larger *g* forces which is applied over the shorter residence time. The most significant difference between the centrifuges and hydrocyclones is that in hydrocyclones the centrifugal force is generated with a pump and there are no other mechanically moving parts. Energy needed for the rotation of the liquid comes from the high velocity of the liquid [22a]. Operation of hydrocyclone is illustrated in Figure 19.

The pressurized slurry is fed tangentially to the hydrocyclone, in which the slurry path involves a double vortex, where liquid is spiraling downward at the outer shell of the device and upward at the center of the device [22a]. The primary vortex at the outer shell carries the suspended material down the axis of hydrocyclone, while the secondary vortex at the center carries the overflow of dilute suspension of fine particles. The underflow of concentrated suspension contains more coarse solids.

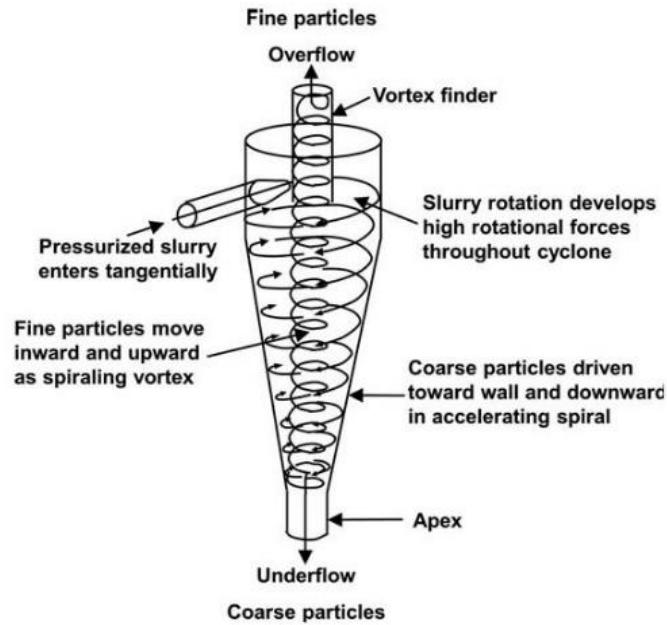


Figure 19. Operation principle of hydrocyclone. [22a]

Typically the distinction between the particles separated and not separated by hydrocyclone is not sharp. This separation problem can be solved by employing hydrocyclones in series as shown in Figure 20. The retention efficiency of solids is high with low diameter hydrocyclones setting limitations to the throughput of the device [22a]. Thus, multiple hydrocyclone units are typically operated in parallel.

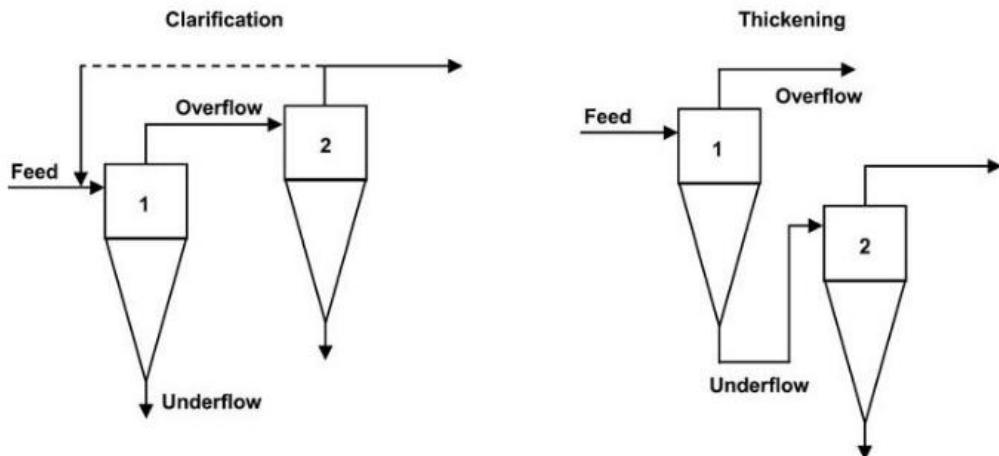


Figure 20. Hydrocyclones in series for (left) clarification and (right) thickening operations. [22a]

Hydrocyclones are utilized in separating solids and liquids from gases as well as solids from liquids. In addition, hydrocyclones can be operated at very high temperatures and pressures [22a]. Mathematical expressions for hydrocyclone separation are given in Ref [22a].

5 CHEMICAL PRECIPITATION

Chemical precipitation is a process, in which the ionic equilibrium is altered by addition of counter-ions to reduce the solubility of ionic constituents in order to produce insoluble precipitates that can be easily removed by sedimentation or filtration. Precipitation is closely related to crystallization, differing from crystallization by the facts that precipitate is usually amorphous, often poorly defined in size and shape, and generally not pure. Precipitates may also exist as aggregates. Precipitation is able to remove a large number of compounds even in one step. Chemical precipitation is primarily used for the removal of metallic cations, but also for removal of anions such as fluoride, cyanide, and phosphate, as well as organic molecules, e.g. the precipitation of phenols and aromatic amines by enzymes [26].

Major precipitation processes include water softening and stabilization, heavy metal removal, fluoride removal, and phosphate removal [26, 27]. In water softening, the divalent cationic species, mainly calcium and magnesium ions, are removed. Heavy metal removal is most widely utilized in the metal plating industry. Processes include the removal of soluble salts of cadmium, chromium, copper, nickel, lead, zinc, etc. In many process metals are also recovered. Metal ion can be removed by hydroxide precipitation, sulfide precipitation, or carbonate precipitation [27]. Phosphates are removed from wastewater to protect surface waters from eutrophication (plant growth stimulated by nutrient addition). Precipitation of fluorides and phosphates are discussed in the following.

5.1 Fluoride precipitation

Fluoride precipitation is a common method applied to high fluoride content wastewaters (>200 mg/L). Fluoride is primarily precipitated from wastewaters as calcium salt using calcium hydroxide as precipitation agent:

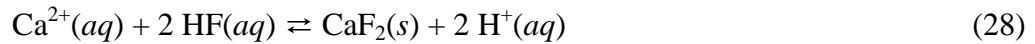


Calcium fluoride is also known as fluorite or fluorspar. Apatite also contains calcium fluoride which, in fertilizer process, reacts with nitric acid yielding calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and hydrofluoric acid (HF) [28]. Hydrofluoric acid reacts further with silica originating from apatite and hexafluorosilicic acid, H_2SiF_6 , is formed. Hexafluorosilicic acid is also known as hydrofluorosilicic acid, fluorosilicic acid, or fluosilicic acid. Fluosilicic acid decomposes due to action of temperature and acids yielding silicon tetrafluoride (SiF_4) and hydrofluoric acid. In the presence of calcium, sodium, and potassium silicofluorides CaSiF_6 , Na_2SiF_6 , and K_2SiF_6 , respectively, are precipitated. Precipitations of silicofluorides are troublesome especially in cold surfaces.

Fluoride, F^- ion, is a weak base and it is a conjugate base of the hydrogen fluoride, HF, which is a weak acid [29]. Chemical equilibrium can be written as follows:



The equation for the overall process is:



From the overall equation we can see that when acidity is increased, the solubility equilibrium of CaF_2 is shifted to the left according to the Le Châtelier's principle, thus solubility of CaF_2 is increasing with increasing acidity, i.e. decreasing pH value. The effect of pH value on solubility of CaF_2 is illustrated in Figure 21.

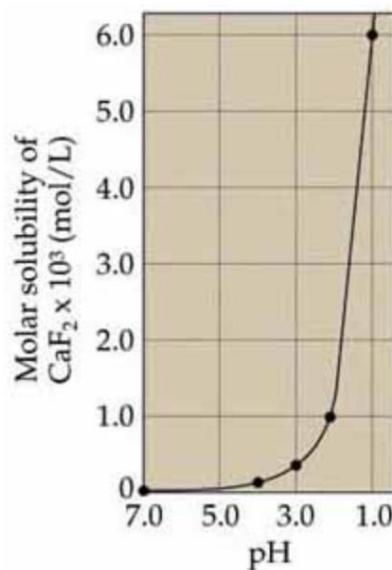


Figure 21. The effect of pH on solubility of CaF_2 . Notice that the pH scale is given with acidity increasing to the right and the vertical scale has been multiplied by 10^3 . [30]

As seen from the solubility–pH diagram, the fluoride precipitation proceeds most efficiently from the reaction mixture with $\text{pH} \geq 6$.

The precipitation of fluoride by calcium compounds, such as CaCl_2 , CaCO_3 (calcite), and $\text{Ca}(\text{OH})_2$, have certain limitations. A chemical comparison of these calcium additives are given in Table 2.

Table 2. Available calcium species for the precipitation of fluoride in the effluents. [31]

Compound	Stoichiometrically available Ca (mass %)	Water solubility (g/100 g H_2O)
CaCl_2	36.11	81.3
$\text{Ca}(\text{OH})_2$	54.09	0.160
CaCO_3	40.04	0.00066

It is noted that while calcium hydroxide contains higher mass concentrations of calcium species than calcium chloride (54.09 % vs. 36.11 %), its solubility is much lower (0.160 g/100 g H_2O vs. 81.3 g/100 g H_2O). Thus, when calcium hydroxide is

added to the effluent, the concentration of calcium species available for interaction with fluoride ions is considerably lower. When considering the fertilizer process, the maximum acceptable chloride concentration in the fertilizer slurry is 10 ppm [9] and thus any addition of chlorides to the process should be avoided. Calcium carbonate has moderate calcium concentration, but it can be regarded almost insoluble to water.

The benefit of calcium hydroxide is that its alkalinity is able to increase the pH of effluent, thus favoring the precipitation of calcium fluoride as its solubility decreases. As calcium hydroxide has low water solubility, larger volumes are required to adequately precipitate the fluoride species. However, Grzmil and Wronkowski [32] have found in their studies that calcium hydroxide is the most efficient precipitant among calcium compounds. Due to its low water solubility, calcium hydroxide is typically added to the reaction tank in a slurry form.

5.2 Phosphate precipitation

Phosphates can be precipitated from wastewaters as metal phosphates by di- or trivalent metal salts into wastewater or by calcium compounds. The precipitation of phosphates by the addition of iron and aluminum salts results on the precipitation of $\text{FePO}_4 \cdot 2 \text{H}_2\text{O}$ (strengeite) and $\text{AlPO}_4 \cdot 2 \text{H}_2\text{O}$ (variscite). The precipitate formation depends on the pH value. Results obtained at pH range from 5 to 6 have been promising, since iron and aluminum phosphates possess the lowest solubility at this pH range. Metal phosphates precipitate as colloids, hence leading to the formation of large sludge quantities. Precipitation with calcium compounds is of great importance in the chemical dephosphation of wastewater [32].

Depending on the composition of wastewater, pH, and the molar ratio of calcium and phosphate ions, the deposition of hydrated dicalcium phosphate ($\text{CaHPO}_4 \cdot 2 \text{H}_2\text{O}$), monetite (CaHPO_4), octacalcium phosphate ($\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5 \text{H}_2\text{O}$), amorphous calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), and tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) may be obtained [32]. Distribution diagram for phosphoric acid, H_3PO_4 , is shown in Figure 22.

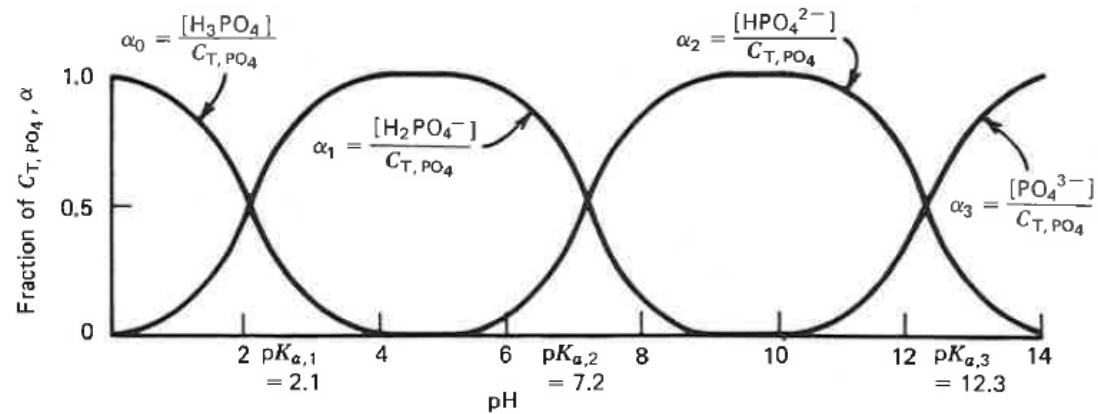


Figure 22. Distribution diagram for H_3PO_4 . [29]

The pH of solution is important as the solubility of phosphates decreases along with increasing pH value. The effective pH value to which calcium hydroxide can be dosed was found to be 9.0. A minimum relation of calcium to phosphate ions should be 1.49 [32]. Precipitation of calcium phosphates is also greatly influenced by the accompanying ions, especially carbonates and magnesium.

5.3 Nitrogen removal by precipitation

As pointed out earlier, most nitrogen compounds are readily dissolved in water implying that the use of chemical precipitation method is severely restricted. Generally, struvite precipitation has been used in wastewater treatment to reduce the phosphate concentration in the effluent, but also chemical precipitation of ammonium in the form of struvite has been studied widely from various types of wastewaters, e.g. landfill leachate, industrial wastewater, and semiconductor wastewater [33].

Struvite or magnesium ammonium phosphate (MAP) is a white orthorhombic crystalline substance consisting of magnesium, ammonium, and phosphate in equal molar concentrations. The basic chemical reaction to form struvite is expressed in Equation 29:



where

$$n = 0, 1, \text{ or } 2.$$

Parameters that influence on the precipitation of struvite are pH, temperature, ionic strength of the solution, and molar ratios of magnesium, ammonium, and phosphate. The optimal $\text{Mg}^{2+} : \text{NH}_4^+ - \text{N} : \text{PO}_4^{3-} - \text{P}$ molar ratio for struvite precipitation ranges from 1 : 1 : 1 to 1.6 : 0.6 : 1 according to different studies [33]. Solubility of struvite has been reported to decrease when the pH of the solution increases so that ammonium nitrogen removal has its optimum at the pH of 9.2.

Struvite can be used as a substitute of phosphate rock in phosphate industry or as agricultural fertilizer. Struvite precipitation has been mainly used for the treatment of wastewater from anaerobic processes [34]. On the other hand, struvite can create problems in process pipes, pumps, and other equipment in wastewater due to crystal formation on critical surfaces. Struvite formation can be controlled by minimizing the concentration levels of any of the three main soluble ions. By precipitating the orthophosphate ion (PO_4^{3-}) with a trivalent metal, such as ferric iron (Fe^{3+}) or aluminum (Al^{3+}) (see Paragraph 5.2), the precipitation of metal orthophosphate will reduce the soluble phosphorus levels in wastewater, thus lowering the potential of struvite crystallization.

Process waters at fertilizer plant contain high concentrations of ammonium nitrogen while concentrations of phosphorus and magnesium are low. Thus, the removal of ammonium nitrogen by struvite precipitation would require substantial additions of low concentration components. Another drawback is the high pH value required for precipitation of struvite and decreasing pH with nitric acid prior to feeding back to the scrubber system. As well, chemical costs for adjusting molar concentrations and increasing pH would become too high.

6 COAGULATION AND FLOCCULATION

The finely dispersed particles of colloidal size (0.001–1 µm) cannot be separated completely by sedimentation or filtration processes. These particles cause the turbidity of water and may consist of minerals such as silica and clays, algae cells, bacteria, viruses, organic detritus, or insoluble pollutants [35]. However, colloidal particles can be removed by utilizing coagulation and flocculation techniques. Coagulation is the removal of finely divided non-settleable solid particles, especially colloids, by aggregation into larger particles occurring through the destabilization of the electrical double layer (EDL). Flocculation, instead, is the formation of even larger particles by the formation of bridges between coagulated particles through the adsorption of large polymer molecules and by other forces [26]. After coagulation and/or flocculation, the aggregates can be removed by separation processes such as sedimentation, flotation, or filtration.

6.1 Colloidal stability

Stability of colloidal particulate matter resists their removal by settling or filtration. The stability of the colloids is due to their size and electrical properties. The factors affecting to the stability are the chemical nature of the colloid and the chemistry of the dispersion medium, e.g. the ionic strength, pH, and organic content of water [1c]. Due to the small colloidal particle size their surface area in relation to the particle mass is very high. As a result, surface phenomena predominate, while gravitational effects are negligible [1c, 36].

Colloidal particles that possess either positive or negative primary charges repulse each other in the solution, thus preventing their agglomeration. Majority of colloids that exist in aqueous environment are negatively charged. A colloidal system as a whole does not have a net charge. Thus, the charges on colloidal particles are counterbalanced by ions of opposite charge (counter-ions) near the surface and in the solution phase. This inclination toward electrical neutrality results in the formation of an electrical double layer around colloidal particles as illustrated in Figure 23.

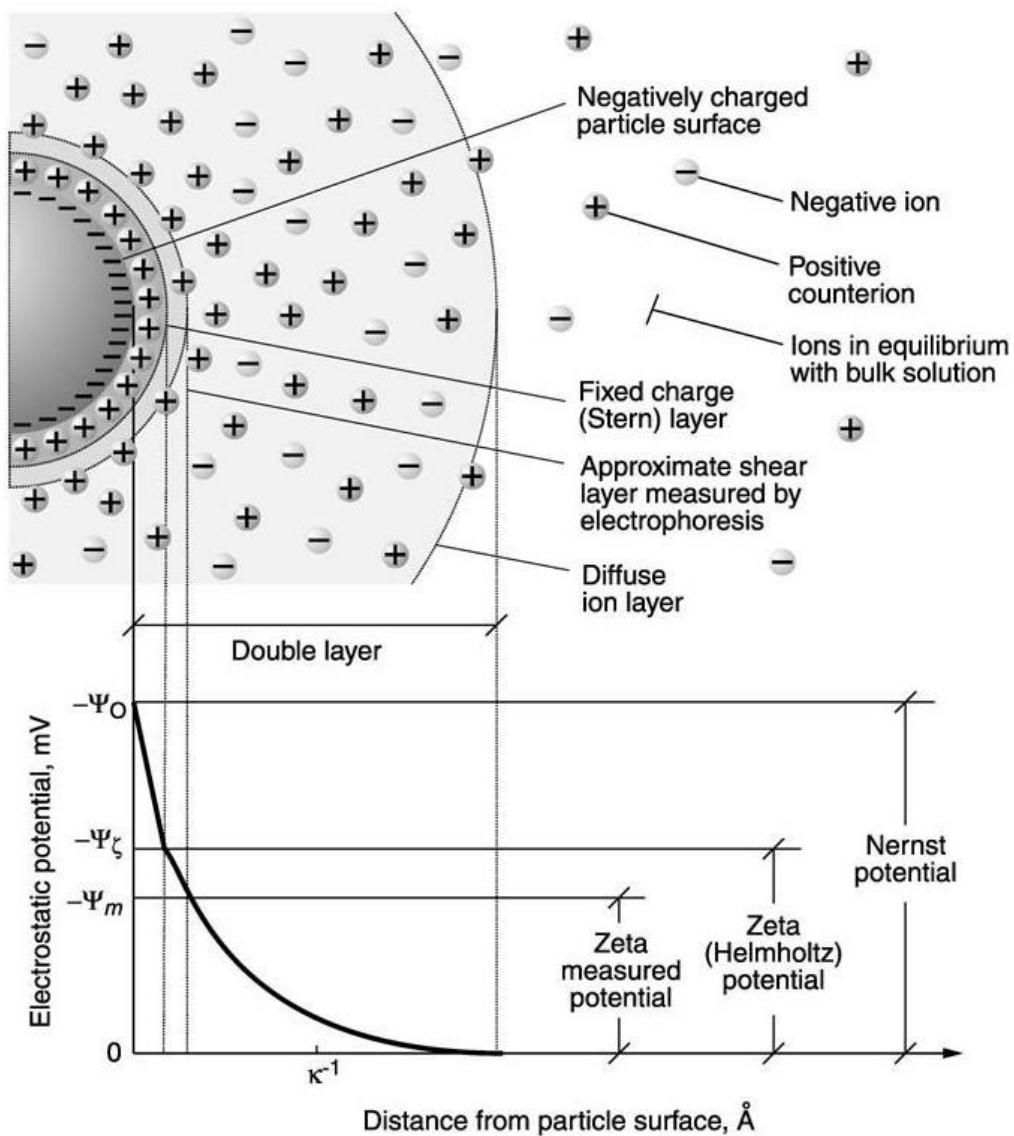


Figure 23. Conceptual representation of the electrical double layer. [37]

The electrical double layer is comprised of a (1) Stern layer (also called fixed charge layer) of oppositely charged ions adsorbed to the surface of colloid particle and (2) a diffuse layer of a mixture of charged ions [1c]. The outer limit of the Stern layer is defined as the shear surface that separates the Stern layer and the diffuse layer and defines the mobile portion of the colloid. The fixed layer including the bound water moves with the colloid particle as a unit. Counter-ions of the fixed layer are electrostatically attracted and are concentrated in the interfacial region, but still they are rather loosely attached and may diffuse away due to thermal agitation, and being

replaced by other ions. These two opposite forces — electrostatic attraction and diffusion — spread the charge over the electrical double layer such that the concentration of counter-ions is greatest at the surface and decreases with distance from the surface. If water contains a high concentration of ions, i.e. high ionic strength, the electrical double layer will be compacted, hence occupying a smaller volume and extending less far into solution [1c, 36].

Due to the primary charge on the particle, an electric potential exists between the surface of the particle and the bulk of the solution. The charge is a maximum at the particle surface decreasing with distance from the surface. When two colloidal particles with similar primary charge approach each other, their electrical double layers induce a repulsive electrostatic force to keep particles apart. The closer the particles are, the greater the repulsive force is. Repulsive forces which keep particles from aggregating are counteracted by an intermolecular attractive force termed van der Waals' force. All molecules and colloidal particles possess van der Waals' force regardless of their charge and composition. The magnitude of van der Waals' force depends on the composition and density of the colloid, but is independent of the aqueous phase composition. The van der Waals' force decreases rapidly when the distance between the particles increases [1c, 36].

Figure 24 illustrates the effect of separating distance between two particles on the net force existing between them. When particles with similar charge approach each other, the repulsive electrostatic forces increase to keep them apart. However, if two particles can be brought sufficiently close each other to overcome the energy barrier, the attractive van der Waals' force will predominate and particles will keep together. Consequently, if the destabilization and coagulation of colloidal particles is desired, the sufficient kinetic energy must be provided to overcome the existing energy barrier, or else the energy barrier must be lowered by some means. The theory of colloidal stability due to attractive and repulsive forces is called the DLVO theory according to findings of Derjaguin, Landau, Verwey, and Overbeek [1c].

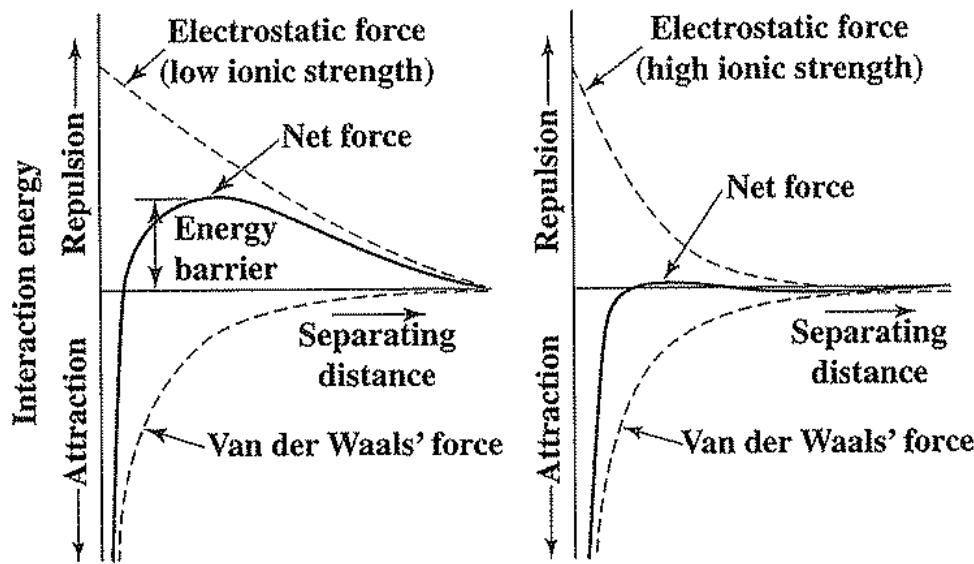


Figure 24. Effect of liquid ionic strength and separating distance between colloidal particles on the forces of interaction between them. [1c]

6.2 Destabilization of colloids

As discussed above, colloids can be stable in water due to electrostatic repulsions between the particles. In coagulation and flocculation processes, particles are destabilized with the addition of inorganic or organic chemicals which have an effect on the properties of electrical double layer. Coagulants are chemicals which reduce the repulsive energy between the particles, i.e. lower the energy barrier. Flocculation occurs when these agglomerated particles attach to each other via weak bonds. Flocculation agents improve floc properties, such as settleability and filterability [1c, 36, 37].

Colloids can be destabilized by the following mechanisms [1c, 36–39]:

- **Compression of electrical double layer.** Addition of high concentration of an electrolyte to a stabilized colloidal dispersion will increase the concentration of ions within the electrical double layer, and hence the thickness of this layer will decrease. The addition of counter-ions possessing higher charge, such as Ca^{2+} instead of Na^+ , will affect similarly resulting in a

greater decrease in charge with distance from the particle interface, thus decreasing or eliminating the potential barrier. Due to reduced or eliminated potential barrier, particles are able to collide and aggregate. Excess of salt concentration does not lead to restabilization of the particles.

- **Charge neutralization.** Destabilization occurs when oppositely charged ions or polymers are adsorbed onto the surfaces of the particles. For example, positively charged organic molecules such as dodecylammonium ion, $C_{12}H_{25}NH_3^+$, is hydrophobic and adsorb readily to negatively charged colloidal particles. Hence, the particle charge may be partially or even completely neutralized. In the case of charge neutralization, the particles no longer repel each other and optimal conditions for agglomeration are created. Trivalent aluminum and iron salts are also examples of coagulants that function in this way. They are partially or totally hydrolyzed in water forming positively charged dibasic, tribasic, or polymeric hydroxides that will readily adsorb onto the particle surface and neutralize surface charges depending on their degree of hydrolysis. Examples of aluminum salt polymers are $Al_6(OH)_{15}^{3+}$ and $Al_7(OH)_{17}^{4+}$ and of iron salt polymers are $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$. Too high coagulant dose can reverse the colloidal charge and restabilize the particles.
- **Entrapment of particles in a precipitate.** When sufficient quantities of Al(III) and Fe(III) salts are added to a solution typically at around neutral pH, they will form metal hydroxide precipitates, such as $Al(OH)_3$ and $Fe(OH)_3$, respectively. The colloidal particles are entrapped in the precipitates either during the precipitate formation or just after. This type of coagulation by enmeshment of colloids in precipitates is commonly called sweep coagulation. Required coagulant dosage is virtually independent of the type and concentration of colloids in the solution.
- **Interparticle bridging.** High molecular mass polymer chains can adsorb onto the particle surface forming bridges between adjacent particles. Adsorption

occurs by electrostatic forces, van der Waals' forces, hydrogen bonding, and chemical bonding. This mechanism is used for the coagulation produced by high molecular mass organic coagulants. The bridging mechanisms for anionic, cationic, and non-ionic organic flocculants differ from each other. Restabilization can occur when the surface is completely covered by the polymer.

In the mining industry, the mineral (anionic) suspensions are generally flocculated with anionic polyelectrolytes for economic reasons. In these suspensions, anionic particles are suspended in hard water containing divalent calcium and magnesium ions. The positively charged calcium and magnesium ions are adsorbed onto the negatively charged particle surface thus forming an ionic double layer. As the cations are facing outward, the anionic flocculant can approach the particle and adsorb on its surface. The bridging is the result of a chemical bond in which the divalent cations link the solid particles with the active groups of the polymer chain. Mineral suspensions cannot be flocculated in very soft water due to the absence of divalent calcium and magnesium ions [38]. Suspensions must be hardened with anhydrous lime before addition of polymer. Alternatively, it is possible to use cationic flocculant. Due to their positive charge, cationic flocculants partially or completely neutralize negative charge on particle surfaces cross-linking the adjacent particles. Bridging with non-ionic synthetic flocculants can only take place via hydrogen bonding.

7 REMOVAL OF MOLECULES AND IONS

Competing processes for ion removal by precipitation include ion exchange, electroprecipitation, and reverse osmosis. When compared to the chemical precipitation, the disadvantages of these processes are higher capital costs and, in the case of electroprecipitation and reverse osmosis higher energy costs for operation. All these processes are better adapted to metal recovery and recycle than chemical precipitation is. Advantages of chemical precipitation are low capital cost and simple operation. Major disadvantages are its operating costs due to the chemical expense

and the disposing of the produced precipitate [26]. In this chapter, the processes for removal of molecules and ions from wastewater are discussed.

7.1 Adsorption

Adsorption and ion exchange are sorption operations where certain components are selectively transferred from the fluid phase to the surface of solid particles. In the adsorption processes, the natural tendency of liquid or gas components to collect at the surface of a solid material is utilized. As a result selective concentration, i.e. adsorption, of one or more components (adsorbates), occurs at the surface of a microporous solid, which is called adsorbent. Primarily, the attractive forces binding the adsorbate are weaker than those of chemical bonds, hence allowing the adsorption to be reversed (regeneration of adsorbent to its original condition) by either raising the temperature of the adsorbent or by reducing the concentration or partial pressure of the adsorbate [22b]. Desorption or regeneration step allows the recovery of valuable adsorbates and enables reuse of the adsorbent. The adsorption–desorption process is illustrated in Figure 25.

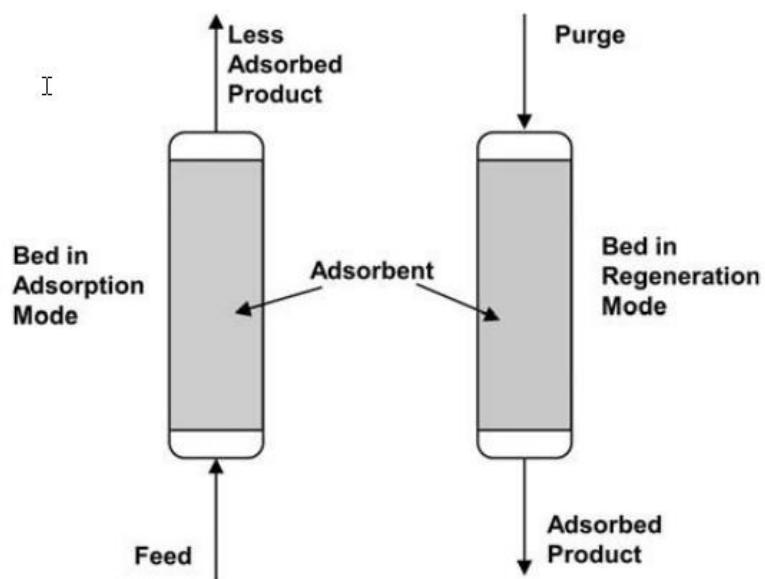


Figure 25. Schematic of an adsorption–desorption process. [22b]

According to Sawyer *et al.* [1d] the adsorption can be divided into three general types, which are physical, chemical, and exchange adsorption. Physical adsorption is relatively non-specific and results from weak attraction forces or van der Waals' forces between molecules. Adsorbed molecule is not attached to a specific site and it can freely move over the adsorbent surface. Physical adsorption is also quite reversible. In chemical adsorption (chemisorption) forces comparable to those resulting in chemical compound formation are present. Chemically adsorbed material typically forms a monolayer, i.e. one molecule thick layer over the adsorbent surface. After the formation of monolayer, the adsorbent is practically exhausted. In general, the adsorbent has to be heated in order to remove the adsorbed material from its surface. The third type of adsorption, exchange adsorption, is described with electrical attraction between the adsorbate and the surface of adsorbent. Ion exchange is also regarded as an exchange adsorption process. In exchange adsorption, ions concentrate at the adsorbent surface due to electrostatic attraction to the surface sites possessing opposite charge. Attraction is mainly dependent on the ion charge and ion size, so that, the greater the charge and the smaller the size, the greater the attraction.

In an earlier study entitled “The removal of ammonium, phosphate, and nitrate by adsorption” [40], the applicability of different adsorbent materials for the simultaneous removal of ammonium, phosphate and, nitrate in wastewater was investigated. The suitability of the adsorption method for removing the ammonium in wastewater at Yara’s Siilinjärvi site was studied as well.

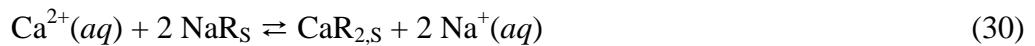
Adsorption of ions possessing both positive and negative charges through one step process proved to be challenging. The results showed that calcined hydrotalcite removed phosphate and nitrate, but did not have a significant effect on ammonium removal. However, the adsorption of nitrate was reduced in the presence of phosphate ions. On the other hand, zeolites and bentonite removed ammonium effectively, also reducing the amount of ammonium from Yara’s water samples. The degree of adsorption decreased with increasing pH value. For adsorption efficiency, the acidic or slightly acidic pH values were most suitable. To overcome the challenges brought by the opposite electrical charges of ions, the mixing of adsorbents were studied.

These experiments gave promising results with the combination of calcined hydrotalcite and clinoptilolite, which is a naturally occurring zeolite [40].

7.2 Ion exchange

Ion-exchange is a process where cations or anions from an aqueous solution are exchanged with cations or anions on a solid ion exchanger. Ion exchange is a reversible process allowing recycling of the ion exchange resin before its replacement. Regeneration is primarily accomplished with concentrated acid, base, or salt solutions [22b].

As an example, water softening by ion exchange takes place in a cation exchange column, in which calcium and magnesium ions are removed. The removal of calcium ions proceeds by the following reaction [22b]:



where R denotes the polymeric ion exchanger resin. Selectivity for divalent cations decreases sharply with ionic concentration, and regeneration can be carried out effectively with a concentrated sodium chloride solution [41].

The first ion exchangers used in water softening were naturally occurring inorganic alumino-silicates (zeolites). Nowadays, synthetic organic polymer resins based on styrene or acrylic acid type monomers are the most widely utilized. Polymeric resins are constructed of a three-dimensional polymeric network with attached ionic functional groups. Ion exchange resins may be categorized by the nature of functional groups attached to a polymer or by the chemistry of the particular polymer in the matrix. Strong acid and strong base resins are styrene–divinyl benzene copolymers with different functional groups as illustrated in Figure 26.

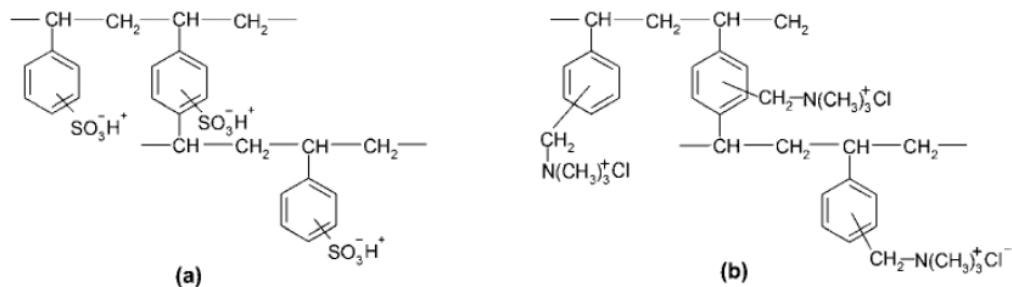


Figure 26. Styrene–divinyl benzene copolymer ion exchange resins: (a) sulfonated cation exchanger and (b) aminated anion exchanger. [22b]

Complete deionization with ion-exchange columns is the classical method of producing ultrapure water for boiler feed, in electronics manufacture, and for other general uses in the chemical industries. In deionization process two exchangers with opposite functionality to remove both cations and anions are used. Ion exchange resins with different functionalities can be loaded either in separate columns or packed in adjacent layers in the same column, or in a mixed bed. In the latter case, the two exchangers are intimately mixed during the loading step. In regeneration step, lighter anion exchanger is typically separated by backwashing from denser cation exchanger. Typically there is a screened distributor at the interface of the two exchangers in order to regenerate them sequentially without removing them from the column as illustrated in Figure 27 [41].

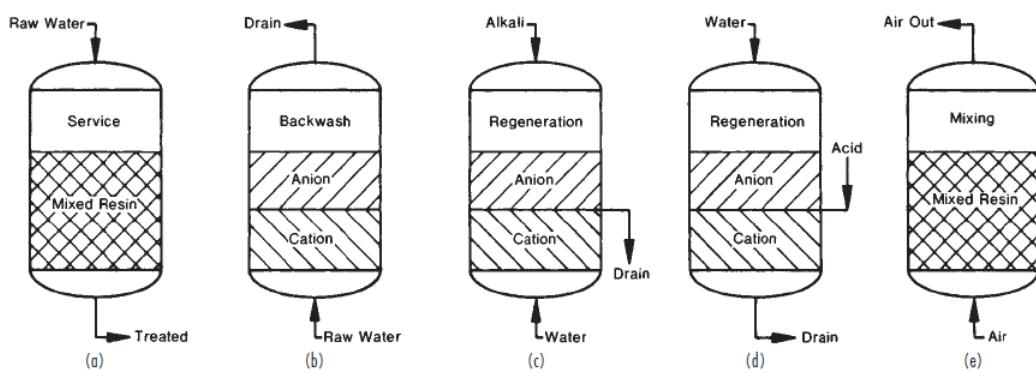


Figure 27. Schematic of a mixed-bed ion exchange and sequential regeneration: (a) service period (loading), (b) backwash period, (c) caustic regeneration, (d) acid regeneration, and (e) resin mixing by compressed air. [41]

Industrial applications of ion exchange are ranging from the purification of low-cost commodities to the purification and treatment of high-cost pharmaceutical derivatives as well as precious metals. Industrial ion exchange systems are operated either in batch, semi-continuous, or continuous mode. Depending on the application and the effluent quality, the systems vary from a simple one column unit to arrays of cation and anion exchangers. A single-column installation is satisfactory if the unit can be shut down for regeneration. In continuous processing two or more columns packed with the same ion exchange resin must be installed in parallel.

7.3 Membrane separation

A membrane is defined as a semi-permeable barrier between two phases that can be either liquid or gaseous. Components permeate from one side of the membrane to the other under the influence of a driving force, which can be a gradient in concentration, pressure, temperature, or electrical potential. A pressure driven membrane process is illustrated in Figure 28.

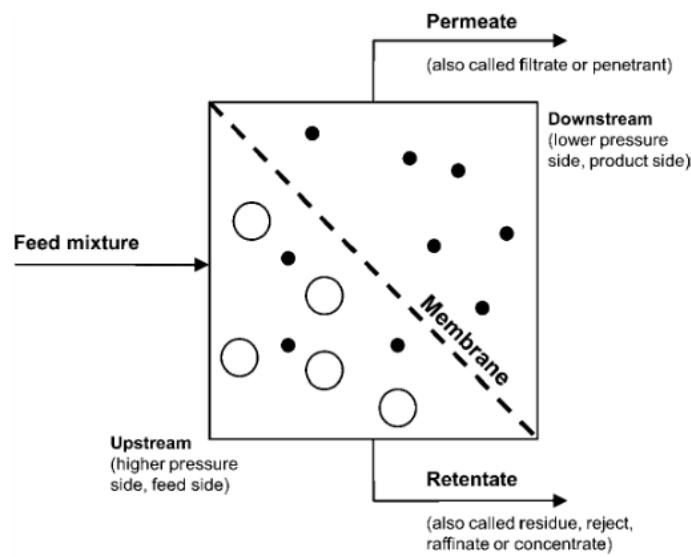


Figure 28. Outline and terminology of a pressure driven membrane process. [22c]

Further classification of membrane processes can be made by the driving force. Dialysis appears to be the only concentration driven membrane process, while the

pressure driven processes are subdivided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO, also hyperfiltration). In general, pressure differences of 0.1–2 bar, 1–10 bar, 10–35 bar, and 15–100 bar are referred to MF, UF, NF, and RO processes, respectively. The applied pressure increases as the membrane pore size decreases to end up dense membranes for the finest separations [42].

Depending on the application membranes with different pore sizes are used. Microfiltration is used to separate ultrafine particles with size range of 0.1–10 µm from liquid and gas streams. Ultrafiltration is able to separate particles with the size of 2–100 nm. Examples of such small particles are proteins and viruses. Nanofiltration separates particles and dissolved molecules smaller than ca. 2 nm. For pressure driven membrane processes, reverse osmosis offers the finest degree of separation as presented in Figure 29.

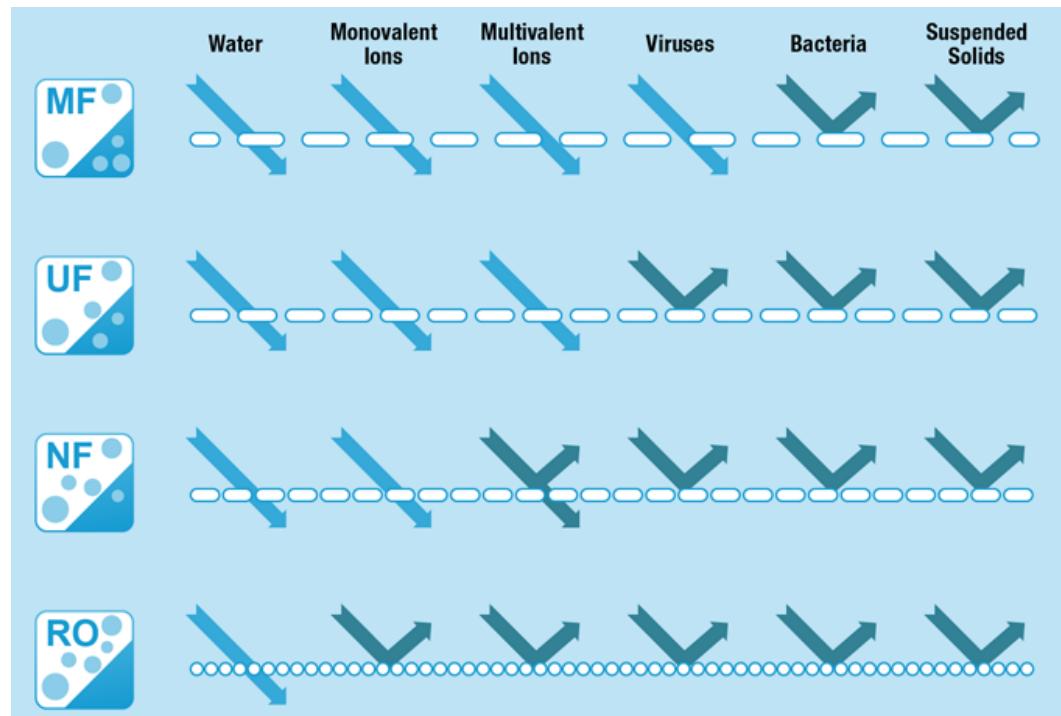


Figure 29. Comparison of membrane processes and their filtration efficiency. [43]

In normal osmosis process, the solvent naturally moves from an area of low solute concentration (high water potential) through a membrane to an area of high solute concentration (low water potential). The movement of a pure solvent is driven to reduce the free energy of the system by equalizing solute concentration on each side of a membrane, thus generation osmotic pressure. In reverse osmosis, the external pressure is applied to reverse the natural flow of pure solvent. The solute is retained on the pressurized side of the membrane while the pure solvent is passing through the membrane.

Membranes used for reverse osmosis have a dense layer in the polymer matrix where the separation takes place. This layer may either comprise the skin of an asymmetric membrane or an inter-facially polymerized layer within a thin film composite membrane [44]. Generally, membranes are designed to allow only water to pass the dense layer and to prevent the passage of solutes such as salt ions. On the high concentration side of the membrane, a pressure of 2–17 bar for fresh water and 40–82 bar for seawater is needed. Natural osmotic pressure of the seawater is around 27 bar which must be overcome [44].

Pretreatment is important when working with nanofiltration and reverse osmosis membranes due to their spiral-wound design. Membrane with spiral-wound design (presented in Figure 30) does not allow backpulsing with water to scour its surface and remove the solids [44]. Membranes are highly susceptible to fouling and loss of production capacity. Membrane feed water should be relatively free from colloidal particulates [45]. In applications of phosphate fertilizer industry the fouling of RO modules mainly due to silicon oxide, calcium fluoride, and calcium sulfate have been pointed out [46].

Advantage of reverse osmosis in desalination systems is relatively low energy consumption. With recent technological advances energy consumption has come down to around 3 kWh per cubic meter [44].

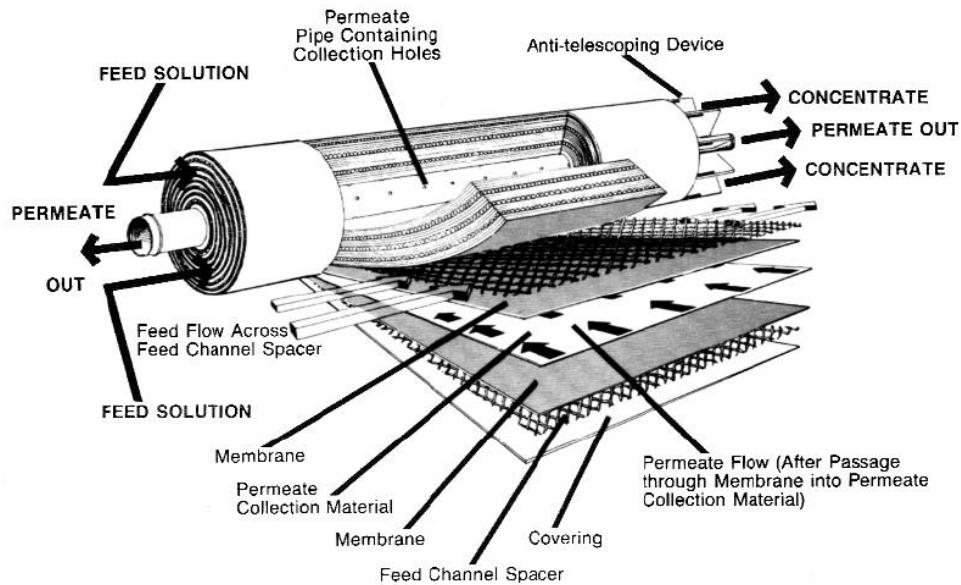


Figure 30. Spiral-wound membrane configuration. [43]

8 PRELIMINARY STUDIES

At first, quality of process waters during the time this thesis was started and analytical methods for process waters analyses are reviewed in this section. Later in this section preliminary precipitation tests with process waters are discussed.

8.1 Analyses of process waters

In normal operation, process waters at fertilizer plant are sampled three times per week. Samples of process waters are collected from the delivery side of the circulation water pump LA 253, which circulates the process water in the circulation water tank LA 250 and feeds process waters also to the inclined plate settler LA 738. Thus, the analytical data of process waters equals to the quality of process waters fed to the inclined plate settler. From now on, the sampling of process waters in this thesis refers to sample collection at the above sampling position unless stated otherwise. Analytical data for process waters during September 2014, i.e. the time when the thesis was started, is presented in Table 3.

Table 3. Analytical data for process waters during September 2014. [47]

Date	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws g/L	K ₂ O-ws g/L	SO ₄ g/L	F-ws mg/L	Density/ 35 °C kg/m ³
1.9.2014	161	129	1.4	2.3	112	1 432	1 323
3.9.2014	162	135	1.4	2.4	101	2 238	1 331
5.9.2014	167	140	1.4	2.3	98	2 365	1 336
8.9.2014	165	145	1.8	2.7	81	2 715	1 332
10.9.2014	170	145	2.0	2.6	91	2 723	1 347
12.9.2014	166	139	3.1	2.8	93	3 665	1 341
15.9.2014	181	153	2.7	2.6	102	2 718	1 365
17.9.2014	167	144	2.4	2.5	87	2 030	1 337
19.09.2014	170	150	2.1	2.4	84	1 946	1 344
22.09.2014	149	127	1.9	2.2	78	1 971	1 304
24.09.2014	182	159	2.2	2.1	87	2 239	1 369
26.09.2014	173	152	3.9	2.3	80	1 951	1 353
29.09.2014	172	153	3.9	2.0	72	2 328	1 352
Average	168	144	2.3	2.4	90	2 332	1 341
Min. value	149	127	1.4	2.0	72	1 432	1 304
Max. value	182	159	3.9	2.8	112	3 665	1 369

ws = water soluble

Typically, water soluble species of ammonium nitrogen (denoted as NH₄-N), nitrate nitrogen (NO₃-N), phosphorus (P₂O₅), potassium (K₂O), sulfate (SO₄), fluoride (F), and density are analyzed in process waters. Chloride is quantified once a week by titration with silver nitrate (AgNO₃) solution [48]. During September 2014, the chloride concentration in all analyzed samples has been 2 g/L, i.e. 2 000 ppm.

The quantities of the primary nutrients in fertilizers are expressed in the form of nitrogen as % N, phosphorus as % P₂O₅ (or in some countries as % P), and potassium as % K₂O (or in some countries as % K) [49, 50]. Total elemental nitrogen (N) can be calculated by adding NH₄-N and NO₃-N. The compound P₂O₅, as such, is never found in fertilizer nor in water, but historically, has been an accepted term for expressing content of phosphorus [51]. The correct chemical name for P₂O₅ is phosphorus pentoxide, which appears as a chemical compound with molecular formula of P₄O₁₀ and undergoes exothermic hydrolysis yielding phosphoric acid. Similarly, for historical reasons potassium oxide (K₂O) has been used for expressing

the potassium content, although it is rarely encountered (never in fertilizer) as such due to its high reactivity.

Water soluble species of NH₄-N, NO₃-N, P₂O₅, and K₂O are quantified with QuAAstro AutoAnalyzer (Seal Analytical). For quantification of K₂O flame photometer (Sherwood Scientific, model 420) is also utilized [52]. Sulfate in process waters is quantified with ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) analyzer (Thermo Scientific iCAP 6500 Duo) [53]. Water soluble fluoride is determined ion selectively by MA235 pH/Ion Analyzer (Mettler Toledo) using F⁻ ion selective electrode [54]. Total fluoride and water soluble sodium, calcium, silicon, magnesium, and aluminum were also determined for chemical precipitation tests. Total fluoride is determined ion selectively with exception of sample being dissolved in hot diluted hydrochloric acid instead of water. Sodium, calcium, silicon, magnesium, and aluminum are quantified with ICP-OES as sulfate. All analyses were performed in the laboratory of Yara Suomi Oy at Siilinjärvi.

As seen in Table 3, the total concentration of dissolved species in fertilizer plant's process waters was 950 g/L as calculated from the average values in September 2014. Mass concentrations of NH₄-N and NO₃-N are converted to mass concentrations of NH₄ and NO₃, respectively. The NH₄-N mass concentration of 168 g/L equals to NH₄ mass concentration of 216 g/L. Similarly, the NO₃-N mass concentration of 144 g/L equals to NO₃ mass concentration of 637 g/L. The total amount of dissolved species is thus 71 % of the mass of process waters. Conversion factors derived from molar masses are 1.29 for NH₄-N to NH₄ and 4.43 for NO₃-N to NO₃. During September 2014 density of process waters was above 1.3 kg/L, the average being almost 1.35 kg/L. In addition to dissolved species, there are solids in process waters. High density of process waters limits the particle separation by sedimentation process because the density difference between the solids and the process waters, i.e. suspending liquid, becomes too small [22a]. As well, dense and almost saturated process waters cannot effectively wash exhaust gases coming from reactors.

8.2 Preliminary precipitation experiments

Preliminary precipitation tests were carried out at Savonia University of Applied Sciences. In these experiments chemical precipitation with calcium hydroxide, potassium hydroxide (KOH), potassium carbonate (K_2CO_3), and potassium bicarbonate ($KHCO_3$, also known potassium hydrogen carbonate) was studied. In addition, precipitation tests at varying pH values and temperatures were performed. Supernatants were separated from precipitates by centrifugation and analyzed. [55] Sample specifications are presented in Table 4.

Table 4. Sample specifications. Sample of process waters (denoted as PW-0109) was collected on September 1, 2014.

Sample	Temperature °C	pH	Agent for pH adjustment and precipitation
PW-0109			Process waters sample/Reference sample
PW-2.5_4	4	2.5	–
PW-4_4	4	4	KOH
PW-6_4	4	6	KOH
PW-Ca_4	4	4	$Ca(OH)_2$
PW-2.5_21	21	2.5	–
PW-4_21	21	4	KOH
PW-6_21	21	6	KOH
PW-Ca_21	21	4	$Ca(OH)_2$

Laboratory results for process waters after the precipitation tests conducted at Savonia are presented in Table 5. Initially, process waters sample PW-0109 contained dissolved matter approximately 890 g/L, thus constituting about 67 % of the sample mass. The pH of the sample was measured to be initially 2.5. Potassium hydroxide and calcium hydroxide were added as 50 % solution (m/v) and 50 % slurry (m/v), respectively, to adjust the pH value to the target value indicated in Table 4. Saturated solutions or slurries of pH adjusting/precipitation agents are typically used to avoid sample dilution which may enhance the solubility thus making precipitation even harder. For example, 50 % KOH solution (m/v) worked well, but 4 M KOH solution proved to be too dilute [55].

Table 5. Analytical data for precipitation tests conducted at Savonia.

Sample	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws g/L	K ₂ O-ws g/L	SO ₄ g/L	F-ws mg/L	F-tot mg/L	Density/ 22 °C* kg/m ³
PW-0109	159	131	1.4	2.4	100	1 742	1 800	1 322
PW-2.5_4	135	115	1.7	1.9	74	607	770	1 282
PW-4_4	135	116	1.5	4.6	73	1 340	1 580	1 285
PW-6_4	134	115	1.6	4.2	74	1 120	1 335	1 283
PW-Ca_4	135	116	1.6	2.0	76	652	855	1 285
PW-2.5_21	149	131	1.5	2.0	76	1 020	1 290	1 313
PW-4_21	148	129	1.5	3.4	81	1 110	1 250	1 309
PW-6_21	150	130	1.3	6.1	77	1 650	1 850	1 313
PW-Ca_21	149	130	1.5	2.1	78	1 140	1 365	1 312

ws = water soluble

* Determined at 22 °C, except reference sample PW-0109 at 35 °C

Precipitations carried out at the temperature of 4 °C showed reduction of ammonium nitrogen of about 15 %, nitrate nitrogen of about 12 %, and sulfate of about 26 %. Type of precipitation agent, whether it was added or not, or pH did not have any effect on those. At room temperature reductions of the ammonium nitrogen, nitrate nitrogen, and sulfate were about 6 %, 1 %, and 22 %, respectively. Thus, the effect of temperature on reduction of ammonium nitrogen, nitrate nitrogen, and sulfate is pronounced over the pH adjustment. At room temperature precipitates were mainly ammonium sulfate ((NH₄)₂SO₄), while at 4 °C ammonium sulfate and ammonium nitrate (NH₄NO₃) were precipitated [55].

On the other hand, the results for fluoride removal are somewhat conflicting. The highest fluoride reductions were achieved at 4 °C with sample without precipitation agent at original pH of 2.5 (F-ws from 1 742 g/L to 607 g/L and F-tot from 1 800 g/L to 770 g/L) and sample with adjustment of pH to 4 using Ca(OH)₂ (F-ws from 1 742 g/L to 652 g/L and F-tot from 1 800 g/L to 855 g/L). Thus, fluoride removal in the former experiment was about 65 % for F-ws and 57 % for F-tot, and in the latter experiment about 63 % and 53 %, respectively. Using potassium hydroxide fluoride concentration is decreasing with increasing pH at 4 °C, but at 21 °C the effect is

opposite. At room temperature the sample at pH 6 differs from all others when regarding the fluoride removal.

Saturated potassium carbonate and potassium bicarbonate solutions were found inappropriate for adjusting pH and precipitation. Potassium carbonate is very effective for pH adjustment, but it is not possible to add sufficient amounts of potassium (as carbonates) for precipitation while maintaining the pH below 8. In order to achieve sufficient potassium amount by adding potassium bicarbonate problems arise from dilution of samples.

Solubility of ammonium sulfate in water is 706 g/L at 0 °C and 780 g/L at 30 °C [56]. For ammonium nitrate the solubility is 1 183 g/L at 0 °C and 2 418 g/L at 30 °C [56]. Assuming that ammonium sulfate precipitates first due to its lower water solubility, the theoretical amounts of ammonium sulfate and ammonium nitrate to be precipitated can be calculated. In 1 liter sample, the theoretical amounts for ammonium sulfate and ammonium nitrate are 138 g and 742 g, respectively, yielding 880 g in total. Due to above assumption, the amount of nitrate remaining in the water would be as low as 5.2 g being approximately 0.9 % of the initial situation.

9 LABORATORY EXPERIMENTS

Laboratory experiments were started with chemical precipitation experiments of process waters. In the next phase coagulants and flocculants were tested followed by testing coagulants and flocculants together. In each section analytical data of supernatants is discussed.

9.1 Chemical precipitation experiments

In first precipitation experiments with process waters calcium carbonate (calcite) and calcium hydroxide were used as precipitation agents. The same precipitation agents had been used also in previous precipitation tests [46]. However, current tests were performed with smaller amounts of precipitation agents. Due to quite rapid increase

of pH when adding calcium hydroxide, dosing was based on the target pH value instead of addition certain amount of precipitation agent. Calcium carbonate was added as dry powder while calcium hydroxide was added as 50 % slurry (m/m). In addition, alusilica (Alufluor) [57] was tested for binding of fluoride. Fennopol A 305 flocculant which have been used at phosphoric acid plant was also tested. Flocculant was used as a 0.1 % solution (m/m). All experiments were carried out at room temperature. In each experiment 200 mL of process waters with original pH of 3.3 was used. Chemical addition was followed by rapid mixing after which samples were allowed to settle for 20 minutes. Supernatants were separated from precipitates by centrifugation of 15 minutes (Eppendorf 5702 centrifuge, RCF 3 000). Sample specifications are given in Table 6.

Table 6. Sample specifications. Process waters sample (denoted as PW-0910-00) was collected on October 9, 2014.

Sample	Target pH	Dosage g	Precipitation agent	Other chemicals (dosage)
PW-0910-00			Process waters sample/Reference sample	
PW-0910-01			Precipitated as such/No addition of chemicals	
PW-0910-02	–	2	CaCO ₃	–
PW-0910-03	–	6	CaCO ₃	–
PW-0910-04	–	10	CaCO ₃	–
PW-0910-05	4	–	Ca(OH) ₂	–
PW-0910-06	6	–	Ca(OH) ₂	–
PW-0910-07	8	–	Ca(OH) ₂	–
PW-0910-08	4	–	Ca(OH) ₂	A 305 (2 mL)
PW-0910-09	6	–	Ca(OH) ₂	A 305 (2 mL)
PW-0910-10	–	–	–	Alusilica (0.25 g)

Analytical data of supernatants is presented in Table 7. Full analytical data of supernatants including also sodium, calcium, silicon, magnesium, and aluminum is presented in Appendix I. According to analyses, process waters sample PW-0910-00 contained dissolved matter approximately 1 018 g/L, thus constituting about 75 % of the sample mass. Precipitations with calcium carbonate showed reduction of ammonium nitrogen of about 10 %, nitrate nitrogen of about 1 %, and sulfate of

about 53 %. Water soluble fluoride had declined of about 7 % and total fluoride of about 10 %. The amount of calcium carbonate seemed to have no effect on the results. Because calcium carbonate is practically insoluble to water, solid calcium carbonate was clearly present in the precipitate.

Table 7. Analytical data of supernatants after precipitation tests.

Sample	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws mg/L	K ₂ O-ws mg/L	SO ₄ g/L	F-ws mg/L	F-tot mg/L	Density/ 35 °C kg/m ³
PW-0910-00	180	152	2 240	2 360	106	1 941	2 200	1 363
PW-0910-01	164	152	2 480	2 050	54	1 757	2 020	1 333
PW-0910-02	163	152	2 430	2 040	50	1 809	1 995	1 330
PW-0910-03	162	150	2 410	2 020	50	1 811	1 980	1 329
PW-0910-04	160	150	2 440	2 020	48	1 799	1 965	1 327
PW-0910-05	156	145	2 510	2 080	49	1 808	1 970	1 320
PW-0910-06	155	145	1 190	2 060	48	409	625	1 314
PW-0910-07	155	144	55	2 050	48	191	405	1 313
PW-0910-08	161	151	2 410	2 010	51	1 773	1 945	1 330
PW-0910-09	159	148	1 170	2 020	51	339	525	1 322
PW-0910-10	163	152	2 430	2 010	53	1 740	1 980	1 331

ws = water soluble

Precipitations with calcium hydroxide yielded to about 14 %, 5 %, and 54 % reduction of ammonium nitrogen, nitrate nitrogen, and sulfate, respectively. On the contrary, pH of the sample had quite drastic effect on fluoride as well as phosphorus reduction. At pH 4, reduction of water soluble fluoride, total fluoride, and phosphorus was about the same level as in precipitations with calcium carbonate. At pH 6 reduction of phosphorus was about 47 %, while water soluble fluoride and total fluoride had reduced about 79 % and 72 %, respectively. Removal of phosphorus and fluoride was the most effective at pH 8 resulting in about 98 % reduction of phosphorus, and about 90 % reduction of water soluble fluoride, and about 82 % reduction of total fluoride. At pH 8, ammonia was clearly released from the sample. Mass concentrations of phosphorus and fluoride remaining in supernatants after precipitation at different pH values in contrast to reference sample are illustrated in Figure 31.

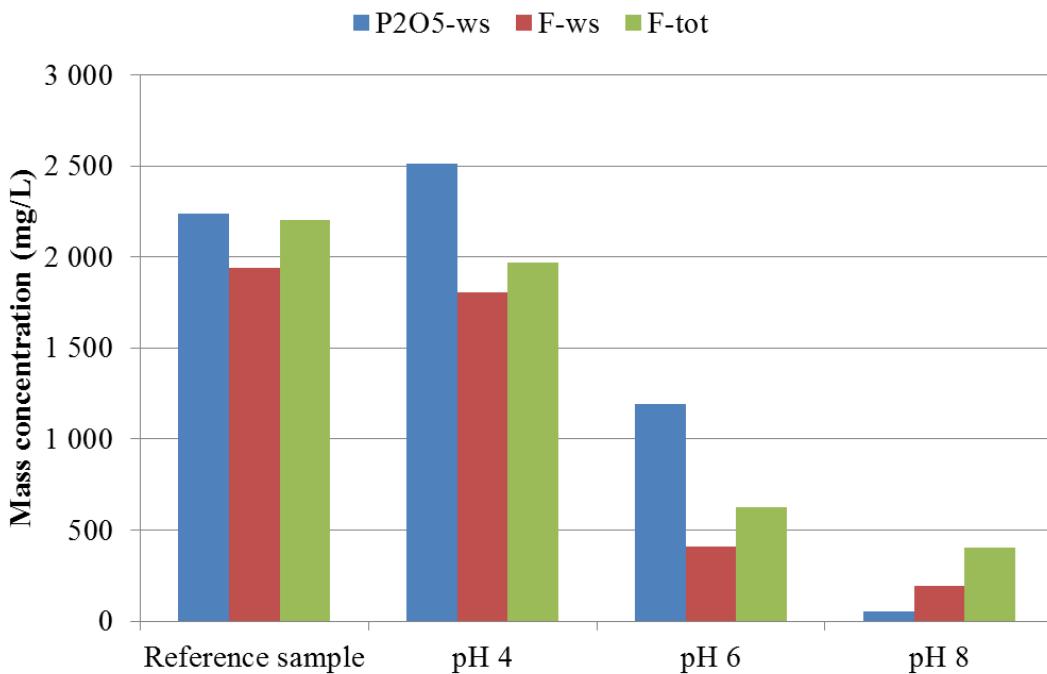


Figure 31. Mass concentrations of phosphorus and fluoride remaining in supernatants after precipitation at different pH values in contrast to reference sample.

Results for water soluble calcium are also interesting. The calcium content is increased at pH 4 and 8 due to addition of calcium hydroxide. At pH 6 water soluble calcium was reduced about 88 % (from 289 mg/L of the reference sample to 35 mg/L) despite the calcium hydroxide addition. At pH 4 the reduction of water soluble silicon was about 7 %, while at pH 6 and 8 the reduction was about 90 %. Water soluble magnesium was reduced about 63 % at pH 4 and about 100 % at pH 6 and 8. Amounts of water soluble aluminum are very small in process waters and after precipitation there was actually no aluminum in the supernatants.

Calcium hydroxide precipitations with Fennopol A 305 flocculant showed very similar trends to above described. The reductions of water soluble species were originated from the changes of pH while flocculant seemed to have no effect on those. Alusilica did not have any significant effect on fluoride removal yielding in about 10 % reduction of water soluble fluoride and total fluoride.

Supernatants were separated from precipitates by centrifuging. After centrifugation supernatants were decanted over the precipitate and their volumes were measured. Precipitates were dried at room temperature to their constant weight. The mass of the solid precipitate and the volume of supernatant decanted after each experiment are presented in Figure 32. Al-Harahsheh *et al.* [58] have observed similar correlation between precipitate masses and supernatant volumes in their studies.

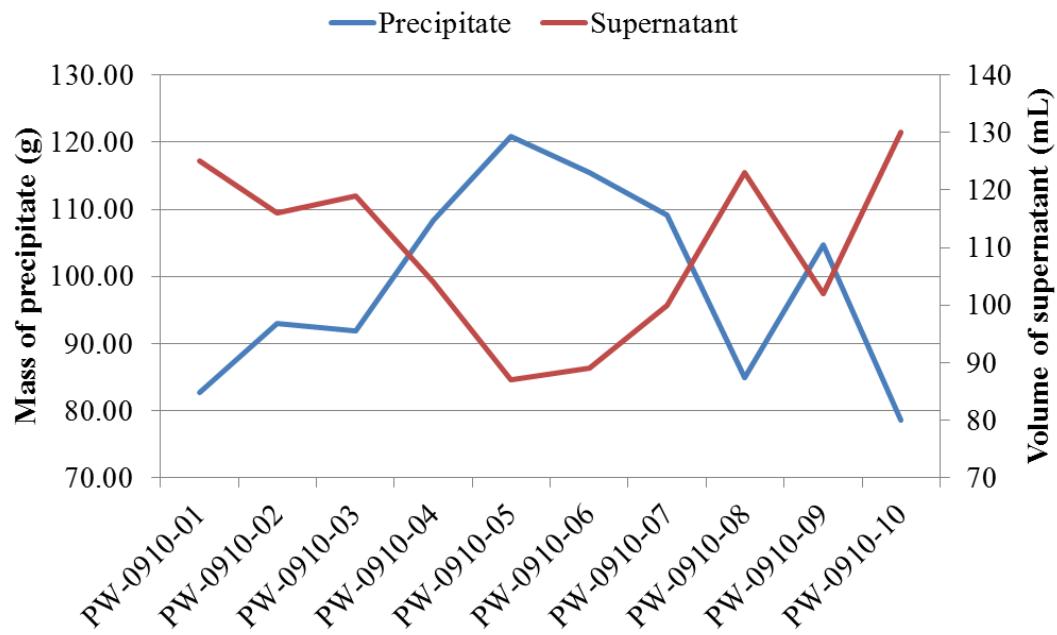


Figure 32. The mass of the solid precipitate and the volume of supernatant decanted after each experiment.

Supplementary precipitation tests were performed using calcium hydroxide as precipitation agent. Calcium hydroxide was added as dry powder or 50 % slurry (m/m). In both cases, dosing of precipitation agent was based on the target pH value. Possibility to bind fluoride with alusilica was tested now with pH adjustment. As well, Fennopol A 305 flocculant (0.1 mass % solution) was tested with different dosages. All experiments were carried out similar to above precipitation tests. Process waters sample pH was 3.3. Supernatants were separated from precipitates by centrifugation of 10 minutes (Hettich Universal 320 centrifuge, RCF 3 420). Sample specifications are given in Table 8.

Table 8. Sample specifications. Process waters sample (denoted as PW-2810-00) was collected on October 28, 2014.

Sample	Target pH	Precipitation agent	Other chemicals (dosage)
PW-2810-00	Process waters sample/Reference sample		
PW-2810-01	Precipitated as such/No addition of chemicals		
PW-2810-02	6	Ca(OH) ₂ slurry	–
PW-2810-03	7	Ca(OH) ₂ slurry	–
PW-2810-04	8	Ca(OH) ₂ slurry	–
PW-2810-05	6	Ca(OH) ₂ powder	–
PW-2810-06	7	Ca(OH) ₂ powder	–
PW-2810-07	8	Ca(OH) ₂ powder	–
PW-2810-08	6	Ca(OH) ₂ slurry	Alusilica (0.25 g)
PW-2810-09	6	Ca(OH) ₂ slurry	A 305 (1 mL)
PW-2810-10	6	Ca(OH) ₂ slurry	A 305 (2 mL)

Analytical data of supernatants is presented in Table 9. Full analytical data of supernatants including also sodium, calcium, silicon, magnesium, and aluminum is presented in Appendix II.

Table 9. Analytical data of supernatants after precipitation tests.

Sample	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws mg/L	K ₂ O-ws mg/L	SO ₄ g/L	F-ws mg/L	F-tot mg/L	Density/ 35 °C kg/m ³
PW-2810-00	165	138	1 290	2 190	97	1 807	2 140	1 334
PW-2810-01	153	136	1 360	1 990	69	1 738	2 070	1 315
PW-2810-02	153	135	625	1 990	70	367	635	1 306
PW-2810-03	152	135	330	1 990	69	215	485	1 305
PW-2810-04	152	135	90	1 970	66	137	430	1 306
PW-2810-05	155	137	440	2 010	73	286	555	1 310
PW-2810-06	154	136	250	1 990	70	182	450	1 308
PW-2810-07	152	137	80	1 990	65	132	410	1 302
PW-2810-08	154	135	605	2 000	76	357	620	1 304
PW-2810-09	154	136	525	2 010	75	339	605	1 313
PW-2810-10	153	134	375	1 990	73	260	525	1 311

ws = water soluble

Process waters sample PW-2810-00 contained dissolved matter approximately 926 g/L, which constituted about 69 % of the sample mass. In precipitations, ammonium nitrogen content was reduced about 8 % with 50 % slurry and about 7 % with dry powder showing slightly higher reduction with increasing pH value. Precipitations at pH 6 with alusilica and flocculant showed average reduction of ammonium nitrate similar to precipitations with calcium hydroxide powder. Nitrate nitrogen reduction varied from about 1 % to 3 % within the experiments. Sulfate removal was enhanced with increasing pH being around 32–33 % at pH 8.

As in earlier experiments, removal of phosphorus was the most efficient at pH 8 showing around 93–94 % reduction. At lower pH values precipitations with dry powder showed clearly higher phosphorus reductions than precipitations with 50 % slurry. Removal of water soluble fluoride and total fluoride was enhanced with increasing pH as well. Fluoride reduction with calcium hydroxide powder was slightly higher at all pH values when compared to reduction with 50 % calcium hydroxide slurry. Mass concentrations of phosphorus and fluoride remaining in supernatants after precipitation at different pH values using $\text{Ca}(\text{OH})_2$ slurry and dry powder as precipitation agents in contrast to reference sample are illustrated in Figure 33.

Precipitations at pH 6 with addition of alusilica and flocculant showed generally the same or slightly higher reductions of phosphorus and fluoride than all other precipitations performed at pH 6. On the other hand, sulfate reduction at pH 6 with alusilica and flocculant was about the same or some lower than precipitations at pH 6 in general.

In precipitations at pH 8 water soluble calcium content increased similar to earlier experiments. At pH 6 and 7 calcium content was decreased despite the addition of calcium hydroxide. Reduction was more pronounced at pH 6 being about 50 % and 61 % with 50 % slurry and dry powder, respectively. At pH 7 the reduction was about 44 % with 50 % slurry, but only 19 % with dry powder. With alusilica the calcium reduction was about the same as with 50 % slurry at pH 6. Flocculant dosage of 1 mL gave calcium reduction of about 55 %, which decreased to about 30 % with 2 mL

flocculant dosage. Removal of water soluble silicon and magnesium was around 92–94 % and 95 %, respectively, within the experiments. Again, water soluble aluminum was barely detectable in process waters sample.

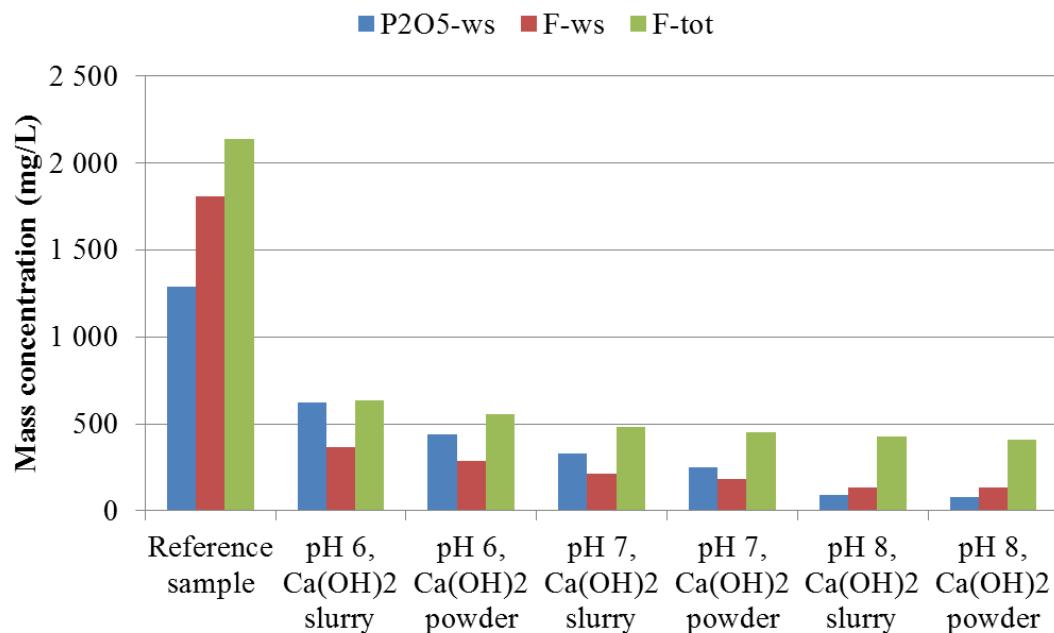


Figure 33. Mass concentrations of phosphorus and fluoride remaining in supernatants after precipitation at different pH values using Ca(OH)₂ slurry and dry powder as precipitation agents in contrast to reference sample.

Volumes of supernatants were measured after centrifugation and precipitates were dried in air to their constant weight. The mass of the solid precipitate and the volume of supernatant decanted after each experiment are presented in Figure 34.

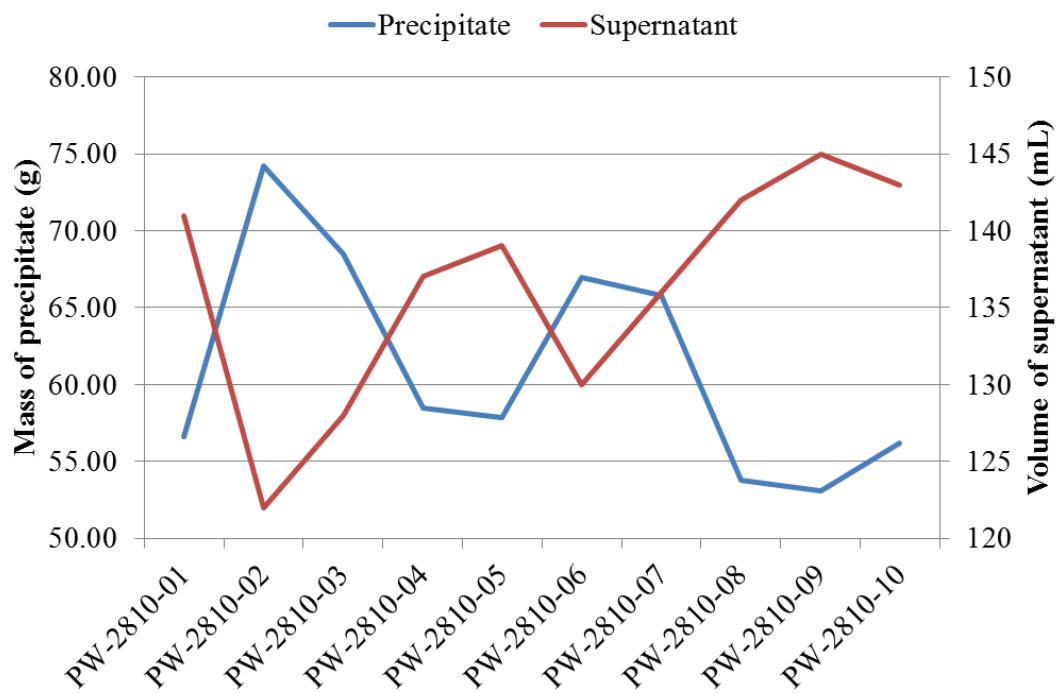


Figure 34. The mass of the solid precipitate and the volume of supernatant decanted after each experiment.

As a summary, calcium hydroxide as precipitation agent showed significant reduction of phosphorus and fluoride. Removal of phosphorus and fluoride was enhanced with increasing pH value. However, ammonia is released at pH 8 or above. Calcium hydroxide was dosed as 50 % slurry (m/m) and dry powder, of which dry powder showed slightly higher reduction of phosphorus and fluoride. Instead, alusilica proved to have no effect on fluoride binding. Either calcium carbonate did not show any significant efficiency in precipitation tests. In experiments where pH was adjusted above 5 it was observed that some ion in process waters has buffering effect around pH 5. A relatively larger addition of pH adjusting agent was needed to overcome this point.

9.2 Coagulant testing

Coagulants are typically used for destabilizing of stable colloidal solutions by neutralizing the primary charges (positive or negative) of colloidal particles.

Neutralization of primary charges allows the colloidal size particles to aggregate into larger particles thus making the settling of these particles possible. Sometimes coagulants are also called primary coagulants or precipitation agents. Coagulants tested here were provided by Kemira Oyj and are presented in Table 10.

Table 10. Overview of coagulants provided by Kemira Oyj.

Product name	Chemical name of the substance	Type	State
Kemira ALG	Aluminum sulfate (alum) $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	Inorganic	Solid
Kemira PIX-105	Ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$	Inorganic	Liquid
Superfloc C-577	Polyamine (PA)	Organic, cationic	Liquid
Superfloc C-592	Poly(diallyldimethylammoniumchloride) (PolyDADMAC)	Organic, cationic	Liquid

Aluminum sulfate was delivered as solid granular powder. Commercially available aluminum sulfate solution contains 4.3 mass % of aluminum. As calculated from the molecular formula solid aluminum sulfate contains about 9.1 mass % of Al. A working solution having aluminum content close to commercial one is prepared by dissolving one mass equivalent of solid aluminum sulfate to one mass equivalent of water resulting in solution with aluminum content of 4.5 mass %. However, due to weak solubility of solid aluminum sulfate in water, the working solution containing about 2.3 mass % of aluminum was decided to use in experiments. Ferric sulfate was ready to use solution containing about 12.6 mass % of Fe.

Superfloc C-577 and Superfloc C-592 coagulants are liquid, cationic polymers of differing molecular weights. They are used as primary coagulants and charge neutralization agents in liquid–solid separation processes in a wide variety of industries. Polymeric coagulants are diluted with water prior to use. Typically, the polymeric coagulants are added as 10 mass % solutions. Product properties of polymeric coagulants are presented in Table 11.

Table 11. Product properties of polymeric coagulants.

	Product name	
	Superfloc C-577	Superfloc C-592
Chemical type	Cationic polyamine	Cationic polyDADMAC
Relative charge	Very high	Very high
Molecular weight	Medium	Very low
Specific gravity/25 °C	1.14–1.18	1.05–1.10
Total solids (%)	49–52	39–41
Viscosity (mPa s)	800	2 000

The shelf lives of Superfloc C-577 and Superfloc C-592 are 12–24 months and 24 months, respectively. The products should be stored at temperatures no higher than 30 °C. Recommended materials of construction include stainless steel, glass fiber, plastic, and glass or epoxy-lined vessels, while iron, copper or aluminum have to be avoided. These organic coagulants should be fed to the system by using a corrosion resistant, positive displacement pump which should be fitted with oil resistant gaskets and seals.

Inorganic coagulants Kemira ALG and Kemira PIX-105 were tested using concentrations of 50 ppm, 100 ppm, 200 ppm, and 500 ppm, while organic coagulants Superfloc C-577 and Superfloc C-592 were tested with concentrations of 20 ppm, 50 ppm, and 100 ppm. The term ppm is an abbreviation of parts per million representing the part of a whole number in units of 1/1 000 000. For example, 1 ppm corresponding to 0.0001 % is equal to 1 mg/kg, 1 g/t, 1 ml/m³, etc. Due to the lower relative charge of inorganic coagulants higher concentrations are used.

All experiments with coagulants were carried out at room temperature. In each experiment 200 mL of process waters with original pH of 3.4 was used. Process waters sample for coagulant testing was collected on November 18, 2014. Coagulants were added by weighting them directly to process waters sample. After addition of coagulant they needed to be dispersed thoroughly and rapidly in the water. Rapid mixing (400 rpm) for 10 seconds was followed by slow mixing process (40 rpm) for 10 minutes in order to give already destabilized particles and chemical precipitates a chance to come in contact and agglomerate into larger and heavier rapid settling

particles. After mixing samples were allowed to settle for 30 minutes. Supernatants were separated from precipitates by centrifugation of 10 minutes (Hettich Universal 320 centrifuge, RCF 3 420). Generally experiments were performed without pH adjustment. Inorganic coagulants with concentration of 200 ppm were tested also with pH adjustment to 6 using 50 % Ca(OH)₂ slurry (m/m), because the optimal pH range for ALG is from about 5 to about 6 and for PIX-105 from about 4 to about 6 [59]. Dissolution of aluminum sulfate and ferric sulfate in water increases the concentration of hydrogen ions, hence the net effect is a drop in pH or the consumption of present alkalinity. Organic coagulants have either very small effect or no effect to the pH value.

Sample specifications and analytical data of supernatants are presented in Appendix III. Reference sample PW-1811-00 contained dissolved matter approximately 925 g/L constituting about 70 % of the sample mass.. In general coagulants seemed to have only minor effects on enhancing the chemical precipitation. On phosphorus removal PIX-105 had effect, but it required substantial concentrations. With PIX-105 concentration of 200 ppm phosphorus reduction was about 14 % and with 500 ppm concentration reduction of phosphorus was about 41 %. With PIX-105 concentration of 200 ppm and pH adjustment to 6 the phosphorus reduction was about 65 %. Earlier precipitations at pH 6 with 50 % calcium hydroxide slurry (m/m) yielded to phosphorus removal of about 52 % and with dry calcium hydroxide powder the phosphorus removal was about 66 % indicating that phosphorus removal with PIX-105 at pH 6 was mainly due to pH adjustment. Similarly with ALG concentration of 200 ppm at pH 6 phosphorus reduction of about 57 % was achieved.

Fluoride reductions with coagulants were typically low. As expected, highest fluoride reductions were achieved with inorganic coagulants using concentrations of 200 ppm at pH 6. In these experiments, water soluble fluoride reduction with ALG was about 90 %, total fluoride reduction being about 85 %. With PIX-105 water soluble fluoride was reduced about 82 % and total fluoride about 80 %. Water soluble calcium, silicon, and magnesium also yielded highest reductions with pH adjusted sample.

Mass concentrations of phosphorus and fluoride remaining in supernatants after precipitation at pH 6 with inorganic coagulants in contrast to reference sample are illustrated in Figure 35.

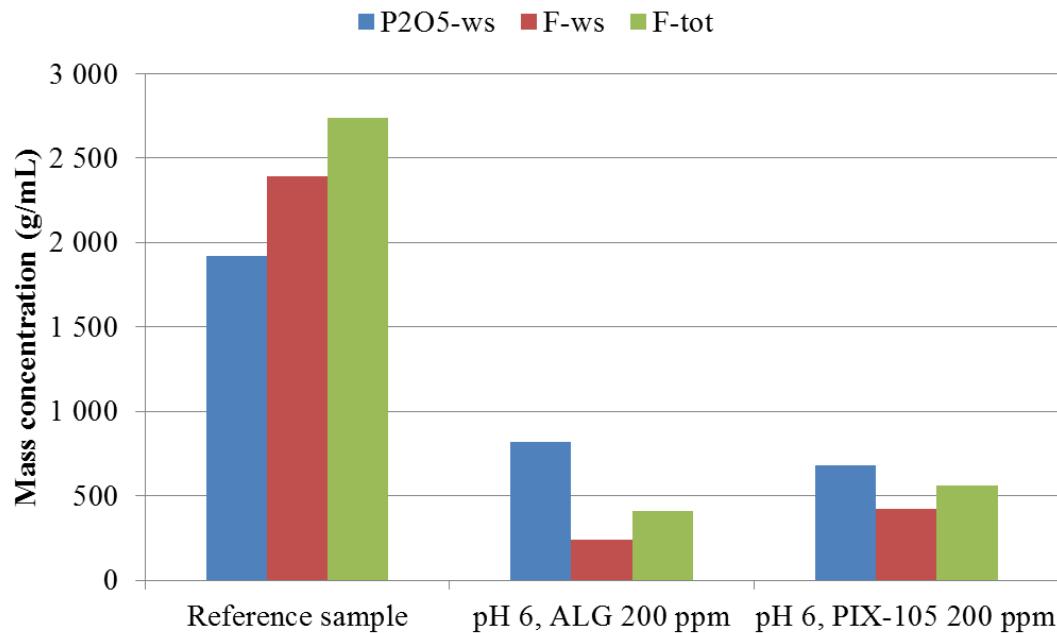


Figure 35. Mass concentrations of phosphorus and fluoride remaining in supernatants after precipitation at pH 6 with inorganic coagulants in contrast to reference sample.

After settling time, the total amount of precipitate with coagulants was generally >150 mL, the original batch size or process waters being 200 mL. Superfloc C-577 yielded relatively turbid supernatants. On the contrary, Superfloc C-592 especially with concentrations of 50 ppm and 100 ppm yielded relatively clear supernatants. As well, aluminum sulfate with concentration of 50 ppm yielded clear supernatant. With higher aluminum sulfate concentrations turbidity of the supernatants was increased. At low concentrations of ferric sulfate, supernatants were turbid, but at concentrations of 200 ppm and 500 ppm they were relatively clear.

9.3 Flocculant testing

The function of flocculation is to allow the formation of larger and denser particles (flocs) by the formation of bridges between coagulated particles, e.g. through the adsorption of large polymer molecules. Flocculants tested here were also provided by Kemira Oyj and are presented in Table 12.

Table 12. Overview of flocculants provided by Kemira Oyj.

Product name	Chemical name of the substance	Type	State
Superfloc N-100	Polyacrylamide	Non-ionic	Solid
Superfloc A-100	Polyacrylamide	Anionic	Solid
Superfloc A-110	Polyacrylamide	Anionic	Solid
Superfloc A-120	Polyacrylamide	Anionic	Solid
Superfloc A-130	Polyacrylamide	Anionic	Solid
Superfloc A-137	Polyacrylamide	Anionic	Solid
Superfloc A-1883RS	Polyacrylamide	Anionic	Emulsion
E-4832	Polyacrylamide	Anionic	Solid
E-4837	Polyacrylamide	Non-ionic	Solid
Superfloc C-490K	Polyacrylamide	Cationic	Solid
Superfloc C-491	Polyacrylamide	Cationic	Solid
Superfloc C-491HMWP	Polyacrylamide	Cationic	Solid
Superfloc C-492	Polyacrylamide	Cationic	Solid
Superfloc C-494	Polyacrylamide	Cationic	Solid

Polyacrylamide (PAM) type flocculant products can be classified into non-ionic polymers and ionic polymers (polyelectrolytes) of which the latter can be further subdivided into anionic and cationic types. The charge density of flocculant product within anionic A-100 series (from Superfloc A-100 to Superfloc A-137) and cationic C-490 series (from Superfloc C-490 to Superfloc C-494) is increasing with the numerical value in the product name. As seen in Table 12 commercial flocculants are typically solid granular powders with exception Superfloc A-1883RS being emulsion. Stock solutions of the flocculants can be prepared up to 0.5 mass % concentrations via an automated make-up unit or on a batch basis. Solutions should be aged 30–60 minutes for maximum effectiveness. Secondary dilution water should be added to

the stock solution prior to the addition point at a ratio up to 10:1. Flocculants are generally used as 0.1 mass % solutions. With Superfloc A-1883RS stock solutions up to 2 mass % can be prepared. Aging of 30 minutes is recommended for maximum effectiveness. Concentration of working solution is typically 0.5 mass %. Stock solutions preserve their efficiency from several days to one week, while working solutions should be used within 24 hours. Solutions are no more corrosive than water.

Flocculant solutions are prepared by stirring the water by magnetic stirrer and slowly adding the granular powder to the vortex. This is very important step to avoid formation of larger clumps which are not dissolved to water. Granules do not dissolve instantly, instead smaller clumps are visible in water. Within aging period with slow stirring clumps are totally dissolved and a clear, viscous solution is obtained.

The shelf life of Superfloc A-1883RS is 9 months when stored at temperatures between 5–30 °C. The shelf life of other flocculant products is 24 months when stored in unopened packages in a dry atmosphere at maximum temperature of 40 °C. Like with organic coagulants, recommended materials of construction include stainless steel, glass fiber, plastic, and glass or epoxy-lined vessels while iron, copper or aluminum have to be avoided. One should also notice that centrifugal pumps are not recommended for transferring of polymeric solutions.

Performance screening of flocculant products is typically made by selecting flocculants of different chemical type (non-ionic, anionic, and cationic) which have different relative charges [60]. If some flocculant seems to work, other flocculants within the same series having varying polymer chain lengths are tested. Here, flocculants Superfloc N-100, Superfloc A-100, Superfloc A-130, Superfloc C-491, and Superfloc C-494 were selected for testing. Product properties of these flocculants are presented in Table 13.

Table 13. Product properties of selected flocculants.

	Product name/Superfloc				
	N-100	A-100	A-130	C-491	C-494
Chemical type	Non-ionic	Anionic	Anionic	Cationic	Cationic
Relative charge	Very low	Low	Medium	Very low	Medium
Molecular weight	High	High	High	High	High
Bulk density (kg/L)	0.72	0.78	0.83	0.75	0.75
Viscosity/25 °C (mPa s)					
0.10 %	25	100	200	60	130
0.25 %	70	250	450	150	300
0.50 %	150	500	900	350	600

Experiments with flocculants were carried out at room temperature. Batch size in each experiment was 200 mL. Flocculants were added by weighting the calculated amount of working solution directly to process waters sample. Flocculant addition was followed by rapid mixing (400 rpm) for 10 seconds and by slow mixing (40 rpm) for 1 minute. After mixing periods samples were allowed to settle for 30 minutes. Supernatants were separated from precipitates by centrifugation of 10 minutes (Hettich Universal 320 centrifuge, RCF 3 420).

First flocculant experiments were performed without pH adjustment. Process waters sample for these tests was collected on November 25, 2014, having pH value of 3.7. Flocculant dosages of 1 ppm, 3 ppm, and 5 ppm were tested. After dosing the flocculant, immediate floc formation was observed. Darker flocs, as long twisting filaments, were formed with all flocculants and with all flocculant concentrations. After settling, two precipitate layers were observed, the white precipitate layer at the bottom and the darker layer containing flocs above it. The volume of floc layer increased with flocculant concentration.

With Superfloc N-100 and Superfloc A-100 the supernatants were relative clear with concentration of 1 ppm and turbidity was increased with increasing flocculant concentration. Instead, Superfloc A-130 with concentration of 5 ppm yielded relatively clear supernatant, while the supernatants at lower concentrations of 1 ppm and 3 ppm were turbid. According to visual observation, the flocs with A-130 were

smaller than with N-100 and A-100. Supernatants with cationic flocculants were relatively turbid at all concentrations. Relative amount of flocs was also lower with these flocculants.

Superfloc N-100 and Superfloc A-100 were selected for further flocculant tests. In these tests pH was adjusted to 6 with 50 % Ca(OH)₂ slurry (m/m) prior to flocculant addition. Process waters sample for these tests was collected on December 10, 2014, having pH value of 1.8. Flocculant concentrations of 1 ppm, 3 ppm, 5 ppm, and 10 ppm were tested. Within these experiments visible floc formation was not observed. However, the settling of precipitate seemed to be improved with increasing flocculant concentration resulting in smaller volume of precipitate and respectively in larger supernatant volume. Average reduction of phosphorus was about 59 %. Water soluble fluoride and total fluoride showed average reduction of 80 % and 81 %, respectively.

As stated out, there was no visible floc formation in the latter flocculation tests. It was noticed that the batch of process waters used in the latter tests contained high amount of solids. Process waters were stored at temperature cabinet to prevent the solids crystallization before performing the precipitation, coagulation, or flocculation tests. Although sample was stored at temperature of 45 °C nearly half of the volume was filled with solids. In the former flocculation tests solids content of process waters was much lower. High solids content in process waters possibly hinder or even prevent floc formation, but more likely it prevents the visual observation of flocs. However, if higher solids content requires higher flocculant concentrations, the adjustment of flocculant dosing as well as monitoring of flocculant performance may prove problematic as quality of process waters fluctuate.

9.4 Combined coagulant–flocculant testing

Few experiments on simultaneous use of coagulants and flocculants were performed. In these experiments the above described procedures for sample preparation were used. When used simultaneously, lower concentrations of coagulants and flocculants

are typically used [60]. Coagulant concentrations of 50 ppm and 100 ppm were utilized, while flocculant concentrations were 1 ppm and 5 ppm. Tests were performed with aluminum sulfate, ferric sulfate, and C-577 coagulants and with N-100 and A-100 flocculants.

Experiments resulted in total precipitate volumes of almost 200 mL indicating that settling had not taken place. In cases where very thin layer of supernatant was separated, they were very turbid. Visible coagulant or floc formation was not observed. Further analyses for the samples of these experiments were not performed. According to above findings it seems evident that combined coagulation–flocculation is not suitable for process waters. Instead, direct flocculation may be utilized to enhance the settling of solids in process waters.

9.5 Flocculation system

A handling system is needed for flocculant utilization in industrial processes. Flocculation system comprises of mixing, storing, and diluting of the polymer as illustrated in Figure 36.

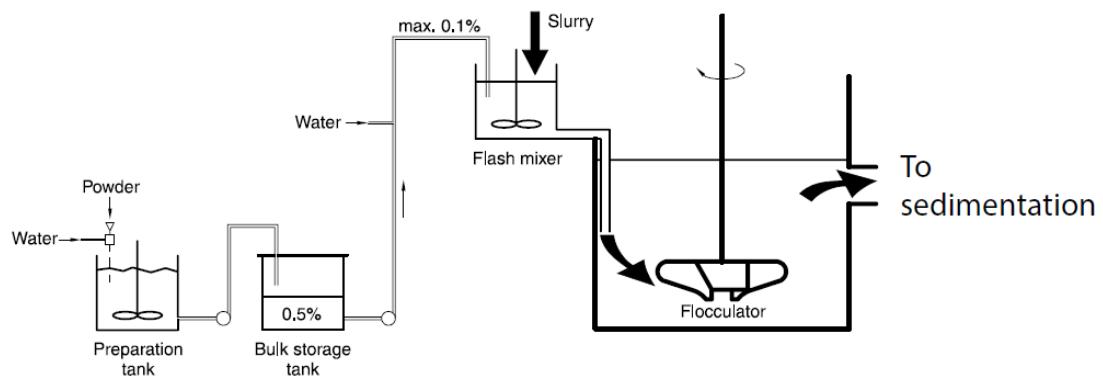


Figure 36. A flocculation system for industrial processes. [17]

First flocculant granules are added to water and mixed thoroughly so that the flocculant polymer is completely dissolved to water. Generally, stock solutions up to 0.5 mass % concentrations can be prepared via an automated make-up unit. Solutions should be aged 30–60 minutes for maximum effectiveness. Secondary dilution water

is added to the stock solution to prepare a working solution having 0.1 mass % concentration. The mixture of dilute flocculant solution is then mixed with the feed slurry using rapid mixing and allowed to condition (or age) under slow mixing before sedimentation or dewatering process.

10 PLATE SETTLER CHARACTERISTICS AND OPERATION

Operation principle of inclined plate settler is described earlier in Paragraph 3.2. In this section earlier studies related to plate settler efficiency are reviewed at first. The characteristics and operation of fertilizer plant's inclined plate settler as well as settling experiments with process waters are also discussed.

10.1 Plate settler studies

Solids removal efficiency of inclined plate settler has been studied earlier at least in two separate phases. In 2006, solids removal efficiency was studied to find out the applicability of the plate settler [61]. In the course of this study four fertilizer grades were in production. Solids content were determined as well as nutrient contents for incoming process waters. Results of analyses are presented in Table 14.

As seen, solids content was fluctuating considerably. Also, solids removal efficiency was varying notably. During this study, the solids content was higher in the overflow than in the feed flow at two points. Total amount of process waters coming to the plate settler was evaluated to be approximately 154 000 m³/a. Two highest values, i.e. 1 600 mg/L and 1 900 mg/L, were written off as they were thought to originate from clogging or some other malfunction in operation. From above results, the solids reduction in plate settler was approximated to be 14 t/a.

Table 14. Solids contents of the plate settler's feed and overflow and nutrient contents of the feed in April 2006.

Sample	Feed					Overflow Solids mg/L
	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws g/L	K ₂ O-ws g/L	Solids mg/L	
4.4.2006	54	45	0.9	1.7	120	61
5.4.2006	—	—	—	—	1 600	460
6.4.2006	92	84	0.9	2.2	1 900	1 600
10.4.2006	—	—	—	—	67	77
11.4.2006	94	88	0.4	1.6	98	100
12.4.2006	—	—	—	—	600	230
13.4.2006	109	99	0.6	1.8	260	210

ws = water soluble

Solids reduction in plate settler has been monitored also between December 2011 and January 2012 [46, 47]. Determined solids contents as well as nutrient contents for incoming process waters are presented in Table 15. All results, including also nutrient contents for plate settler's overflow are presented in Appendix IV.

Table 15. Solids contents of the plate settler's feed and overflow and nutrient contents of the feed between December 2011 and January 2012. [47]

Sample	Feed					Overflow Solids mg/L
	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws g/L	K ₂ O-ws g/L	Solids mg/L	
14.12.2011	119	94	0.7	1.8	223	180
16.12.2011	97	77	0.9	1.7	1 754	1 247
21.12.2011	68	51	0.4	1.3	118	125
23.12.2011	71	54	0.4	1.3	238	187
28.12.2011	78	58	0.7	1.9	165	128
30.12.2011	76	58	0.8	1.9	345	155
4.1.2012	104	77	1.0	2.4	331	343
11.1.2012	134	104	1.4	2.6	970	956
13.1.2012	142	109	1.6	2.6	624	644
18.1.2012	125	97	1.2	2.3	498	472
20.1.2012	123	93	1.1	2.2	925	918
25.1.2012	130	94	1.2	1.7	440	518
27.1.2012	123	91	1.5	1.8	1 039	1 669

ws = water soluble

As seen from the results in Table 15 there was fluctuation in quality of process waters coming to the plate settler. Especially, solids content was fluctuating considerably. As well, solids removal efficiency was varying notably. Generally, the solids reduction was very small and at some points the solids content in the overflow has been even higher than in the feed flow. By excluding the observations where solids content was higher in the overflow than in the feed flow, solids reduction has varied from about 1 % to 55 %, the average being about 19 %.

The samples of process waters collected from different points of inclined plate settler were analyzed also in the beginning of this thesis. The results are presented in Table 16.

Table 16. Analytical data for process waters from inclined plate settler. The samples were collected on September 16, 2014.

Sample	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws g/L	K ₂ O-ws g/L	SO ₄ mg/L	F-ws 2 282	Density/ 35 °C kg/m ³
LA 738 feed	172	150	2.6	2.6	86	2 282	1 349
LA 738 overflow	173	149	2.6	2.5	85	2 269	1 346
LA 738 underflow	173	150	2.6	2.5	87	2 294	1 351

ws = water soluble

As expected, the reduction of dissolved species does not take place in inclined plate settler. The solids were not analyzed and thus the solids reduction between the feed and the overflow is not available. When comparing with earlier results, it can be observed that nutrient content, especially NH₄-N and NO₃-N, in process waters has been risen. Fluoride content in process waters has also been risen. Instead, it seems that sulfate has almost retained its level.

Fluctuation of process water quality in the closed circulation mainly results from changes in process conditions. When fertilizer grade in production is changed, raw materials and/or their feed ratio as well as process conditions (e.g. pH) are changed. Thus, also the chemical composition of exhaust gases from reactors to scrubber system differs between the grades.

10.2 Plate settler characteristics

Initially, any documents or drawings related to the fertilizer plant's inclined plate settler were not found. As well, the history of the settler is a bit unclear. According to process operators, the plate settler has been in use at fertilizer plant since the late 1980's. Within this study a 3D laser mapping for the plate settler was conducted. A 3D model of the plate settler is presented in Figure 37.

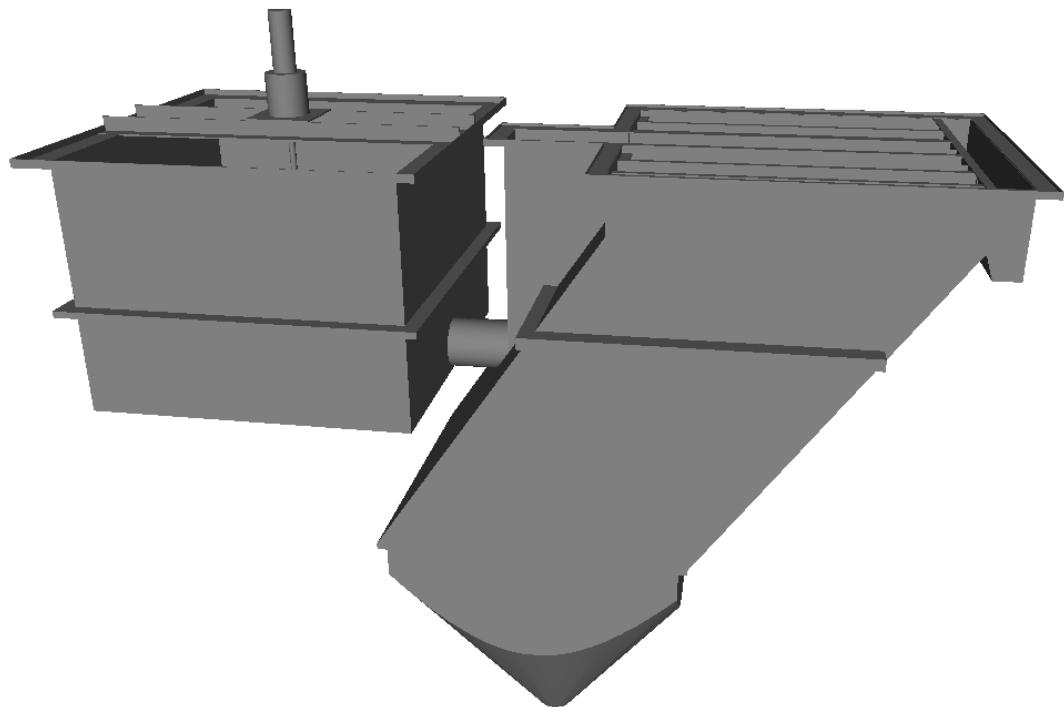


Figure 37. 3D model of the fertilizer plant's inclined plate settler.

There are two plate packs on both sides of the influent channel. Inclination angle of the plates is 55°. Both packs are constructed of 30 plates. The length of a single plate is 2 500 mm and total width 700 mm (350 mm + 350 mm). The sectional drawing of a single plate is illustrated in Figure 38. The perpendicular distance between the plates is 50 mm. Total plate area is 105 m² (Equation 22) and total projected surface area is about 60 m² (Equation 19). The cross section of the plate packs is shown in Figure 39.

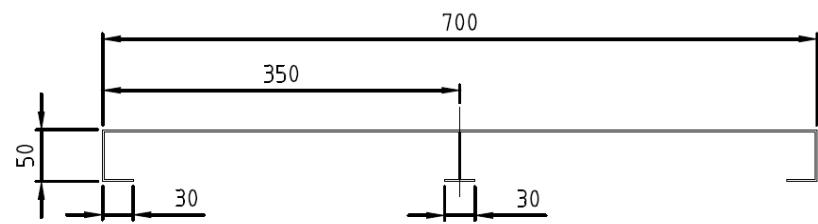


Figure 38. Sectional drawing of a single plate.

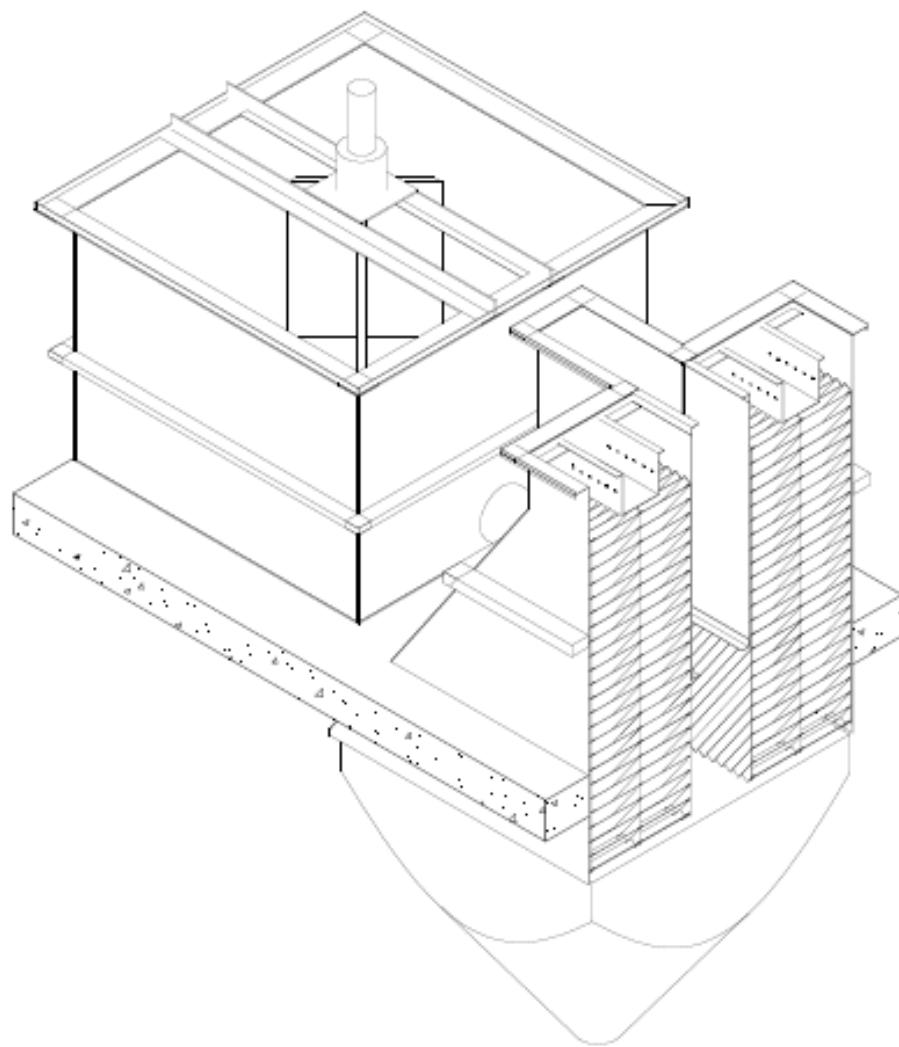


Figure 39. Cross section of the plate packs.

Above each plate pack there is a full-length overflow launder with flow distribution orifices. Distance between the bottom of the overflow launder and the upper edge of the plate pack is about 70 mm. There are total of 60 flow distribution orifices in each overflow launder, 30 in both sides of one launder. Diameter of orifices is 17 mm and the distance between two orifices is 60 mm. Flow distribution orifices are at the height of 120 mm measured from the bottom of the launder. Side view of the overflow launder is illustrated in Figure 40.

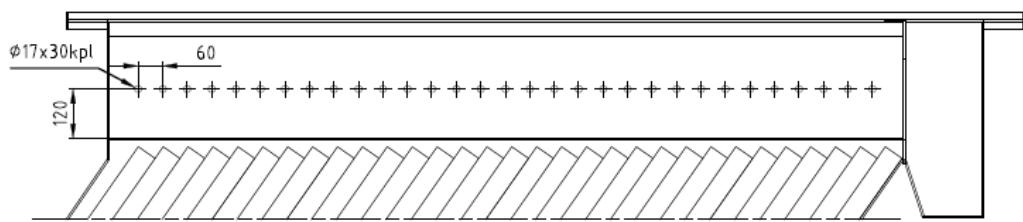


Figure 40. Side view of the overflow launder showing flow distribution orifices.

10.3 Settling tests

Settling tests with process waters were performed in order to find out the effect of direct flocculation on settling velocity as well as to find out the theoretical maximum of process waters feed to the inclined plate settler. Settling tests were performed with and without pH adjustment. Flocculant Superfloc N-100 with concentrations of 1 ppm and 5 ppm was selected for settling tests. Calcium hydroxide as a 50 % slurry (m/m) was used for pH adjustment.

Settling tests were carried out at room temperature in 500 mL measuring glass. Process waters sample was collected on February 17, 2015, having pH value of 3.2. Batch size in each experiment was 500 mL. Process waters were stored at temperature of 45 °C to prevent crystallization, but each batch was cooled down to room temperature prior to pH adjustment and flocculant addition. Flocculant was added by weighting the calculated amount of 0.1 mass % working solution directly to process waters sample. Flocculant addition was followed by rapid mixing (400 rpm)

for 10 seconds and by slow mixing (40 rpm) for 1 minute. After mixing period sample was transferred to the measuring glass and allowed to settle.

Progress of settling of untreated process waters could not be observed because supernatant was not clarified and hence it was not possible to observe the interface between the clarified supernatant and settling suspension. After the settling time of 30 minutes total volume of the precipitate was 205 mL. Instead, process waters samples with pH adjustment and flocculant addition showed relatively clear interfaces between the supernatant and settling suspension. Results of these settling tests are presented in Figure 41.

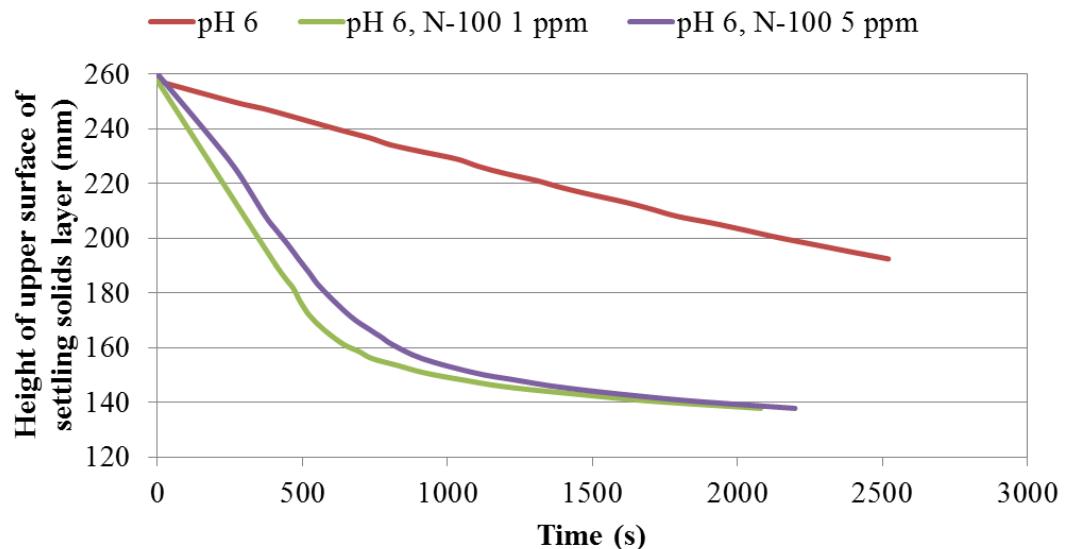


Figure 41. Progress of settling as a function of time. At starting point ($t = 0$), solids are fully mixed in the suspension after which solids start to settle.

As seen in Figure 41 the settling of pH adjusted sample as a function of time proceeded almost linearly up to about 30 minutes after which the velocity was slightly decreased. The settling velocity calculated from linear part was about 0.10 m/h. At first, the settling of pH adjusted samples with flocculant addition was more rapid, the settling velocity slowing down later due to the precipitate layer on the bottom restricting further settling. Actually, the settling at lower settling velocity region was due to the compression of precipitate layer. As seen, the settling with

1 ppm flocculant concentration occurred more rapidly than with flocculant concentration of 5 ppm. Settling velocities calculated from linear part of the curves with flocculant concentrations of 1 ppm and 5 ppm were 0.54 m/h and 0.44 m/h, respectively.

Supernatant samples were collected with a syringe above the precipitate layer and analyzed. As supernatants were not separated by centrifugation, analytical data corresponds to the overflow quality. Analytical data of supernatants is presented in Table 17.

Table 17. Analytical data of supernatants after settling tests.

Sample	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws mg/L	K ₂ O-ws g/L	SO ₄ mg/L	F-ws mg/L	F-tot mg/L	Solids mg/L
Reference sample	167	145	1 420	2 200	85	1 185	1 370	728
Untreated sample	153	141	1 520	2 020	54	1 240	1 470	298
pH 6	154	142	750	2 010	55	219	460	440
pH 6, N-100 1 ppm	154	142	760	2 010	55	225	465	486
pH 6, N-100 5 ppm	154	142	740	2 010	56	239	475	570

ws = water soluble

Process waters sample contained dissolved matter approximately 948 g/L, which constituted about 71 % of the sample mass. With pH adjusted samples the average reduction of phosphorus was about 47 %. Water soluble fluoride and total fluoride showed average reduction of 81 % and 66 %, respectively. Solids content was reduced with untreated sample of about 59 %. With pH adjusted sample reduction in solids content was about 40 %, with 1 ppm N-100 about 33 %, and with 5 ppm N-100 about 22 %.

The results regarding the reduction of solids content are a bit overwhelming, because turbidity of the supernatant in untreated sample was high, while with flocculated samples supernatants were less turbid. Due to supernatant sampling with syringe

precipitate may naturally end up to the sample increasing the solids content. However, this is unlikely because supernatants were visually checked after sampling.

10.4 Evaluation of plate settler operation

Design principles of inclined plate settlers are presented earlier in Paragraph 3.6. Based on the equations presented there and the results of settling tests, the operation of inclined plate settler can be evaluated. Surface overflow rate based on horizontally projected plate area or the overflow velocity based on the total plate area can be calculated when the dimensions of the plates, the inclination angle, and influent feed are known. Typically used maximum influent feed to the inclined plate settler has been $20 \text{ m}^3/\text{h}$. The horizontally projected plate area and the total plate area are:

$$A_{tp} = n \cdot L \cdot w \cdot \cos \theta = 2 \cdot 30 \cdot 2.5m \cdot 0.7m \cdot \cos(55^\circ) = 60.2m^2 \quad (19)$$

$$A_{tot} = n \cdot L \cdot w = 2 \cdot 30 \cdot 2.5m \cdot 0.7m = 105m^2 \quad (22)$$

And surface overflow rate and overflow velocity:

$$v_o = \frac{Q}{A_{tp}} = \frac{20m^3/h}{60.2m^2} = 0.33m/h \quad (17)$$

$$v_{ov} = \frac{Q}{A_{tot}} = \frac{20m^3/h}{105m^2} = 0.19m/h \quad (21)$$

All particles with $v_s \geq v_o$ or $v_{sy} \geq v_{ov}$ will be removed from the suspension. The settling velocity in the y direction, i.e. v_{sy} , can be calculated by Equation 15 presented earlier. The operation of inclined plate settler with suspensions having different settling velocities is presented in Table 18.

Table 18. Operation of inclined plate settler with suspensions of different settling velocities.

	Suspension treatment		
	pH 6	pH 6, N-100 1 ppm	pH 6, N-100 5 ppm
Settling velocity v_s (m/h)	0.10	0.54	0.44
Surface overflow rate v_o (m/h)	0.33	0.33	0.33
Settling velocity, y direction v_{sy} (m/h)	0.06	0.31	0.25
Overflow velocity v_{ov} (m/h)	0.19	0.19	0.19
Operation	Not working	Working	Working

As seen in Table 18, the inclined plate settler is able to remove particles from flocculated suspensions, while settling velocity of pH adjusted suspension is too slow. The vertical settling velocity determined in batch settling experiments gives a good estimation of settler operation, but it does not correlate for 100 % removal of particles. After settling tests supernatants contained particles whose settling velocity was much lower than those presented in Table 18.

Taking into account the above velocity rules, it is also possible to evaluate the minimum plate efficiency for inclined plate settler operation in cases of flocculated suspensions. The rules are fulfilled with minimum plate efficiency of 62 % and 76 % for pH adjusted suspension having N-100 flocculant 1 ppm and 5 ppm, respectively. Similarly, maximum influent feed can be also evaluated. For suspension with 1 ppm and 5 ppm flocculant concentration maximum influent feed would be $32 \text{ m}^3/\text{h}$ and $26 \text{ m}^3/\text{h}$, respectively.

For optimal operation of inclined plate settler, the filling time of sludge hopper relative to sludge removal is critical. Amount of sludge removed should be at least the same as incoming sludge amount. Inclined plate settler should be operated so that time interval between sludge removals is as close to filling time as possible [62]. At Uusikaupunki the inclined plate settler is having the sludge hopper volume of 1.5 m^3 . Because the dimensions of that plate settler are very close to the dimensions of plate

settler at Siilinjärvi, sludge hopper volume is assumed to be 1.5 m^3 . With influent feed of $20 \text{ m}^3/\text{h}$ of flocculated suspension, the sludge pump should be able to remove the sludge amount of about 180 L/min if operated continuously. With higher sludge pump output, periodic sludge removal is possible. Above evaluation is based on the sludge or precipitate contents observed in settling tests.

In practice, the precipitates cause clogging of inclined plate settler quite often. Precipitation from saturated solutions takes place especially when warm process waters cools down. Precipitate contains ammonium nitrate, ammonium phosphate, ammonium sulfate, and insoluble particles of apatite and gypsum among others [63]. During the time the precipitate becomes very hard clogging the sludge hopper and spaces between the plates. Most likely, clogging results from too slow settling of non-flocculated solids/precipitates and/or insufficient sludge removal. Recently, the plate settler has been operated only with one plate pack, the other being completely removed from the settler. This naturally worsens the separation of solids because flow conditions become uneven and short-circuiting of suspension is allowed. In addition plates in packs are bent and scratched promoting the precipitate adhering to the plate surface. During maintenance operations one should avoid damaging the plates. Instead of mechanical removal of clogging, washing should be used. In addition, few extra openings allowing overflow have been made. As well, these openings allow a route for short-circuiting and make flow conditions uneven by reducing the hydraulic back pressure.

In order to find out the flow conditions in inclined plate settler, modeling with computational fluid dynamics (CFD) should be performed. With CFD study it would be possible to optimize the structural issues affecting to the performance of inclined plate settler, such as:

- Location of the feed of process waters to the settler with respect to plate assembly and sludge hopper in order to reduce the risk of disturbing previously settled solids

- Plate design for influent entry to reduce the risk of disturbing previously settled solids
- Design of the collection channels (flow distribution orifices) for creating the pressure drop across the collection channels to ensure uniform flow distribution across the plates in order to utilize the full area for settling

10.5 Cost estimation

Calcium hydroxide either as a 50 % slurry (m/m) or as a dry powder was used as precipitation agent as well as for pH adjustment. The amount of 50 % $\text{Ca}(\text{OH})_2$ slurry needed for pH adjustment was weighted. An average amount of 50 % $\text{Ca}(\text{OH})_2$ slurry for increasing pH from 3.2 to about 6 was 5.1 g/L. This equals to 5.1 kg/m³. Supposing the influent feed of 20 m³/h to the plate settler throughout the year the total influent feed would be 175 200 m³/a. The total amount of 50 % slurry needed for pH adjustment would then be about 898 t/a of which the amount of $\text{Ca}(\text{OH})_2$ is about 449 t/a. Currently, the price of calcium hydroxide is 140.65 €/t including the carriage [64]. Thus, total cost of calcium hydroxide per year would be about 63 k€.

Consumption of Superfloc N-100 flocculant is about 228 kg/a with flocculant dosage of 1 ppm and influent feed of 20 m³/h. Price of polyacrylicamide flocculants is 2–4 €/kg depending on the product quality and the volume needed [65]. Assuming the flocculant price of 4 €/kg, total annual cost would be 910 €.

In earlier plate settler studies the yearly influent feed was estimated to be 154 000 m³ [61] and total cost of calcium hydroxide would then be about 56 k€/a. In earlier precipitation tests [46] with process waters performed with specific amounts of calcium hydroxide it was concluded that dosage of 20 g/L would be optimal. With this amount, the yearly consumption of calcium hydroxide was calculated to be 3 504 tons and total cost without carriage to be about 526 k€/a. It can be concluded that the yearly cost for chemical precipitation by adjusting pH to the target value of 6, is almost 8 times less.

As mentioned earlier, buffering effect was observed when exceeding pH 5 in process waters. In case precipitation at around pH 5 would give acceptable results, cost savings could be achieved due to lower chemical consumption.

11 CONCLUSIONS

The focus of this thesis was on performance intensification of fertilizer plant's inclined plate settler and enhancing the chemical precipitation of dissolved fluorine, phosphorus, and nitrogen in process waters. Precipitation tests were carried out mainly using 50 % calcium hydroxide slurry (m/m) as a precipitation agent. Calcium hydroxide as a dry powder and calcium carbonate were tested as well. Calcium hydroxide is advantageous precipitation agent because it increases pH of the solution thus enhancing the precipitation of fluoride and phosphate compounds as their solubility decreases with increasing pH value.

In precipitation tests process waters contained dissolved matter from about 69 % to about 75 % by mass. Calcium hydroxide yielded significant reduction of phosphorus and fluoride. Their reduction was enhanced with increasing pH value. At pH 6 reduction of phosphorus was around 50 % with calcium hydroxide slurry, while almost 80 % of water soluble fluoride and over 70 % of total fluoride were removed. Removal of phosphorus and fluoride was the most effective at pH 8 where phosphorus was reduced by 93–98 % and reduction of water soluble fluoride and total fluoride was over 90 % and about 80 %, respectively. Reduction of phosphorus and fluoride was slightly improved when calcium hydroxide was dosed as dry powder. Instead, calcium carbonate did not show any significant efficiency in precipitation tests.

Instead, most nitrogen compounds are readily dissolved in water making precipitation a severely restricted method for nitrogen removal. Precipitation with calcium hydroxide yielded ammonium nitrogen reduction from 6 % to 14 % and nitrate nitrogen from 0 % to 5 %. Precipitation of ammonium nitrogen as magnesium ammonium phosphate (struvite) is not a valid method due to high molar concentration

of ammonium nitrogen in process waters. Depending on the batch of process waters, the molar concentration of ammonium nitrogen was 2 300–3 100 times higher than the molar concentration of magnesium, while optimal $Mg^{2+} : NH_4^+ \cdot N$ ratio would be 1 or even higher.

The most potential alternatives for nitrogen removal are adsorption, ion exchange, and membrane separation techniques, especially reverse osmosis. Generally adsorption and ion exchange are regarded as techniques of medium operational costs, and reverse osmosis as high operational cost technique. To remove both cations and anions by adsorption and ion exchange, adsorbents and ion exchange resins, respectively, with different functionalities are required. Those can be loaded either in separate columns, or packed in adjacent layers in the same column, or in a mixed bed. High molar concentration of dissolved species in process waters increases the osmotic pressure and may limit utilization of reverse osmosis for nitrogen removal. Chemical precipitation and solids removal are needed prior to utilization of any of these techniques.

Separation of solids by fertilizer plant's inclined plate settler is inadequate. Very hard precipitates are clogging the sludge hopper and spaces between the plates. Most likely, clogging results from too slow settling of non-flocculated solids/precipitates and/or insufficient sludge removal. As well, modifications such as removing the other plate pack completely and making of few extra openings allow short-circuiting of the suspension and make flow conditions uneven as the hydraulic back pressure is reduced. Results below apply to the plate settler which is equipped with both plate packs and short-circuiting of suspension is prevented.

Sizing calculations for inclined plate settler and settling tests showed that the inclined plate settler is able to remove particles from flocculated suspensions, while settling velocity of pH adjusted non-flocculated suspension was too slow. Batch settling experiments were performed with non-ionic Superfloc N-100 flocculant. Flocculant dosage of 1 ppm gave slightly higher settling velocity than 5 ppm flocculant dosage. According to the velocity rules, maximum influent feed to the inclined plate settler with 1 ppm flocculant dosage is $32 \text{ m}^3/\text{h}$ supposing 100 % plate efficiency. That is, if

influent feed is $20 \text{ m}^3/\text{h}$, velocity rules are fulfilled even with plate efficiency of 62 %.

Calcium hydroxide is needed about 450 t/a by assuming that influent feed to the plate settler is $20 \text{ m}^3/\text{h}$ and pH is adjusted to 6. The annual cost of calcium hydroxide would then be about 63 k€. Amount of Superfloc N-100 flocculant needed is about 230 kg/a with influent feed of $20 \text{ m}^3/\text{h}$ and flocculant dosage of 1 ppm. Thus, annual cost of flocculant would be about 900 €.

As a summary, to intensify the operation of inclined plate settler using influent feed of $20 \text{ m}^3/\text{h}$, pH of the process waters should be adjusted to 6 and Superfloc N-100 flocculant with concentration of 1 ppm should be added to ensure sufficient settling velocity. By this treatment phosphorus concentration is reduced about 50 % and water soluble fluoride and total fluoride about 80 % and over 70 %, respectively. Total annual chemical cost including calcium hydroxide and flocculant would be around 64 k€. In addition, the proper operation of plate settler requires that both plate packs are in place and short-circuiting of suspension is prevented.

Solids, colloidal size particles, and ions and molecules cannot be removed in one stage process. Solids can be removed by gravity settling, e.g. inclined plate settler, while colloidal size particles needs to be coagulated and/or flocculated prior to gravity settling. Fluoride and phosphate ions can be removed quite effectively by precipitation with calcium hydroxide. Removal of nitrogen compounds — ammonium and nitrate — is not straightforward. Adsorption, ion exchange, or reverse osmosis might be suitable technique for removing of those.

To find out the flow conditions in inclined plate settler, modeling with computational fluid dynamics (CFD) should be performed in continuation studies. With information obtained from CFD study the structural issues that affect to flow conditions and performance of inclined plate settler could be optimized. As well, precipitation with calcium hydroxide should be studied around pH 5 due to buffering effect. If precipitation at pH 5 would result sufficient removal of phosphate and fluoride, annual cost for calcium hydroxide would be lower. It would also be profitable to test

suitability of adsorbents, ion exchange resins, and membranes in laboratory scale for removal of ammonium, nitrate, and other remaining ions. As well, a detailed study of compounds formed during precipitation is needed in order to evaluate their stability in the reactor conditions as underflow slurry from the plate settler is fed back to the fertilizer reactor.

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APPENDIX I 1 (1)

Analytical data of chemical precipitation tests for process waters collected on October 9, 2014.

Sample	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws mg/L	K ₂ O-ws mg/L	SO ₄ g/L	F-ws mg/L	F-tot mg/L	Na-ws mg/L	Ca-ws mg/L	Si-ws mg/L	Mg-ws mg/L	Al-ws mg/L	Density/35 °C kg/m ³
PW-0910-00	180	152	2 240	2 360	106	1 941	2 200	158	289	413	135	5	1 363
PW-0910-01	164	152	2 480	2 050	54	1 757	2 020	171	212	387	71	0	1 333
PW-0910-02	163	152	2 430	2 040	50	1 809	1 995	172	370	383	56	0	1 330
PW-0910-03	162	150	2 410	2 020	50	1 811	1 980	171	381	384	52	0	1 329
PW-0910-04	160	150	2 440	2 020	48	1 799	1 965	176	391	386	52	0	1 327
PW-0910-05	156	145	2 510	2 080	49	1 808	1 970	181	368	385	50	0	1 320
PW-0910-06	155	145	1 190	2 060	48	409	625	176	35	45	0	0	1 314
PW-0910-07	155	144	55	2 050	48	191	405	171	334	41	5	0	1 313
PW-0910-08	161	151	2 410	2 010	51	1 773	1 945	172	352	388	60	0	1 330
PW-0910-09	159	148	1 170	2 020	51	339	525	169	49	46	0	0	1 322
PW-0910-10	163	152	2 430	2 010	53	1 740	1 980	169	208	387	64	11	1 331

ws = water soluble

APPENDIX II 1 (1)

Analytical data of chemical precipitation tests for process waters collected on October 28, 2014.

Sample	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws mg/L	K ₂ O-ws mg/L	SO ₄ g/L	F-ws mg/L	F-tot mg/L	Na-ws mg/L	Ca-ws mg/L	Si-ws mg/L	Mg-ws mg/L	Al-ws mg/L	Density/35 °C kg/m ³
PW-2810-00	165	138	1 290	2 190	97	1 807	2 140	124	205	379	93	5	1 334
PW-2810-01	153	136	1 360	1 990	69	1 738	2 070	135	208	356	75	5	1 315
PW-2810-02	153	135	625	1 990	70	367	635	129	103	30	5	0	1 306
PW-2810-03	152	135	330	1 990	69	215	485	128	114	23	5	0	1 305
PW-2810-04	152	135	90	1 970	66	137	430	128	364	26	5	0	1 306
PW-2810-05	155	137	440	2 010	73	286	555	128	80	24	5	0	1 310
PW-2810-06	154	136	250	1 990	70	182	450	127	167	24	5	0	1 308
PW-2810-07	152	137	80	1 990	65	132	410	128	388	22	5	0	1 302
PW-2810-08	154	135	605	2 000	76	357	620	123	102	30	5	5	1 304
PW-2810-09	154	136	525	2 010	75	339	605	123	92	28	5	0	1 313
PW-2810-10	153	134	375	1 990	73	260	525	125	143	30	5	0	1 311

ws = water soluble

APPENDIX III 1 (2)

Sample specifications and analytical data of coagulation tests for process waters collected on November 18, 2014.

Sample	Target pH	Precipitation agent	Other chemicals (dosage)
PW-1811-00		Process waters sample/Reference sample	
PW-1811-01		Precipitated as such/No addition of chemicals	
PW-1811-02	–	–	C-577 (20 ppm)
PW-1811-03	–	–	C-577 (50 ppm)
PW-1811-04	–	–	C-577 (100 ppm)
PW-1811-05	–	–	C-592 (20 ppm)
PW-1811-06	–	–	C-592 (50 ppm)
PW-1811-07	–	–	C-592 (100 ppm)
PW-1811-08	–	–	ALG (50 ppm)
PW-1811-09	–	–	ALG (100 ppm)
PW-1811-10	–	–	ALG (200 ppm)
PW-1811-11	6	Ca(OH) ₂ slurry	ALG (200 ppm)
PW-1811-12	–		ALG (500 ppm)
PW-1811-13	–		PIX-105 (50 ppm)
PW-1811-14	–		PIX-105 (100 ppm)
PW-1811-15	–		PIX-105 (200 ppm)
PW-1811-16	6	Ca(OH) ₂ slurry	PIX-105 (200 ppm)
PW-1811-17	–		PIX-105 (500 ppm)

APPENDIX III 2 (2)

Sample specifications and analytical data of coagulation tests for process waters collected on November 18, 2014 (continued).

Sample	NH ₄ -N-ws g/L	NO ₃ -N-ws g/L	P ₂ O ₅ -ws mg/L	K ₂ O-ws mg/L	SO ₄ g/L	F-ws mg/L	F-tot mg/L	Na-ws mg/L	Ca-ws mg/L	Si-ws mg/L	Mg-ws mg/L	Al-ws mg/L	Density/35 °C kg/m ³
PW-1811-00	164	137	1920	1780	100	2390	2740	122	245	552	125	5	1330
PW-1811-01	156	137	2020	1610	77	2156	2515	129	203	509	71	5	1316
PW-1811-02	154	133	1960	1590	83	2125	2510	136	201	501	68	5	1312
PW-1811-03	154	132	1980	1570	83	2073	2425	136	205	486	73	5	1311
PW-1811-04	154	136	1980	1540	83	2014	2350	125	202	474	72	5	1312
PW-1811-05	155	133	2040	1530	81	2204	2535	130	209	521	74	5	1313
PW-1811-06	154	133	2010	1530	83	2276	2440	128	205	510	76	5	1311
PW-1811-07	154	132	2010	1520	85	2260	2520	127	207	510	76	5	1310
PW-1811-08	154	132	2010	1510	85	2283	2555	126	208	519	80	51	1311
PW-1811-09	153	130	1980	1510	89	2246	2420	126	207	509	80	103	1308
PW-1811-10	154	130	1960	1520	91	2219	2445	125	205	492	76	198	1313
PW-1811-11	153	129	820	1490	93	239	410	115	125	22	5	7	1307
PW-1811-12	153	127	1870	1510	97	2007	2440	123	198	485	71	497	1311
PW-1811-13	153	131	1970	1470	83	2178	2370	127	199	504	73	5	1312
PW-1811-14	153	130	1810	1480	85	2125	2385	126	199	492	77	5	1311
PW-1811-15	153	130	1650	1480	87	2101	2320	127	200	490	82	5	1309
PW-1811-16	154	130	680	1470	89	424	560	115	26	22	5	0	1308
PW-1811-17	154	129	1140	1470	94	2122	2275	123	200	503	92	5	1308

ws = water soluble

Analytical data of inclined plate settler studies between December 2011 and January 2012.

Sample	Feed							Overflow						
	NH ₄ -N-	NO ₃ -N-	P ₂ O ₅ -	K ₂ O-	SO ₄	F	Solids	NH ₄ -N-	NO ₃ -N-	P ₂ O ₅ -	K ₂ O-	F	Solids	
	ws g/L	ws g/L	ws g/L	ws g/L	g/L	mg/L	mg/L	ws g/L	ws g/L	ws g/L	ws g/L	mg/L	mg/L	
14.12.2011	119	94	0.7	1.8	100	480	223	120	94	0.7	1.8	490	180	
16.12.2011	97	77	0.9	1.7		520	1 754	97	76	0.8	1.7	440	1 247	
21.12.2011	68	51	0.4	1.3	59	258	118	68	51	0.4	1.3	254	125	
23.12.2011	71	54	0.4	1.3		289	238	71	53	0.4	1.3	304	187	
28.12.2011	78	58	0.7	1.9	68	474	165	78	58	0.7	1.9	442	128	
30.12.2011	76	58	0.8	1.9		396	345	77	58	0.8	2.0	359	155	
4.1.2012	104	77	1.0	2.4	98	561	331	104	76	1.0	2.3	558	343	
11.1.2012	134	104	1.4	2.6	107	560	970	134	103	1.4	2.6	577	956	
13.1.2012	142	109	1.6	2.6		625	624	141	108	1.6	2.6	615	644	
18.1.2012	125	97	1.2	2.3	104	617	498	127	98	1.2	2.3	628	472	
20.1.2012	123	93	1.1	2.2		757	925	124	94	1.1	2.2	766	918	
25.1.2012	130	94	1.2	1.7	129	521	440	130	94	1.2	1.7	539	518	
27.1.2012	123	91	1.5	1.8		885	1 039	120	89	1.6	1.8	951	1 669	

ws = water soluble