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# Treatment of Acid Mine Drainage by flocculation, sedimentation and flotation

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Norwegian University of  
Science and Technology

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Master's Thesis in Water Supply and Wastewater Systems

# Treatment of Acid Mine Drainage by flocculation, sedimentation and flotation

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# Abstract

Acid Mine Drainage (AMD) and as consequence Metal Leaching (ML) is known to cause environmental pollution affecting many areas with historic or current mining industries. The Killingdal Area by the Trondheim fjord in Norway is suffering from it. The water is being collected and treated following chemical precipitation, flocculation and sedimentation. The treated water, when discharged to the recipient, needs to fulfil the requirements set out by the Norwegian Environment Agency's discharge permit by 2021.

The present study aims to improve the actual treatment train of the Killingdal site in terms of Suspended Solid Removal (SSR) and sludge volume and quality. Study I analyses the solubility of metals in the raw water by pH modification. This was done by a titration sequence and scanning the metal content (Al, Fe, Ni, Cd, Pb, Cr, Zn and Cu) dissolved in the water with an Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Study II pretends to Improve the flocculation step by analyzing the polymer type (EPIDMA and PAM) and dose and see how this affected the SSR (Sedimentation or flotation) and the sludge quality. The experiments were carried out by a series of jar tests. The variables of study were the: Polymer type, polymer dosage and two different SSR methods. SSR efficiency was evaluated by measuring the turbidity of the water and the metal content in the treated water. Sludge quality was evaluated according to the dewaterability with a Capillary Suction Time (CST).

Experimental results showed that in Study I, the optimal pH for the maximum removal of dissolved metals in the water was between 9 and 10. Study II showed that both SSR unit treatments (sedimentation and flotation) give satisfactory results. EPIDMA polymer is adequate for sedimentation and the optimal dose is 8.3mg/L. PAM works better for the flotation and the optimal dose for SSR is between 5 and 10 mg/L. Neither sedimentation nor flotation fulfill the requirements of the metals limit discharge to the fjord despite the optimization. In the flotation; quantitative results for the sludge conditioning are not clear neither its performance nor its quality, however the qualitative results look very promising.

Further studies need to be done to confirm this last conclusion. Since the SSR do not fulfill the environmental requirements, another treatment unit need to be added to the train. The lime step should be evaluated in another set of experiments to compare the sludge quality. The design of the sedimentation and flotation units scaled to the pilot need to be studied. Bio-sulfidogenic reactors could be a potential solution to lower the content of metals in the treated water and in the SSR sludge product.

Keywords: Acid mine drainage (AMD), Metal Leaching (ML), chemical precipitation, flocculation, sedimentation, flotation, sludge management.

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# Abbreviations

AF	Security Factors
AMD	Acid Mine Drainage
ARD	Acid Rock Drainage
CST	Capillary Suction Time
Eq.	Equation
EPIDMA	cationic Epichlorohydrin-dimethylamine copolymer
EPS	Extra Polymeric Substance
Fig.	Figure
ICP	Inductively Coupled Plasma Mass Spectrometry
ISO	International Organization for Standardization
Me	Metal
ML	Metal Leaching
NGI	Norwegian Institute for Water Research
NTNU	Norwegian University of Science and Technology
PAM	Cationic Polyacrylamide
SS	Suspended Solid
SSR	Solid Suspended Removal
VS	Volatile Solids

# 1. Introduction

The Killingdal area is located in Trondheim along the coast of Ilsvika. Nowadays it is an urban and recreational area, but 10 years ago it used to be an abandoned ore processing facility. The facility, that belonged to *Killingdal Grubeslskap AS*, was in operation from 1891 to 1986. The activity consisted in purifying ores such as pyrite, sphalerite and chalcopyrite and extracting concentrate of Zinc, Copper and Iron. After the closure of the activity, the site became mostly property of the *Trondheim Kommune*.

Several studies were pursued to explore the levels of contamination in sediments and water of the area. The results revealed the presence of Acid Mine Drainage (AMD) and a considerable amount of heavy Metals Leaching (ML) through the site. The main reason behind this pollution was due to an improper management of the wastes during and after the activity of the Killingdal processing plant. AMD is known to be formed when sulfidic minerals are exposed and react with air and water to form sulfuric acid and dissolved iron. The acid runoff further dissolves heavy metals that are present in the surroundings. The hazards associated to AMD are mainly: A harmful effect to aquatic organisms, corroding effect of infrastructures and contaminated soil and drinking water.

Having seen the potential hazard of the leak into the *Trondheimsfjorden*, in 2009 *Trondheim kommune* started a clean-up plan. The goal was to eliminate the health and safety risks associated with the area, minimizing the leaching from the area to the Trondheim fjord and creating an infiltration system to accumulate all the polluted runoff in a safe place where it could be treated. This place turned out to be an underground tunnel, remnant of the buildings and structures of the facility. In 2018 a provisional treatment process for the AMD was installed and activated in there. The pilot is still in improvement phase. Various tests and cleaning solutions have been carried out. However, the treated water is still not fulfilling the requirements set out in the Norwegian Environment Agency's discharge permit by 2021. The current implemented treatment, which is based in chemical precipitation and solid suspended removal (SSR) by gravity separation (sedimentation), reduced the content of heavy metals in the water but it needs to be further optimized and standardized.

The available literature suggests different typical treatment solutions for the problem. However, most do not fit the dimensions of the underground tunnel. In addition to the water treatment it is important to contemplate the sludge quality, production and handling. This makes the selection and dimensioning of treatment solutions even more challenging. Therefore, it was suggested, to *Trondheim Kommune*, flotation as a potential alternative for the suspended solid removal part (instead of the sedimentation) and that could be feasible to work, as well, after the chemical precipitation step that exists. Flotation was thought to be a good alternative worth studying due to the high efficiency of the technique, the resultant compact volume of sludge and the easy handling that it is supposed to perform compared to the sedimentation.

The **aim** of the project is the improvement and optimization of the treatment of the actual pilot of acid mine drainage and metal leaching at the Killingdal site. As a previous step, in order to perform a chemical treatment, it is important to remove as much heavy metals from the water

as possible, make them precipitate to be able to proceed to the next step, the flocculation. Chemical precipitation of the metals it is dependent on the pH, however each metal has different constants of solubility. Having read the literature and the background of the case study, the **hypothesis of Study I** is that to have the least amount of metals dissolved in the raw water, the pH should be 9 or more. The **objective of the study I** consisted in evaluating the solubility of metals in the raw water and at different levels of pH. By knowing the optimal pH, it will be possible to proceed to the next steps of the chemical treatment. Which would be flocculation and SSR and it is what study II will focus on. The **hypothesis of study II** is that flotation, as well as sedimentation, can treat efficiently the AMD, but flotation can fulfil better the requirements and the dimensions of the site, as well as improve the sludge quality, production and handling. For both treatment steps, flocculation and SSR, it will be necessary to optimize the parameters. Many parameters are involved in it, as it will be explained in the literature review section, but only some have been selected for the study. For that, the main **objectives of study II** will be: Firstly, to evaluate polymer type and dose on the efficiency of the subsequent separation treatment (sedimentation or Flotation). This step will be done with Jar tests. Secondly, to evaluate the type of separation treatment that should be selected, sedimentation or flotation, or both and finally to Evaluate how the treatment pilot operation can be optimized.

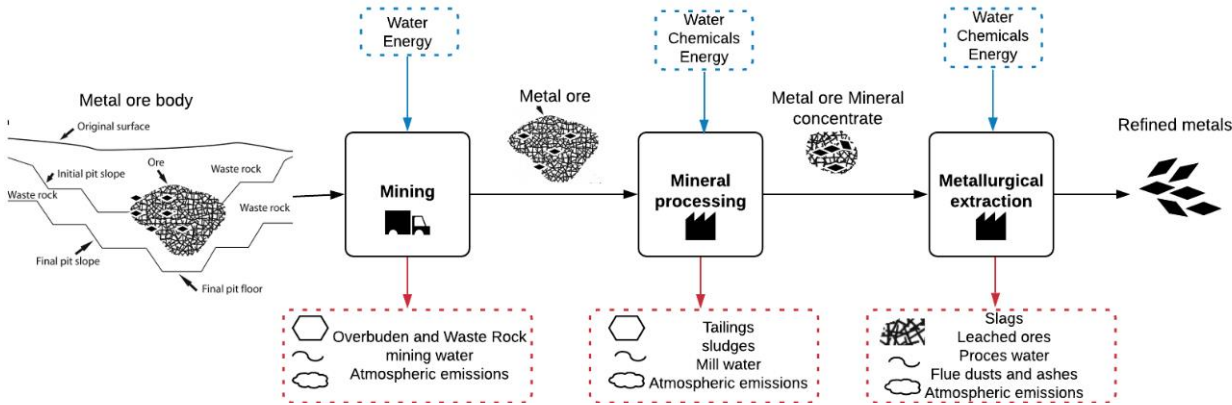
Regarding the document's structure, it will start with a chapter that will focus on the background definitions of the case study and the case study itself, to understand the problem description. It will be followed by the theory of the actual project, which will be the literature review that has been done in order to pursue the experimental part and solve the objectives mentioned above. The material and methodology of the experiments will show the practical work done. The results of the experiments will be shown and explained while being discussed and compared with the literature and similar studies. Finally, some conclusions will be extracted.

# 2. Acid Mine drainage

This chapter will concentrate in section 2.1 describing: The background reasons for AMD to be originated, the characteristics of it and its potential impacts to the environment to understand the importance of it to be treated. This section will be useful for understanding the origin of the case study. Section 2.2 will give an overview of the possible treatments after AMD is originated and an introduction to this thesis, since it is focused in one of the treatments. Both section 2.1 and 2.2 will be the introduction to the final section 2.3 which will be the case study that is what the treatment process of this thesis is based on.

## 2.1. Origin, characteristics and environmental impacts of AMD

**The mining industry** include mining, mineral processing and metallurgical extraction. Mining is the first operation which involves the extraction of the desired material from the ground. One or more component parts of the mined material are possible to recover by mineral processing. Mineral processing physically separate and concentrate the ore mineral from the ore body. Metallurgical extraction aims to destroy the crystallographic bonds in the ore mineral in order to recover the element that is wanted, which is normally a metal. These three activities produce many by-products or unwanted outcomes that have no current economic value called mine wastes, those can be solid, liquid or gas (G Lottermoser, 2010). Since only a very small part of valuable component is extracted from metal ores bodies, the mining industry creates a lot of wastes. It can be seen the following figure 2.1.



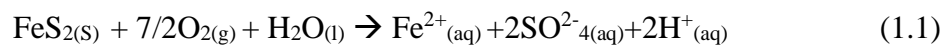
**Figure 2-1:** Simplified flow diagram of inputs and outputs of the mining industry and possible sources of AMD

**Mine wastes** include mining wastes, processing wastes and metallurgical wastes and those produce solid, liquid, and gaseous wastes. In the case of the mineral processing wastes and the metallurgical extraction, the physical and chemical characteristics of the processing wastes vary depending on the mineralogy, geochemistry of the treated resource, type of processing technology and process chemicals (G Lottermoser, 2010). Mine wastes contain few amounts of ore minerals, since it is the product, but it contains bigger amounts when the mine or the processing facility has been abandoned with all the storage of metal ore, concentrate or refined minerals. Good closing and waste management of the mines and the facilities is very important to avoid further impacts in the environment.

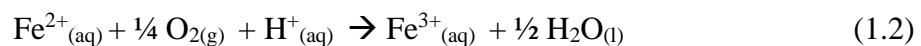
When the treated resource that is a major portion of the rock constitutes **sulphides minerals** such as Pyrite ( $\text{FeS}_2$ ), Chalcopyrite ( $\text{CuFeS}_2$ ), Arsenopyrite ( $\text{FeAsS}$ ), Sphalerite ( $\text{ZnS}$ ), Millerites ( $\text{NiS}$ ), Galena ( $\text{PbS}$ )..., (G Lottermoser, 2010) the mining and processing of these resource can expose the sulphides to a weathering process. This can produce a dangerous mine water waste liquid that is referred more specifically in the literature as Acid Mine Drainage (AMD) or acid rock drainage (ARD) (Igarashi *et al.*, 2020).

**Acid mine drainage** can occur from natural or man-made sources. From the latter ones, the most common are: Waste rock and tailings coming from mining activities such as mining, quarrying and mineral processing (Tremblay and Hogan, 2001). When sulphides are exposed to oxygen, water and catalysed by microorganisms (e.g. Thiobacilli). The oxidation is performed causing as product acidoc water. It is generated by the degradation of sulphides creating a set of acid production reactions. The most studied sulphide oxidation is the Pyrite ( $\text{FeS}_2$ ). It can occur with the presence of a microorganisms (biotic), without microorganism (abiotic) and caused by oxygen (direct oxidation) or caused by oxygen and iron (indirect oxidation). It is possibly a combination of all. (G Lottermoser, 2010).

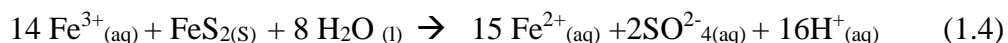
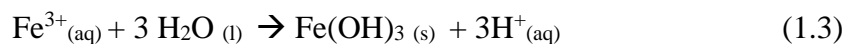
It is commonly accepted that disulphide weathering and especially **the oxidation of pyrite** are the initial reactions in the formation of AMD and metalliferous leachate (ML). The reaction mechanisms of pyrite weathering are thoroughly studied. The first step that takes place is the oxidation of the pyrite ( $\text{FeS}_2$ ) by oxygen, where dissolved iron, sulphate and protons are produced (see Eq 1.1) (Kefeni, Msagati and Mamba, 2017)



The oxidation of pyrite creates an increase of dissolved solids in the water and lowers the pH. If the conditions, that depend on: The oxidation conditions and the  $\text{O}_2$  concentration, the pH and the bacterial activity, are sufficient, most of the  $\text{Fe}^{2+}$  will be oxidized to  $\text{Fe}^{3+}$  (Eq. 1.2). This step is the rate-limiting process since it is very slow at pH below 5. Acidophilic bacteria can help catalyze it (Kefeni, Msagati and Mamba, 2017).



The third step will consist in the precipitation of  $\text{Fe}^{3+}$  as hydroxide as shown in Eq. 1.3. This step is pH dependent and it will happen when the pH is between 2.3 and 3.5. However, there is a part of  $\text{Fe}^{3+}$  that do not precipitate and this residual precipitate may take part in the oxidation of pyrite as it is shown in Eq. 1.4 (Kefeni, Msagati and Mamba, 2017).

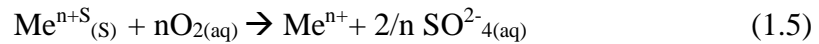


As it can be seen, in the overall reaction procures protons leading to releases of acid into mine water. If no buffering material occur in the natural environment the pH reaches extremely low values (Wolkersdorfer, 2006).

Since pyrite is always found with other minerals, mine water is commonly enriched in many elements forming multi-metal solutions. The oxidation of sulphide minerals does not only create acid, but it also liberates those metals in the surrounding and sulphates from the pyrite

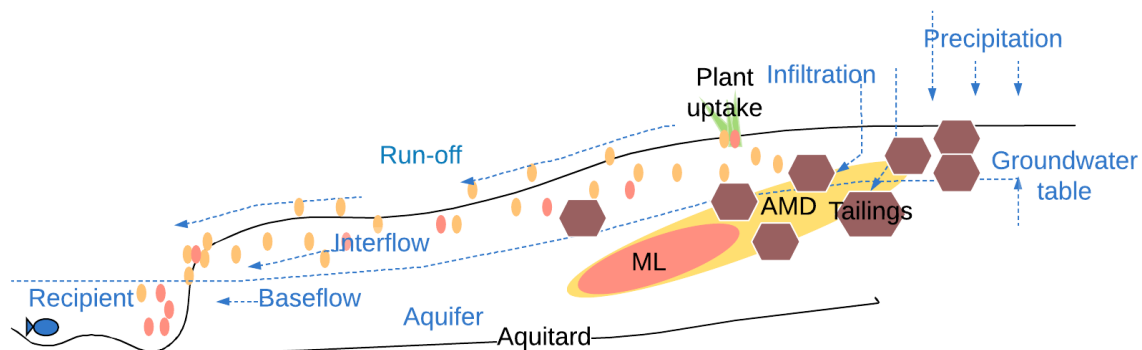


reactions into waters and accelerates the **Metal Leaching** of other elements from gangue minerals (minerals not considered valuable, due to the little amount, and that are within the ore mixture). Most of those minerals are stable at the  $E_H$ -pH conditions and the ground water before mining. When oxygen enters the ore veins, the stable conditions change and those mineral phases start to oxidise to more mobile species, which are then transported into water (Wolkersdorfer, 2006). Eq. 1.5 shows the mechanism. There is a second process that is induced by disulphide oxidation and the lowering of the pH.



The predominant mine water constituents are:  $\text{SO}^{2-}_4$ , heavy metals (Fe, Cu, Pb, Zn, Cd, Co, Cr, Ni, Hg), metalloids (As, Sb), and other elements (Al, Mn, Si, Ca, Na, K, Mg, Ba, F) that were in the surrounding environment. Those constituents are harmful to the creatures and plants when their concentrations go beyond the permissible limits and normally those limits are at very low metal ions concentration (Harsha, Senthil and Panda, 2019).

to sum up, AMD interacts with rocks containing different types of mineral ore and easily provoking the solubility of toxic metals. This happens due to low pH. The environmental pollution will be caused by AMD and the geology of the site (Fig.2.2) (Kefeni, Msagati and Mamba, 2017). Due to rain- and snowmelt-induced flush out from weathered mine tailings, the flood episodes were expected to produce high concentrations of ML. From the waste sites, the hazardous pollutants will travel through the rest of the soil, recipients and therefore be toxic to aquatic biota, which will eventually reverberate in the rest of the food chain.



**Figure 2-2:** Simplified cross-section of a sulfidic waste rock dump and conceptual process of AMD generation and development in an environment close to a recipient

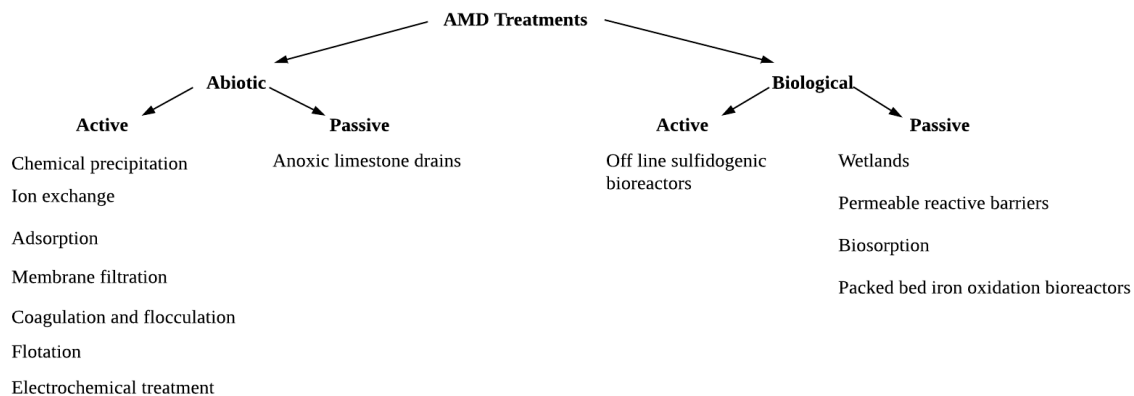
The main possible **environmental impacts** if the AMD is not prevented or treated is A) Damage to the terrestrial ecosystems by: soil acidification, accumulation of toxic elements in the soil, soil erosion, damage of the soil biota, loss of soil fertility, plant contamination, food chain contamination. B) Damage of aquatic ecosystems: Water acidification, polluted recipients, damage to aquatic biota, food chain contamination. C) Damage to human ecosystem: Damage of the structures due to corrosion, non-potable water, loss of potential nourishing intake from the area affecting the economy of agriculture or aquaculture on site.

## 2.2. Treatment methods for Acid Mine Drainage

As pre-control measure there is the possibility to predict, through lab, field or numerical methods, the potential of the tailings to cause AMD and ML. Further research needs to put emphasis on it in order to prevent the event to happen and manage the tailings with the least probability of environmental risk (Tremblay and Hogan, 2001).

When the site has the potential to be contaminated from acidic drainage, the measures to prevent and control it are the recommended procedure since these can eliminate or minimize the acid generation. However, if the it is an historic site (such as closed mines and areas with tailings) where the prevention and control technologies cannot be effectively applied the most cost-effective approach is long-term active treatment, especially in mines where a neutral chemical treatment is required over the long term. (Tremblay and Hogan, 2001).

Various techniques to remediate AMD have been studied throughout the years. As it can be seen in Fig. 2.3. the most common way of classifying the measures is dividing them into active and passive processes. The former usually it is referred to the continuous application of alkaline chemicals to neutralise and then the removal the metals through techniques such: Precipitation, ion exchange, adsorption, filtration, coagulation and flocculation, flotation and other treatments. Passive processes normally consist in natural and constructed wetland ecosystems, but there are other alternatives. Passive systems require less maintenance than the active systems. The subdivision of technologies it is often done depending on the biological activities and the ones that are not, which are named: Abiotic. In the following figure there is the recompilation of the different techniques that can be applied to treat AMD (Johnson and Hallberg, 2005).



**Figure 2-3:** Simplified diagram of the AMD treatments classification in Abiotic, Biological, Active and Passive.

The technologies available for removal of heavy metals and dissolved inorganic substances include chemical precipitation, carbon adsorption, ion exchange, reverse osmosis... Of these technologies, chemical precipitation is most commonly employed for most of the metals (Metcalf & Eddy, 2003).

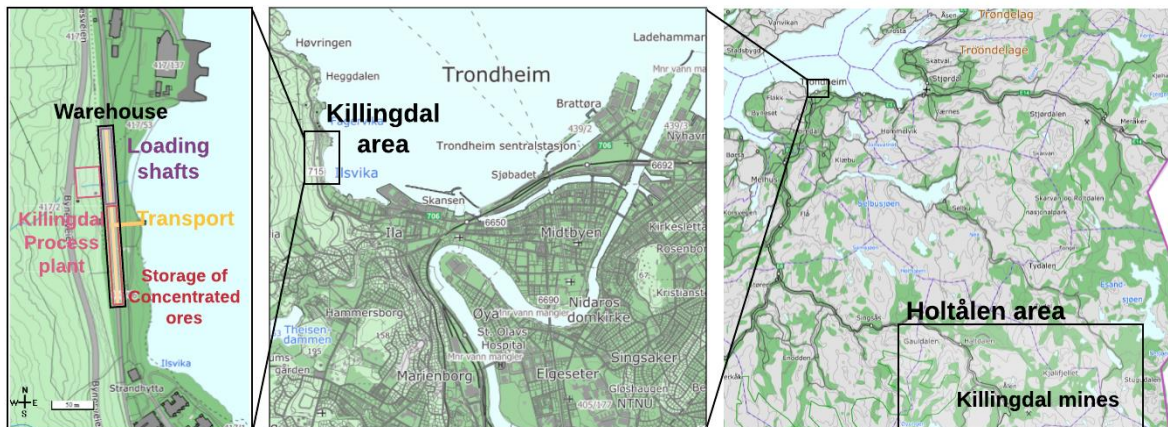
AMD treatment technologies are site specific, and multiple remediation strategies are commonly needed to achieve successful treatment of AMD waters. The first objective in all techniques is to neutralize the acid drainage and the second is to reduce the concentration of

contaminants that are a concern for the environment, so the effluent quality is acceptable to release or recycle/recover the materials of interest, if possible.

The treatment system should be adapted to site-specific conditions, acidic drainage collection and storm water management system, limits on the timing and quality of the treated discharge, among other factors (Tremblay and Hogan, 2001). From the technologies mentioned above, they can stand alone, but most often they are combined.

### 2.3. The case study

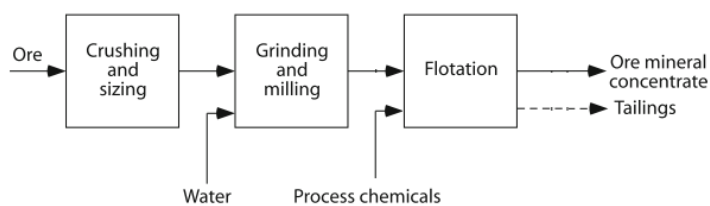
The Killingdal area is the name for the area located in the West of Ilsvika, in Trondheim (Fig. 2.4). The name originates from the *Killingdal Grubeselskap AS* mining company, which was in operation from 1953 to 1986 and had an ore processing facility in the area. The Pyrite ore deposits blended with copper and zinc were extracted from the mines in the region of Holtålen in Fig. 2.4, right, 130 km away from Trondheim, where transported by rail to the Killingdal area where they were processed and afterwards shipped to the clients. (Multiconsult, 2015).



**Figure 2-4:** Situation of the Killingdal area (Left) in Trondheim (Center). Situation of Trondheim and the Killingdal mines in Norway (Right).

The **facility** was divided mainly by the processing plant, the warehouse and a transport tunnel to ship the ores to the clients (Fig.2.4). When the ore arrived by rail this was dumped from freight wagons into the unloading shafts at the North end. Under the warehouse and in the unloading shafts there was a transport tunnel that had a conveyor belt. The ores passed through this tunnel to the process plant, and the finished product (concentrated ores) were transported from the warehouse in the South, to a shipping dock that lay by the sea. At each end of the transport tunnel, there was also a drainage tunnel. The creek was led through the process plant building and the unloading shafts and flows into the fjord (Multiconsult 2015 (Multiconsult 2011)).

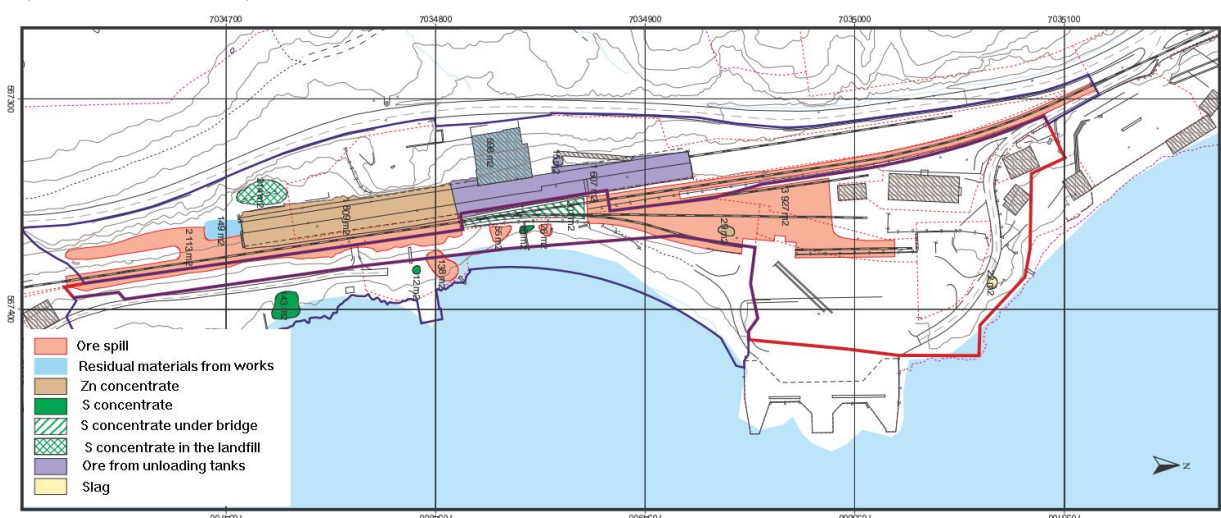
The processing plant was based on flotation. It is a process where finely ground ore are suspended in a liquid and one adds chemicals to separate the ore minerals from the outlet (waste) (Fig. 2.5). The tailings were left in the terrain or sent out in the fjord, while ore mineral concentrates (Zn, Cu, S concentrates) were stored and ready to ship out (Multiconsult, 2015).



**Figure 2-5:** Simplified Flow chart of mineral processing in Killingdal, in which ore is processed to yield an ore mineral concentrate and tailings

The mining company went bankrupt and Trondheim Municipality took over as the landowner of the plant and the area. After the closure, several attempts were made to find new uses for the plant, however due to contamination, it was found unsuitable. Thus, the plant was left unused for years. After pursuing several studies on the **levels of contamination in the area** the results showed the presence of acid mine drainage and a considerable amount of heavy metals in the site during and after the activity of the Killingdal processing plant.

After the activity of the plant in the Killingdal area relatively extensive environmental engineering basic studies were carried out in this area (by NTNU students in 2003 and Rambøll in 2004), and it revealed significant deposits of product residues such as ore concentrates and masses of heavy metals in the former production and warehouse building and outdoors in the site. It was estimated that 4600 tonnes were deposited in the area: 90 tonnes of ore debris left in the warehouse and several piles of zinc and sulfur concentrate were scattered in the area (Kommune, 1996).



**Figure 2-6:** Situation of the waste products of the killingdal facility activity after closure. Ore debris and concentrate, masses of heavy metals and slag in the Killingdal area (Trondheim Kommune, 2009)

As for the ore concentrates found were: Fine-grained and persistent mainly (>10%) of Pyrite ( $\text{FeS}_2$ ) and Sphalerite ( $\text{ZnS}$ ), with subordinate (1-10%) Pyrrhotite ( $\text{FeS}$ ) and Chalcopyrite ( $\text{CuFeS}_2$ ). Accessory minerals (<1%) in the ore are: Bournonite ( $\text{PbCuSbS}_3$ ), Molybdenite ( $\text{MoS}_2$ ), Mackinawite ( $\text{Ni,Fe}_9\text{S}_8$ ), Tetrahedrite ( $(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$ ), Arsenopyrite ( $\text{FeAsS}$ ), Galena ( $\text{PbS}$ ) and Covellinte ( $\text{CuS}$ ). The quality on the ore (content) is determined at 45% sulfur, 5.5% zinc, 1.7% copper and 0.4% lead (NGU, 2016a).

**A clean-up work and monitoring** was pursued by the Municipality since during the active period of the plant and posteriorly, the Killingdal area was a source of pollution to the harbour

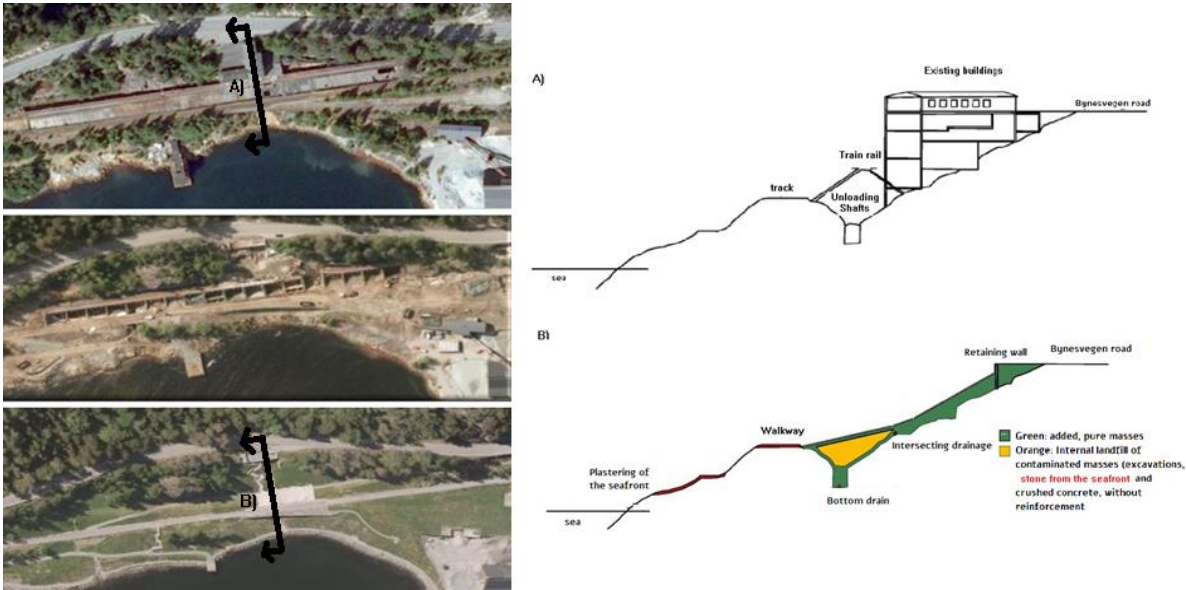


area. In 2002, landowners received an order from Klif (the Climate and pollution Agency), now the Environmental Directorate, to carry out environmental studies. (Multiconsult 2009). According to the Pollution Control Act, the present landowner is responsible for the pollution, although this one was not responsible for the origin of it (Multiconsult, 2011)

The area was supposed to be accessible to public traffic and able for residential purposes, but many risks were associated to it and therefore in 2009 Trondheim municipality engaged a consultancy group to prepare an action plan of urban development. It consisted in demolition of the warehouse, cleaning up of the contaminated soil and urbanize the area (Multiconsult, 2009).

From April 2010 to January 2011, some measures were taken to clean up the contaminated land (Fig.2.7, left). The goal was to eliminate the health and safety risks associated with the area as well as stopping or minimizing the leaching from the area to the Trondheim fjord.

After several years of planning, 2015 began work on dredging and coverage, and was completed in 2016. The control of the sulfide oxidation in of the mine was using in-pit disposal. The coverage consisted of an acid resistant material laid above the bottom layer of the pure masses filled of contaminated masses. The sealing of the contaminated masses is carried if a layer of bentonite, a cloth and then sand. The distance from deposited masses in state class 4 to finished terrain surface must be at least 100 cm. A layer of masses in state class 3 can be laid over the masses in state class 4, up to 0.5 meters below the finished terrain surface The top layer should consist of clean, draining masses (35 cm) and a growth soil layer (10 cm)



**Figure 2-7:** (Left) Pictures of the clean-up works evolution in Killingdal area. (Right) Cross-section of Killingdal area A) before clean-up work B) after clean-up work. (Engebretsen, J., 2017)

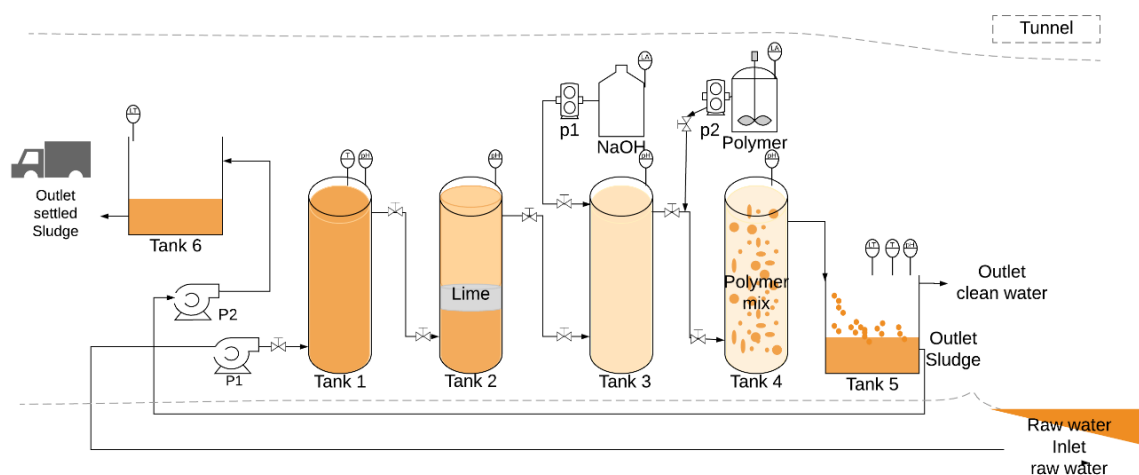
At the same time as an action plan was drawn up for Killingdal, the municipality of Trondheim started planning for another project: Cleaner Harbor. Much of the pollution in the Nyhavna, Brattøra and the channel is caused by previous industry and shipping traffic, with high values of copper and polyaromatic hydrocarbons (PAH) (Trondheim municipality 2016). In the westernmost parts of the harbor pool, Ilsvika and Fagervika, the Killingdal plant contributed to the leaching of copper, zinc, lead and mercury to a large extent. The pollution originated both from runoff from land and from an estimated 1.4 million

tonnes of tailings were deposited in the sea during the period the processing mining plant was in operation (Trondheim municipality, 2011). The project was to clean the port area around Trondheim.

The discharges to the fjord were monitored until October 2011. It was then proposed monthly sampling for three years, with reporting to the Environment Directorate in January 2015 (Multiconsult, 2015). It was assumed that the clean-up work carried out in 2010-2011 would be sufficient to prevent further pollution from the area. However, monitoring from 2011 to 2015 showed increasing concentrations of heavy metals in the seepage water being discharged to the sea from the tunnel in the area. At the same time, Trondheim municipality was instructed by the Environment Directorate (Miljødirektoratet) to limit or stop emissions from Killingdal to the recipient, Trondheim Fjord, by 2021.

In 2016, among other important measures were taken to significantly reduce stream water that infiltrated polluted masses and ended up in the tunnel. The amount of water entering the tunnel today is therefore at its lowest. In 2017 a study conducted by Rambøll and in collaboration with the municipality of Trondheim and Vikelv Water Treatment Plant (VIVA) started with the aim to treat the AMD. All the polluted runoff is concentrated in the tunnel that use to be to ship the minerals (Rambøll, 2017).

In 2018 a **provisional treatment process** for the AMD was activated in the tunnel and it is still in improvement phase. Nowadays, there are 5 pilot tanks. There is a pump taking the water from the tunnel to a continuous-flow group of upflow reactors. The first tank is collecting the volume that will be treated in the second tank. The inlet of tank 2 is in the bottom and the water to treat goes through crushed limestone ( $\text{CaCO}_3(\text{s})$ ) The water flow rate is high, since high velocity of the water particles can prevent settlement onto lime. Also, it is in anoxic conditions to prevent the settlement of the iron deposits on the limestone filters (Rambøll, 2017). The effluent is in the top of the tank. The lime is used to raise the pH so it will gradually dissolve in the acidic mine water, neutralizing the water and increasing the buffer capacity in form of the addition of Sodium hydroxide ( $\text{NaOH}$ ) in tank 3. Tank 4 will contain the polymer mix to create bigger flocs and allow the separation solid - liquid. Next step, tank 5 consists in the sedimentation of the particles.



**Figure 2-8:** Conceptual representation of the current pilot treatment plant in the tunnel Killindal area

The treatment of the pilot have to be adjusted to the regulations of discharge of the Trondheim fjord and have special attention to the metal concentration that is sent to the recipients. For that it needs to follow the Norwegian water and sediment regulations.

**Norwegian Water Regulations (vannforskriftene)** is the adaptation of the EU Water Directive in Norway which the aim is managing water bodies according to the same principles across Europe. The environmental goal for natural water bodies of surface water is that the condition should not deteriorate, and that they should have at least good ecological and chemical state, and for groundwater at least good chemical and quantitative state. Some indices and parts of the classification system are still based on limited access to data and efforts are being made to expand the data base to ensure an even better basis for the environmental objectives and assessment of the state of the environment (Miljødirektoratet, 2018).

The classification shall be based on measurements of the state of ecological quality elements, such as aquatic chemical conditions, aquatic plants, invertebrates (bottom animals) and fish. Ecological status of surface water shows the current state of the environment in the water body, both in terms of species composition, structure and behavior of the ecosystem being groundwater an exception. Ecological status is divided into five classes: very good, good, moderate, poor and very poor ecological state. Very good condition is the condition you want in a body of water with minimal human impact (Miljødirektoratet, 2018).

**Table 2-1:** Ecological status divided in condition classes and its description

I	II	III	IV	V
Background	Good	Moderate	Dangerous	Very dangerous
Background level	No toxic effects	Chronic effects for long term exposure	Acute toxic effects for short term exposure	Extensive toxic effects
Upper limit: Background	Upper limit: AA-QS, PNEC	Upper limit: MAC-QS, PNEC acute	Upper limit: PNEC acute*AF	

The upper limit for Class I represents background values, and the state of nature where such data exists. For most of the anthropogenic toxins and where the toxins do not have a natural source, the upper limit for Class I is set to zero. The upper limit for Class IV is based on acute toxicity without safety factors, and is the limit for more extensive acute toxic effects. All class boundaries outside the upper limit of Class I are calculated based on risk/effect.

Regarding the Norwegian condition classes for coastal waters and sediments the limit values and class limits (with the exception of Class I) are determined on the basis of available information on the environmental toxins from ecotoxicological laboratory tests. Security factors (AF) are used to ensure adequate protection where there is not enough data. By applying safety factors, you take into account any organisms that are more sensitive than those used in laboratory tests. The safety factor is lower the more different types of organisms the substance has been tested on.

The sediment classification system is intended for use with fine-grained sediment consisting of clay and / or silt. As environmental toxins are mainly associated with small particles and organic matter, sediments with deposits of gravel or coarse sand will not be suitable for evaluation through this system. The limit values are also adapted to Norwegian conditions. Among other

things, the content of organic carbon in the sediment is 1%, which is lower than that used in the EU. This is because the content of organic carbon is lower in Norway than in many EU countries.

Regarding the Water and sediments quality in the Killingdal area, In 2018 The Miljødirektoratet monitored the sediments quality of Killingdal area and the water quality of the coast of Fagervika, where the runoff of the Killingdal area drains (marked area in fig. 2.9).



**Figure 2-9:** Sediments monitored area (left) and water monitored area (right) (Miljødirektoratet, 2018).

Nowadays, as it can be seen in the left picture of Fig.2.9 the area of Killingdal shows a potential impact on its sediments and a red mark of sever pollution in the waterfront. Results from concentrations in water samples are classified according to Miljødirektoratet, 2018. The different state classes are given in table. 2.1. The comments from the water measurement are of the area’s ecological condition is poor (orange) and the chemical quality of the water is poor (red). The area shows a great degree of impact with unknown detected effect yet.

It is stated that there is organic pollution coming from urban transport and chemical pollution from coastal transport and slag coming from Killingdal mines. The water has presence of organic pollutants and heavy metals. Therefore, the bad ecological and chemical conditions of the coastal water in the area is a consequence of the acid mine drainage and heavy metals that have been seeping during all these years from the unmanaged tailings of the killingdal mines.

The municipality provided some **data of the actual metal concentrations** that contain the water in the tunnel (Table 2.2). Since the pilot of the treatment plant it is installed some progress has been made in the results of the quality of the treated water and sediments, however it must be improved. The following figure shows the quantities of heavy metals and the condition class that they fall in according to the Norwegian condition classes (see appendix A)

**Table 2-2:** Metal concentrations present in the tunnel water and the sediments of the tunnel according to the Trondheim Kommune in 2020 painted according to the class that they are in.

	Tunnel water (µg/L)	Sediments (mg/kg TS)
Fe	13479	213423
Cu	16281	102013
Zn	8572	73154
Pb	21	308
Cd	29	228
Cr	4	50
As	6	39262
Ni	31	173



## 3. Literature review

This part contains the search and evaluation of the available literature and the specific theories and terms used during the process of the design of the experimental protocol. In addition, it contains the theory that will be used for a better interpretation and analysis of the obtained results in the project.

### 3.1. Chemical active treatment of the AMD

In chapter 2 it is described the main features of AMD water quality. As a general knowledge of the water quality; surface and ground water contain many suspended solids: Inorganic and organic particles. Inorganic particulate constituents, including clay, silt, and mineral oxides that typically enter surface by natural erosion processes. It will contain very fine colloidal and dissolved organic constituents such as humic acids. In the case of sulphide mine water it contains in addition: Minerals, secondary minerals, ferric ( $\text{Fe}^{3+}$ ) precipitates causing turbidity and dissolved trace metals (Pb, Zn, Cu, Fe, Cd, Cr, Ni, As,...) and acidic water (G Lottermoser, 2010).

The conventional active chemical treatment of contaminated mine water comprises: 1) the neutralization of the acidity and 2) precipitate out the solubility of the trace metals. These two steps are effective and by far the most widely used process in industry because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates (Fu and Wang, 2011). In addition, is necessary to remove suspended solids, which cause turbidity, and to prevent discolouration of receiving water by red-yellow-ochrous precipitates. The products of mine water treatment will be the treated water and some form of solid residue called sludge. The efficacy of a treatment process can be considered in terms of the chemistry of the resultant water, the nature of the sludge (volume, toxicity, long-term stability, disposal requirements) and whether any marketable products can be recovered from the process to set against costs (ex: Recoverable metals or drinkable water) (Brown, Barley and Wood, 2002).

For any water treatment there is a first stage where experiments are carried in laboratory scale and then those scale into the pilot. A pilot plant is a physical model of the system as a whole, that is: Rapid-mix, flocculation and settling, and rapid filtration, and therefore is the most accurate means to assess the effects of coagulation. The laboratory scale and the pilot plant are complementary tools for the operation of the treatment. The laboratory tests, for instance jar test, for initial screening and the pilot plant for final assessment and fine tuning (Hendricks, 2011)

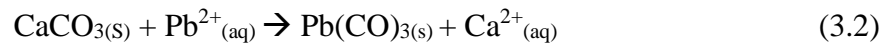
#### 3.1.1. pH modification and solution chemistry of heavy metals

*pH modification or Neutralization* are terms for the removal of excess acidity or alkalinity by treatment with a chemical of the opposite composition (Metcalf & Eddy, 2003). The basis of pH modification treatment is to raise the pH of the AMD causing first iron, and then other metals, to precipitate out of solution.

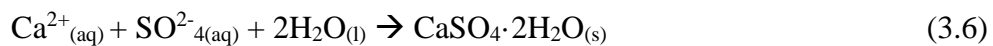
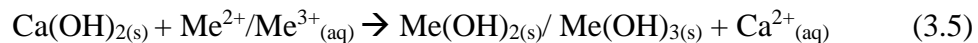
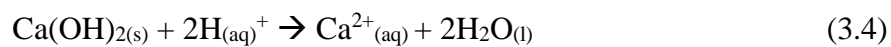
A *Neutralizing agent* is often needed to perform the pH modification. It important to note that excessive neutralization can also lead to enhanced dissolution of metals and metalloids and to waters with high metal and metalloid concentration. Neutralization of AMD water should raise the pH only to values necessary to precipitate and adsorb metals (G Lottermoser, 2010).

Some of the main chemical compounds used as neutralizing agents are Limestone or lime ( $\text{CaCO}_3$ ), Quicklime ( $\text{CaO}$ ), hydratated lime ( $\text{Ca(OH)}_2$ ), dolomite ( $\text{CaMg(CO}_3)_2$ ), caustic magnesia ( $\text{Mg(OH)}_2$ ), magnesite ( $\text{MgCO}_3$ ), soda ash ( $\text{Na}_2\text{CO}_3$ ), caustic soda ( $\text{NaOH}$ ), ammonia ( $\text{NH}_3$ ), kiln dust (largely  $\text{CaO}$  and  $\text{Ca(OH)}_2$ ), coal fly ash (largely  $\text{CaCO}_3$  and  $\text{CaO}$ )... Each neutralizing agent has advantages or disadvantages. However, the most common are Lime ( $\text{CaCO}_3$ ) or hydratated lime ( $\text{Ca(OH)}_2$ ), and caustic soda ( $\text{NaOH}$ ).

*Lime* neutralization is efficient for removing metals such as cadmium, copper, iron, lead, nickel and zinc from solution. Is a low cost material, easy to use, and it creates a dense, easily handled sludge. Nevertheless, it has a slow reaction times and coating of the limestone particles with iron precipitates. In the reaction of limestone with AMD waters, hydrogens ions are consumed, bicarbonate ions generated, and dissolved metals are converted into sparingly soluble minerals such as hydroxides, carbonates and sulphates (G Lottermoser, 2010):



*Hydrated lime* is also effective, easy and safe to use and inexpensive. However, it creates a voluminous sludge. Metals are precipitated in the form of metal hydroxides (Eq.3.5), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}_{(s)}$ ) is formed if sufficient sulfate is in the solution (G Lottermoser, 2010):



*Caustic soda* or *Sodium hydroxide* is especially effective for treating AMD. Caustic soda can raise the pH up to 10. The major disadvantages of caustic soda is that is costly, dangerous to handle and have poor sludge properties(G Lottermoser, 2010).

Since in the case study the main neutralizing agents are Caustic soda and Hydrated Lime, some advantages and disadvantages are exposed here in the following table 3.1.

**Table 3-1:** Advantages and disadvantages of lime and Caustic soda based on (G Lottermoser, 2010)

<b>Treatment</b>	<b>Advantages</b>	<b>Disadvantages</b>
Lime	Least expensive, Can coprecipitate high concentrations of sulfate ions Fewer safety issues Imparts a buffering capacity on wastewater Reliable treatment	Dust, slow to dissolve and must be made into a slurry Slurry must be pumped and can obstruct piping More sludge and is fluffier and difficult to handle Not effective in presence of chelating agents
Sodium hydroxide	Does not need to be mixed in storage Readily dissolve, does not clog piping, less maintenance than lime, does not need to be hydrated Sulfate in waste stream can interfere with reaction	Hydroxides reprecipitate if pH changes More expensive than lime No buffering capacity imparted on wastewater More sludge and is fluffier and difficult to handle

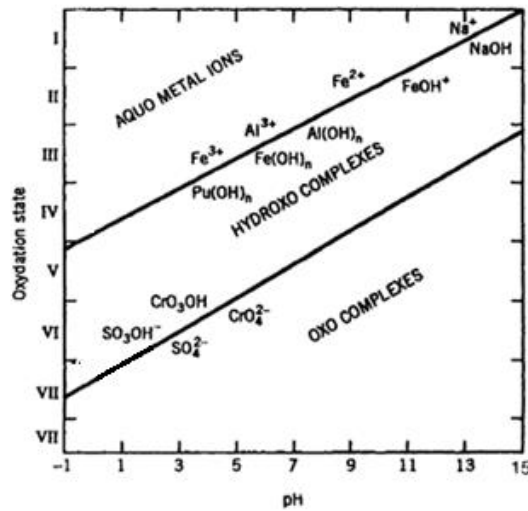
The addition of the agent should be with a dosage and active mixing. This is essential in order to prevent armouring of the reagent particles with reaction products such as metal hydroxides. These precipitates inhibit the neutralization reactions and cause excessive reagent consumption (G Lottermoser, 2010). Also, it is recommended to take into account the formation or tendency to develop calcium carbonate scale since it can cause more sludge formation (Metcalf & Eddy, 2003).

*Precipitation* of the heavy metals is a consequence of the acidity results of the neutralization. The precipitation has generally been observed to occur in three steps: 1) Nucleation, 2) Crystal growth, and 3) Agglomeration and ripening of the solids (Jenkins and Snoeyink, 1980). Key variables in the precipitation process are: 1) Solubility product ( $K_{sp}$ ), 2) temperature, 3) particle charge and 4) time (Hendricks, 2011).

*Solubility of product* is the equilibrium between concentrations of particular ions in solution and the solid precipitate. To remove an undesired cation from solution, an anion may be added so that the solubility product of the precipitate product is exceeded (Critten *et al.*, 2004).

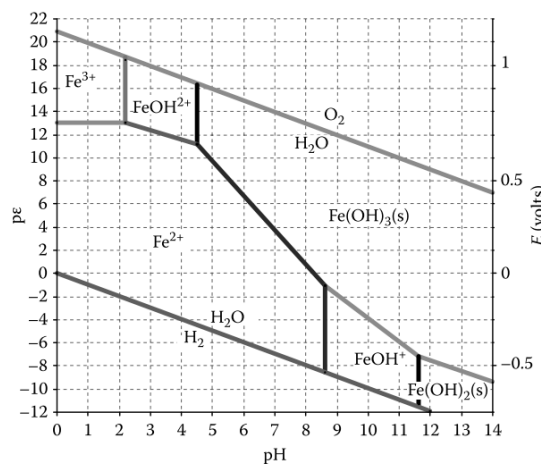
The *chemistry of metal ions* may be complex since there are different valence states and complexes that may form. The precipitation is principally controlled the variables mentioned above, but also by the speciation and concentration of elements and ligands and chelating agents, oxidation state of mineral components and redox of the system. Further, the chemical equation used to explain the precipitation–dissolution reaction is normally expressed related to the pH. The concentration of the dominant species present may be plotted together for a graphical presentation of solubility. *The Predominance diagrams* ( $p\varepsilon$ – $pH$  or  $E_H$ – $pH$ ) determine predominant chemical species at various pH values and is useful when analysing redox equilibria, for reactions in which both electron and proton transfer occur. The axes show the pH and the electrical potential. Acid-base complexation, and precipitation reactions and oxidation states can also be displayed on these diagrams because oxidants and reductants are involved in these types of reactions (Critten *et al.*, 2004).

*Metals ions* are in continuous search of a partner. All metal cations in water are hydrated forming aquo complexes. Metal ions with charge +1 are generally coordinated with water molecules. Most +2 ions are also coordinated with water up to pH values of 6-12. Most +3 metal ions are already coordinated with OH<sup>-</sup> ions within the pH range of natural waters. For +4 the aquo ions have become too acidic and are out of the accessible pH range of aqueous solutions with few exceptions. At high pH the association can be with O<sup>2-</sup> groups forming then oxo-complexes (Fig. 3.1) (Stumm and J.Morgan, 2013).



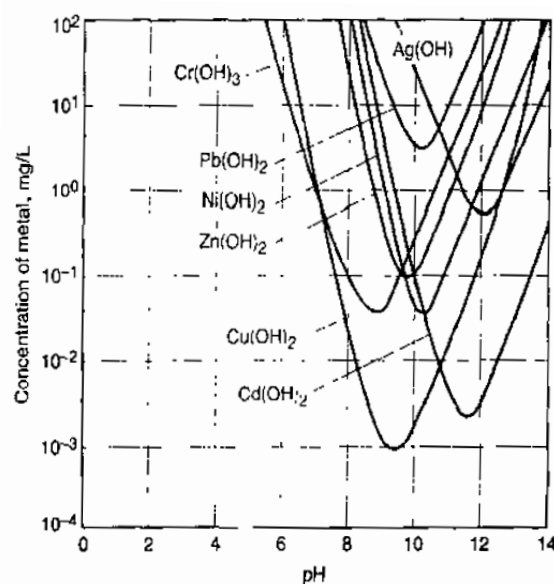
**Figure 3-1:** Illustration in where hydrolysis complexes of different common metals elements take part when dissolved in water. Low oxidation elements stay in complex with water as aquo complexes. When oxidation state and/or pH increases, hydroxo and oxo complexes become more dominant. Adaptation of (Stumm and J.Morgan, 2013)

A typical example, but especially relevant for acidic wastewaters with remnants of the oxidation of pyrite and that contain dissolved iron in the form of ferric (Fe<sup>3+</sup>) and ferrous (Fe<sup>2+</sup>) ions, ferric hydroxide (Fe(OH)<sub>3</sub>) will precipitate upon addition of a base (OH<sup>-</sup>) at a pH of approximately 7 (Fig.3.2). Under these conditions, ferric hydroxide will tend to increase sludge generation through flocculation of suspended solids and colloidal solids (WEF, 1998).



**Figure 3-2:**  $pE - pH$  diagram for Fe<sup>2+</sup> - Fe<sup>3+</sup> system (25°C) from (Metcalf & Eddy, 2003).

Trace metals can react with many other compounds that are preferred ligands than water. If the element concentration is high, two or more central atoms converge and become one large multinuclear complex (Stumm and J.Morgan, 2013). Common precipitants in the removal of metals by chemical precipitation include hydroxide (OH) and Sulfide ( $S^{2-}$ ). Carbonate ( $CO_3^{2-}$ ) has also been used in some special cases (Metcalf & Eddy, 2003). In wastewater treatment facilities most of the metals are precipitated as metal hydroxides through the addition of lime or caustic soda to a pH of minimum solubility. However, several of these compounds are amphoteric (capable of either accepting or donating proton) and exhibit a point of minimum solubility. The pH value at minimum solubility varies with the metal in question as it can be seen in the figure 3.3 (Metcalf & Eddy, 2003). The solid line in Fig. 3.3 represents the total metal in solution in equilibrium with the precipitate, but this location of the minimum solubility will vary also depending on the constituents in the wastewater, so these curves are guide.



**Figure 3-3:** Reference guide curve of residual soluble metal concentration as function of pH for the precipitation of metals as Hydroxides (Stumm and J.Morgan, 2013)

The free ion of metal is usually the most toxic, but in fact most trace elements, particularly metals, do not exist in soluble forms for a long time in water. Rather, they are present mainly as suspended colloids or are fixed by organic and mineral substance. Thus the mobility of metals in the environment depends on a more or less complex network of interactions between aqueous and heterogenous chemical reactions, as well as particle coagulation and flocculation phenomena. (Brown, Barley and Wood, 2002).

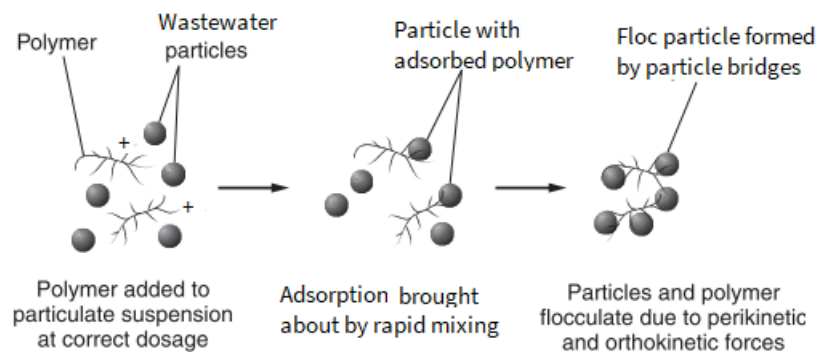
### 3.1.2. Flocculation

*Flocculation* is the unit process in which it is promoted that destabilized and smaller particles aggregate into larger masses (floc agglomerations) due to collisions between them. Collisions are caused by random thermal motion (Brownian motion) and different velocity gradients. With the addition of a flocculant the particles can aggregate to it and promote the flocculation (Metcalf & Eddy, 2003). The Flocculation term is used, as well, when a chemical is added to

contribute to charge neutralization and the subsequent agglomeration. After Flocculation the suspended solids are readily removed by other process such as gravity settling, flotation or filtration (Critten *et al.*, 2004).

*Small particles (or primary particles)* are generally less than 1µm of diameter. Those can be heavy metals that are in colloid suspension, fixed by organic and mineral substance or microorganisms. Colloidal particles typically have a net negative surface charge. The size of colloids (about 0.01 to 1µm) is such that the attractive body forces between particles are considerably less than the repelling forces of the electrical charge. Under these stable conditions. Another type of primary particles are the *microflocs*, which are chemical flocs. Those are formed from a chemical agent such as alum, ferric ion, lime... Most of the primary particles may settle very slowly because of its small particle size (Hendricks, 2011).

*The flocculant* is a chemical agent added just before the flocculation intending to create microflocs from colloidal particles, contributing to *charge neutralization*, and subsequently developing *interparticle bridging*, aid in floc growth and toughness (shear resistance). Most flocculants are polymers that have ionized charges, also called polyelectrolytes. Cationic polymers are considered to be the most common since they help colloids to attach (Hendricks, 2011).



**Figure 3-4:** Sketch of interparticle bridging with correct dosage and mixing of organic polymers inspired by (Critten *et al.*, 2004)

The mixing intensity must be sufficient and adequate to bring about the adsorption of the polymer onto the colloidal particles and to prevent the polymer to fold back and it will not be possible to perform interparticle polymer bridges. A bridge is formed when two or more particles become adsorbed along the length of the polymer during the flocculation process. Bridget particles become intertwined three-dimensional particles grows until the can be removed easily (Metcalf & Eddy, 2003).

Organic polymers can be dived in into two categories: natural or synthetic. Natural include polymers of biological origin and those derived from starch products such as cellulose derivatives and alginates. Synthetic polyelectrolytes are simple monomers that are polymerized into high-molecular-weight substances. Depending on whether the charge, when placed in water, is negative, positive or natural, those polymers are classifies as anionic, cationic and non-ionic respectively (Metcalf & Eddy, 2003).

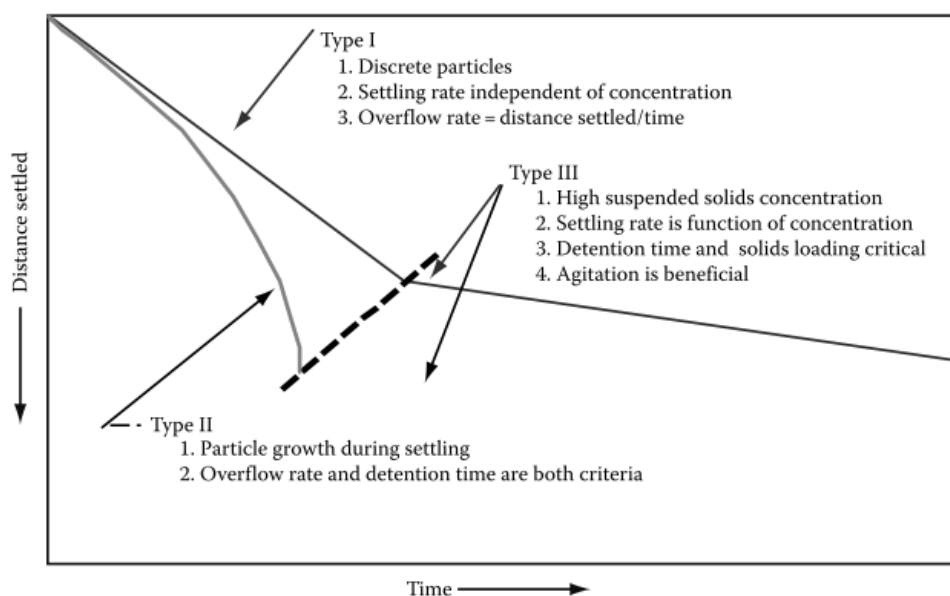
## 3.2. Suspended Solids removal methods

Removal of particles is required because those reduce the clarity of water causing turbidity, preventing the presence of infectious agents that were attached to the particles and also of the toxic compounds adsorbed to their external surfaces. The degree of clarification of water, and therefore for a better suspended solids removal is obtained depending on the previous steps in the treatment train. For instance the quality and the quantity of chemicals used, mixing times, and the care with which the process is monitored and controlled. The removal method will be chosen according to the nature of the suspension that need to be removed. There are many methods to remove particulate matter such as: Straining, gravity separation, flotation, filtration, reverse osmosis...(Metcalf & Eddy, 2003). The most common method to remove flocs formed in flocculation processes is by sedimentation, flotation or filtration. This study is going to focus in the first two.

### 3.2.1. Sedimentation

*Sedimentation* or *gravity settling* unit consists in removing flocs or settleable particles from a suspension by gravity. Sedimentation normally occurs in a basin. For the sedimentation basins is basic to have notions of the *suspension characteristics* and *basin hydraulics*.

Regarding the *characterisation of suspension*, there are four types of settling behaviour in suspensions: Type I) Discrete: The fall velocity of the particles is constant (straight line in the fig. ), particles follow settle in accordance with Stoke's law. Type II) Flocculent: The particles grow in size and, thus, their fall velocity increase. As the particles that approach the bottom of the basin, their concentrations, for both types I and II suspensions, increase so much that the particles start to interfere with each other promoting a new type of suspension which is Type III) Hindered. The last type is IV) Compression: The solids are supported by particles below and consolidation is being formed. Hindered is the type that is the most predominant in the settling units (Hendricks, 2011). The following figure provides and overview of settling characteristics and design guidelines for various settling situations.



**Figure 3-5:** Settling velocities of three types of suspensions (Hendricks, 2011).

Separation of flocculant settleable solids by gravity it is type II: Flocculent suspensions such as metal hydroxides. Normally it consists in particles greater than 0.5mm generally and there is particle growth during settling. Such particles, as they collide with others, agglomerate, and fall at higher velocity. In according to Stoke's law, velocity increases as the square of the diameter). As explained before, but focusing on flocculation in sedimentation, there some principal mechanisms: 1) Differences in the settling velocities of particles and coalesce between them. 2) Velocity gradients within the liquid that cause particles in a region of a higher velocity to overtake those in paths moving slower. Also, 3) flocculation tends to have a sweeping effect in which large particles settling at a velocity faster than smaller particles tend to sweep some of the smaller particles from suspension. 4) in the settling zone occurs hindered settling, meaning that the settling velocities of particles are affected by the presence of other particles due to the movement of the fluid displaced by other neighbouring particles that are in motion. This only happen when there is high concentration of flocs around (Metcalf & Eddy, 2003).

Regarding *the hydraulics of settling basin*, settling in real basins is affected by flow patters that deviate from the ideal basin. Real flow is characterised by *short circuiting* and *dead zones*. Short circuiting means that a portion of the flow entering the basin reaches the basin exit much quicker than the detention time. At the same time, the dead zones result in a portion of the flow leaving the basin much later than the supposed detention time. The design of the inlet and outlet are important to determine the flow patterns. It is important to avoid shortcutting and dead zones. Density currents will also affect the hydraulics.

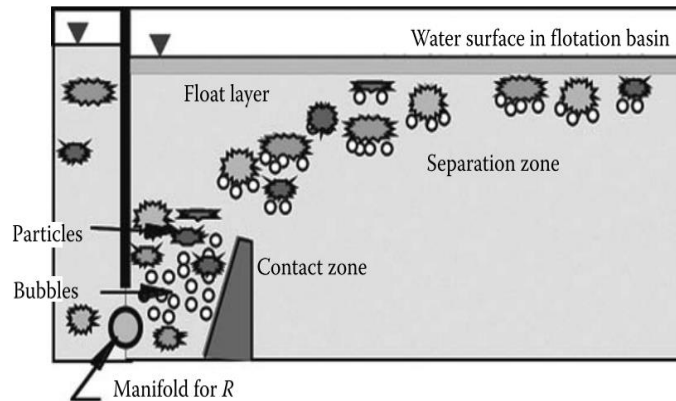
With chemical precipitation, it is possible to remove 80 to 90% of the Total Suspended Solids (TSS) including some colloidal particles, 50 to 80 % of the BOD and 80 to 90% of the bacteria (Metcalf & Eddy, 2003).

### **3.2.2. Dissolved Air Flotation (DAF)**

Flotation is a unit operation in which solids are made to float to the surface on account of their adhering to small air bubbles that rises to the surface and subsequently separate out from the water. (Sincero and Sincero, 2003). Flotation is also considered as a sludge thickening process.

Is a technique to remove fine particles and flocculent particles or flocs with specific gravity less than water or very low settling velocities. So, the wastewater is normally coagulated and flocculated prior to entering the DAF basin. After flocculation, the water with flocs will go to the flotation basin. Meanwhile the saturator is generating water that has dissolved oxygen from air put under pressure (3-8 kPa) (Hendricks, 2011). The water with generated fine bubbles (typically between 40 to 70  $\mu\text{m}$  of diameter) is introduced from the bottom of the basin that contains the water to be treated. As the bubbles move upward through the water, they go to the contact zone of the flotation basin. Bubbles become attached to particulate matter and floc particles, and the buoyant force of the combined particle and air bubbles causes the aggregated particles to rise to the surface. Thus, particles that are heavier than the liquid can be made to float (Fig. 3.6).





**Figure 3-6:** Illustration of flotation basin showing contact zone and separation once (Critten *et al.*, 2004)

The float layer collects at the effluent end of the basin and is removed into a float collection trough. Float removal is accomplished either with a mechanical skimming device or hydraulically by solids overflow into the collection trough. The hydraulic removal of float is achieved by temporarily prohibiting water from leaving the basin, which causes the water level in the basin to rise and float to overflow into the float collection trough. The clarified water leaves at the bottom of the separation zone. The solids and the water may be further processed. The solids will undergo a process of thickening and the water might go under filtering (Critten *et al.*, 2004).

### 3.3. Sludge handling and processing methods

There are several **types of sludge** with specific characteristics, those depend on the pollution extracted and the course of the water treatments performed. The type of sludge will be influenced by the choice of conditioning chemical to use previously and the choice of thickening and/or dewatering methods and equipment.

The physio-chemical sludge is the result of a physical and chemical treatment. Usually it is composed of flocs produced by the chemical treatment. The characteristics of this sludge is the direct result of the chemicals used and of course the pollutants in the water.

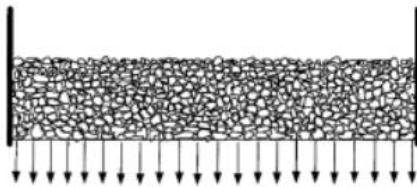
The parameters that influence the dewatering abilities of sludge are: The concentration of the sludge (g/L) and the organic matter content (%), which is comparable to the Volatile Solids content (VS). The higher the VS the more difficult is dewatering. The dryness achieved will be low, the mechanical properties will be low. In that case is recommended to add a thickening step in order to achieve a better dewatering. The higher is the colloidal nature, the more difficult it is to dewater, that is why is better to add a chemical such a coagulant or a flocculant previously. Those help in improving the conditioning of the sludge before proceeding to the next steps of thickening and dewatering.

**Sludge conditioning** is normally performed by *Dewatering aids* or *conditioning chemicals* that help in enhancing the sludge treatability and readability before thickening and dewatering. The most common chemical are minerals such as iron salts and lime and organic chemicals such as coagulants and flocculants. This is further explained in the previous sections (). There are two test methods to evaluate the sludge conditioning and dewatering performance according to

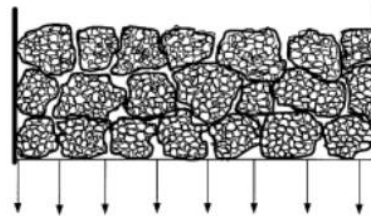
mixing speed and time, dose and type. Capillary suction time (CST) and specific resistance in filtration (SRF) are two popular parameters in evaluating sludge dewaterability. Specific resistance to filtration (SRF) test developed by Coakley and Jones (1956) it remains difficult and expensive. Capillary Suction time (CST) is widely used, is simple and inexpensive. Nevertheless both CST and SRF are empirical and lacking in accuracy (Wei *et al.*, 2018).

The characteristics of the sludge cake in sedimentation is shown in fig. The sludge cake formation will effect the sludge dewatering. In one hand, we can have an unaggregated particle bed as we see in figure A., which normally forms a dense compact bed with smaller pore spaces through which drainage of liquid is slow. On the other hand, the aggregated particle bed Fig. B. forms a more open bed with larger pore spaces through which liquid can drain faster (Gray, 2015).

**A) Unaggregated particle bed**



**B) Aggregated particle bed**



**Figure 3-7:** Schematic illustration of the nature of sediment bed formed by a A) Dispersed suspension and a B) Aggregates suspension. Adaptation of (Gray, 2015)

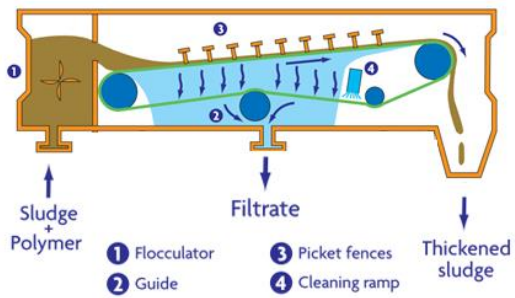
**Dynamic thickening** of the sludge it is normally done before dewatering in order to increase the dry solid content and facilitate the dewatering step. It is a way to lower the volume and therefore the number of truckloads. There are four types to thicken sludge dynamically: Flotation, gravity belt and drum filter.

- **Flotation**, as mentioned previously, it consists in applying pressurised to create micro-bubbles and so those get attach to the particles, these have then a lower density and float to the surface. The thickened sludge is the evacuated in the overflow, and the underflow water can be further treated until it fulfils the requirements.
- **Gravity belt or filtration belt** is a system in where the flocculated sludge flows over a belt with porous that is conveyed at a certain speed. The is drained through the pores of the belt. At the end of the conveyer belt the sludge it is thickened, and the filtrated water is separated. The belt have picket fences which usually enhance the gravity drainage. It needs militainment in cleaning the belt to prevent pore plugging. The thickened sludge is sent to a temporary storage tank before dewatering.
- **Thickening drum or screw drum** has the same principle as the gravity belt. The water is removed because of gravity drainage of the free water through a grid. The difference is that the sludge conveying is done with a screw.

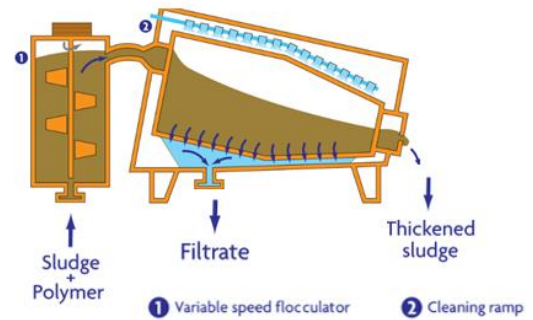
**Sludge dewatering** can be performed by belt filter presses, centrifuge, frame filter press dewatering.

- There are different **Belt filter presses** types, but they all have the same principle and characteristics. The conditioned sludge, with flocs and free water in between the flocs goes to a gravity drainage zone where is drained on a first and lower belt by gravity. The drainage is helped by picket fences that lay freely on the belt. A water line then is created, where all the water freed of the system converges and is eliminated. The sludge continues to a compression zone, where then is pressed between two filter belts. With the arrival of the top belt a progressive pressurization takes place. Once is pressed, the sludge has a compact aspect which is called sludge cake. The case is then scraped off from the surface of the two belts that separate at this level. There is a high pressure washing station that is continuously cleaning the belts.
- The **centrifuge** operating principle it is based in the centrifugal force. The flocculated sludge is injected inside the centrifuge bowl through an injection pipe. The bowl rotates at very high speed (3500 rpm) and the particles are flattened against the bowl's sides in the clarification zone. The sludge particles are then pushed by an Archimedean screw towards the end of the bowl's cone in the sludge spin-dry zone. The clarified liquid is evacuated at the other end of the bowl by overflow.
- **Frame filter press.** The operating principle is filtration and it works in batch cycles. A cycle consist in the conditioning sludge entering in the filtration chambers that have a high pressure pump. The sludge fills each chamber and the water starts to seep out. Once all the chambers are filled, the sludge continues to be pumped in and the pressure then increases up to 15 bars. The filtrate flows into the channels placed in each frame and is evacuated in a main pipe. The sludge injection flow reduces when the pressure increases. Then there is the opening phase, that once the press has stopped, the central core is purged of the liquid sludge inside. The jack that presses the frames together is released. The chambers are opened sequentially, and the cake falls below into a skip or on to a conveyor. Frame filter press dewater sludge at a higher level of dryness than the previous techniques seen above

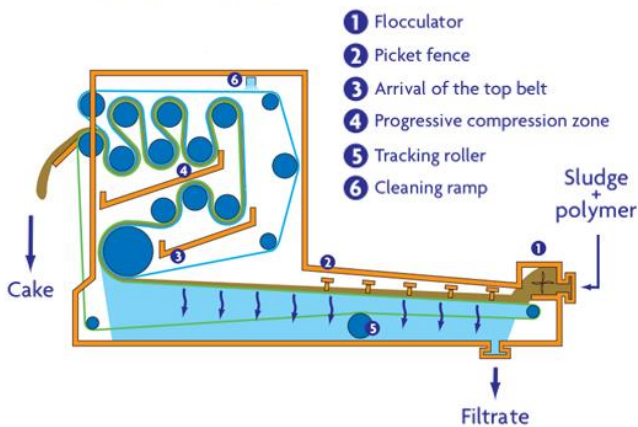
**A) Gravity belt or filter belt**



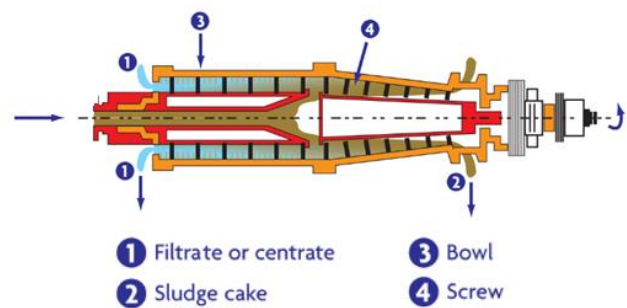
**B) Thickening drum or screw drum**



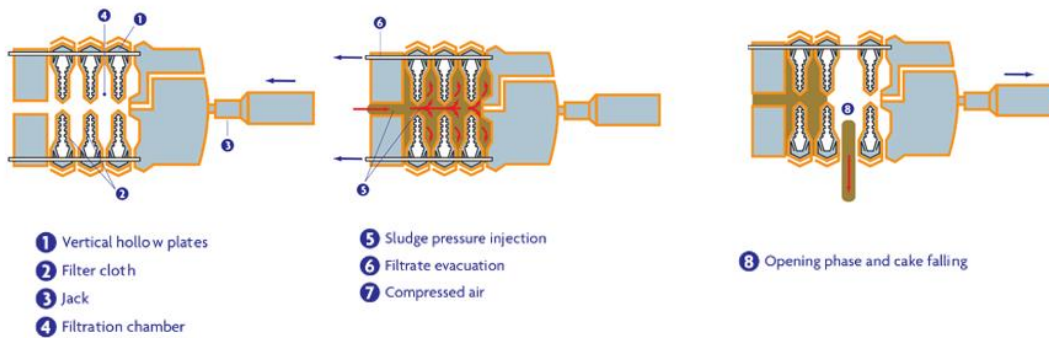
**C) Belt filter press**



**D) Centrifuge**



**E) Frame filter press**



**Figure 3-8:** Representation and parts of different sludge thickening ( A) Gravity belt or filtre belt and B) Thickening drum or screw drum) and Dewatering technologies ( C) Belt filtre press, D) Centrifuge and E) Frame filter press) .

## 4. Materials and Methods

This chapter presents the methodological approach; Explaining why and how the choices of method and design are suited to fulfil the objectives and to answer the hypothesis stated previously in chapter 1. The chapter aims to answer how the supply information and data has been collected and interpreted. In addition, it has been intended to give explanation on the selection of the methods with its strength and weaknesses.

### 4.1. Set up

In the beginning of March, the Municipality gave access to the tunnel, where the water to treat gets collected. The experiments of this project have been carried out there so the temperature and the conditions were adapted to the case study. All the necessary materials and equipment were brought to killingdal and set up as in the following figure 4.1.



Figure 4-1: Setting up of the experiments carried out in the project

### 4.2. Sampling and study material

The raw **water sampling** has been a concern due to change in the flow and apparent change in the chemical properties during the period of measurements of the current project. The variation in the properties of the raw water has been reported in previous studies in Killingdal (Engebretsen, 2017), where specially in Spring, the water table varies a lot influencing in the AMD quality.

Knowing that, the sampling in the **Study I** have been done taking the raw water from the inlet of the pilot plant the following days: 10<sup>th</sup> of March, 4<sup>th</sup> of April and 27<sup>th</sup> of May. Although the inlet of the pilot is pumping the water from the tunnel, it was also interesting to take a sample of the raw water directly from the tunnel to see if there were any differences in the levels of heavy metals. The sample was taken; however, we did not obtain the results from the analytical laboratory and there was no possibility to repeat it.

The samples of raw water for **Study II** have been taken, as well, from the inlet of the pilot. In that case it made more sense since the objective is improving the treatment of the pilot. The trial and the experimental attempts for the study started in March, April was in standby and in May the experimental protocol was finally well set. A big batch of water from the inlet of the pilot was taken. It was taken enough water to proceed several and enough repetition times with all the flocculation-sedimentation and flocculation-flotation experiments. In that way the water in all the experiments of study II had the same properties and it would be possible to see the differences of the effects of the different treatments.

**For both studies** the taken samples were **filtered and not filtered**. The aim is to look to the dissolved metals in water. Those metals in an unacidified sample are the ones that pass through a 0.45 µm membrane filter. Suspended metals in an unacidified sample are retained by a 0.45-µm membrane filter. Total metals are the sum of the concentrations of metals in the dissolved and suspended fractions. So, by comparing filtered and unfiltered it is possible to see respectively the theoretical and the real amount of metals that are in the sample.

Regarding the **chemical agents**, for **Study I** it was used **sodium hydroxide** (0.1M and 1M NaOH) to rise the pH at the different studied pH. Eventually some **chloridric acid** (0.1M and 1M HCl) was used to adjust the pH. Although in the current pilot, managed by the municipality, it is used both lime and NaOH to adjust the pH in the current study it has been selected NaOH alone. NaOH is easier to manage in a laboratory scale and give similar results. However, in further studies it will be interesting to combine both. As for the **Study II**, Sodium hydroxide was used again to adjust the pH at the pH established as optimal and then two different polymers were tried out for the flocculation stage.

The selected **flocculants** were chosen following the recommendation of experts in Trondheim Municipality. Through the read literature, the main criteria for selecting the flocculants was that they should be cationic polyelectrolytes, commercially available to be able to scale into the pilot, and that they were not highly toxic. The used polymers in this study have been a **cationic Epichlorohydrin-diamethylamine copolymer (EPIDMA)** commercially known as Superfloc C-577 supplied by *Kemira Oyj* and a **cationic polyacrylamide (PAM)** named N-SEP438 by *Norwegian Technology*. The companies were contacted to see if they could supply the data sheet of the chemical. For this second polymer it has been difficult to find details about the data since the supplier did not want to provide confidential information, therefore some basic information for the study is lacking. The main information of the polymers is gathered and summarized in Appendix B.

**Flocculants stock solution preparation** had to be done in the case of both polymers since they were given in the solid form and in order to dose them is preferable to have them the liquid state. Polymers are difficult to dissolve, and because of their diversity Polymer suppliers often offer recommendations on dissolving and feeding their polymer.

For the **EPIDMA polymer** it was recommended by the supplier to be diluted in 1:10 (Table 4.1). The municipality had a prepared dilution of 0.5g/L and this was the one that was used to proceed with the dosing in the experiments. In the beginning there was a confusion and it was understood that it was 0.3g/L, this made some of the results of the polymer dosage change, but the curve of the results was still good. For the **PAM polymer** the standard stock solution for polyelectrolytes it is between 0.5 - 1 % (B.A. and Napier-Munn, 2006), however the chosen solution was 0.1% since it was hard to homogenize the polymer into the water. The end stock solution of PAM was then 1g/L.

To calculate the **Flocculant dosage** into the raw water to evaluate the different effects of different dosages was done with the following formula 4.1:

$$C_1 \cdot V_1 = C_2 \cdot V_2 \quad (4.1)$$

Being,

C<sub>1</sub>: Concentration of the stock solution (mg/L)

V<sub>1</sub>: Volume of the dosage to have C<sub>2</sub> (L)

C<sub>2</sub>: Concentration of dosage that we want to add (mg/L)

V<sub>2</sub>: Volume to treat with dosage C<sub>2</sub>. Jars are 2L.

### 4.3. Experimental protocol

In both **Study I and II**, a series of **jar test** have been performed to optimize the chemical treatment, looking at the effect of pH, polymer type on the efficiency of the subsequent separation treatment by sedimentation and flotation. Jar tests is a procedure normally used to study the effect of flocculant addition to water, used to determine required doses and operating conditions for effective flocculation (Critten *et al.*, 2004).

#### 4.3.1. Study I: Solubility of metals in Killingdal's mine water

The objective of the study is to find the Optimal pH, meaning the pH were there are less heavy metals soluble in the water, specially Cu and Zn. We proceeded to **Titration**. It is a common technique where a solution of known concentration is used to determine the concentration of an unknown solution. In this experiment, titration will be used to look at the effect of change of the soluble heavy metals in the water in the different pH.

The **titration protocol** was: 1) prepare 2L Jars with raw water, 2) Take sample of the raw water filtered and not filtered, 3) Measure initial turbidity and pH, 4) Adjust pH with (0.1M or 1M) NaOH and (0.1M or 1M) HCl each jar at different wanted pH: 5, 6, 7, 8, 9, 10, 11, while stirring at 40 rpm 5) Turn the stirrers off and let the particles settle for 30 min. After letting the water settle, the next step was 5) proceeding to the measure the change of turbidity and pH of the water. 6) extract a sample with a syringe with and another without filter from the top of the jar. 7) The samples were sent to the analytical laboratory to see the metal concentration. As mentioned in section 4.2, many samples of the titration were lost in the analytical laboratory, so the results are not fully complete.

The **recorded parameters**: Temperature, Initial, adjusted and final pH and initial and final turbidity, stirring time and velocity, reaction and settling time and Finally, initial and final metal concentration of Al, Fe, S, Ca, Ni, Cd, Pb, Cr, Mo and especially Zn and Cu. Mercury and Arsenic have not been included in this thesis since the previous monitoring of the area showed that the concentrations were lower and acceptable.

#### 4.3.2. Study II: Suspended solids removal and sludge quality

The **treatment by Sedimentation protocol** started by 1) taking a sample of the raw water filtered and non-filtered, 2) Measure initial turbidity and pH, 3) Then the pH was adjusted at the optimal found in the titration while stirring at a gentle speed of 40 rpm. 4) The EPIDMA

polymer dosage (0.8, 1.6, 5, 8.3, 16.6 and 33.2 mg/L) was added while stirring in rapid mixing at 150 rpm during 1 min. Then the stirring speed was decreased at 50 rpm during 15 min. It was further decreased at slow mixing: 20 rpm during 5 min. 5) The stirrers were then turn off and the flocs were let to settle for 30 min in a settling funnel. 6) The funnel measured the volume of the settled sludge. 7) 3 samples of the sludge were taken to measure the dewaterability with a capillary suction time (CST)

The **recorded parameters**: Temperature, Initial, adjusted and final pH after adding polymer, polymer dose, initial and final turbidity, stirring time and velocity, reaction and settling time and Finally, initial and final metal concentration of Zn and Cu. Volume in the funnel and dewaterability of the sludge.

The **Treatment by flotation** or **Dissolved air flotation (DAF) protocol** started by 1) the set-up of the air saturator following the Manual of the Platypus Jar Tester For all the experiments the air was compressed at 5 bars during 120 sec. 2) The jar test starts, following the same protocol as the sedimentation, but using PAM polymer for the different dosages (0.5, 1.5, 3, 5 and 10 mg/L). 3) After performing flocculation in a volume of 2L Jars ( $V_J$ ), 600mL of the treated water were the decanted volume ( $V_D$ ) removed from each jar with the jar manifold and then flotation was started. 4) The saturated water outlet valve was open and normally a volume 1800 mL ( $V_{SW}$ ) was transferred in total to the 4 Jars to perform the flotation. 5) Some samples of sludge were taken to measure the CST.

The **recorded parameters**: The same as in the precipitation in addition to those: Saturator pressure, Volume of treated water ( $V_J$ ), Volume of decanted water ( $V_D$ ), Volume of saturated water transferred ( $V_{SW}$ ) and Recycle rate (Eq. 4.2).

$$\text{Recycle rate (\%)} = \frac{V_{SW}}{V_J - V_D + V_{SW}} \cdot 100 \quad (4.2)$$



A summary of the experiment protocol is represented in the following flow diagram:

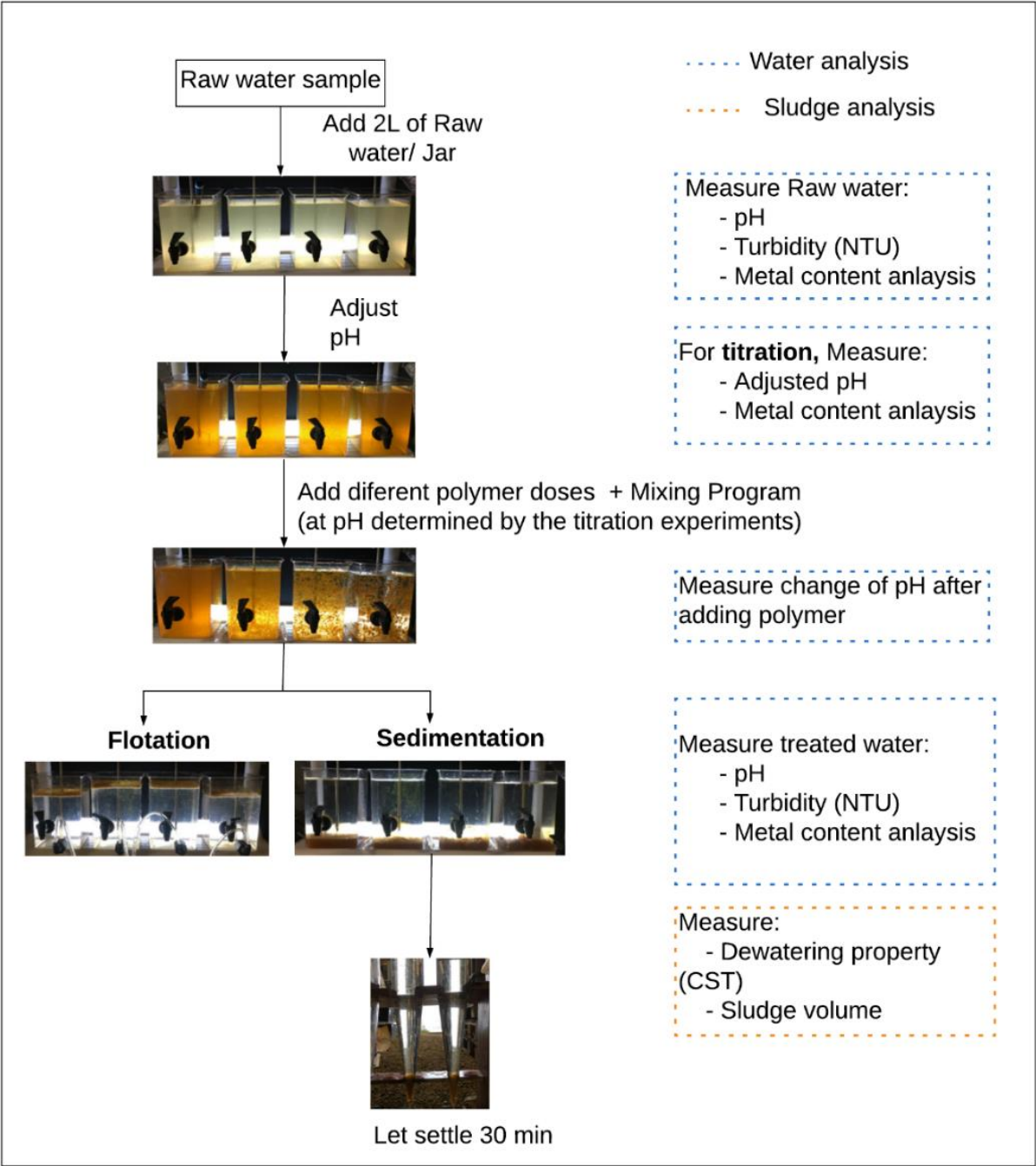


Figure 4-2: Schematic flow of the general protocol and the taken measures.

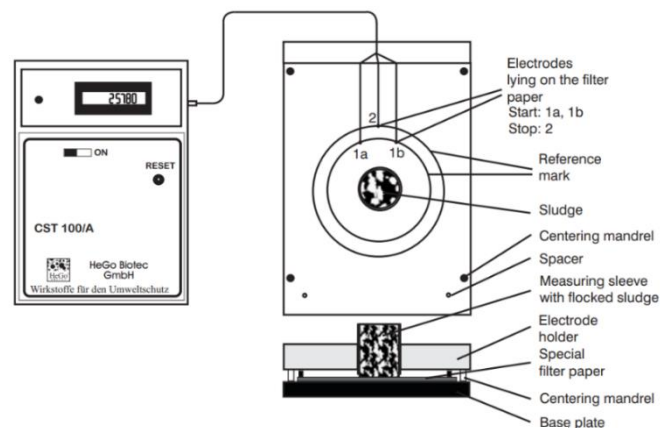
#### 4.4. Analysis Equipment

The **turbidity** which is the reduction in clarity of water caused by the scattering of visible light by particles (Critten *et al.*, 2004), was measured through a **turbidimeter** Turbiquant® 1500.

The **pH** was measured with a pH meter *Hach Sension+*. Provides good measurements with quickly responding electrodes. However, the measurements of the device are set up for +25 °C and our measurements were done at less than +8°C. This could be a problem since the measurements might not be totally accurate.

**Trace metals analysis** was conducted by **Inductively Coupled Plasma Mass Spectrometry (ICP-MS)** by either *ELEMENT 2* from *Thermo Fisher* or *Agilent - 8800 ICP-MS Triple Quad* at NTNU by Syverin Lierhagen. There are many ways to analyse elements in the environment. ICP-MS is a method that has shown itself as a reliable and versatile technique. This method is a combination of the ICP part, being a plasma ion source where the elements in the sample are transformed to ions, combined with a mass spectrometer that detects the ions. Results delivered show the total concentrations of the different preselected elements that are in the sample. Before going to the ICP-MS, the trace metals must be well dissolved. To make sure that the solids are completely dissolved it was added concentrated nitric acid (HNO<sub>3</sub>) to the samples and then put to an UltraClave. Then dilution with pure water and the sample is ready to analyse. The results were reported with the RSD values that represents the uncertainty in the value it corresponds to, and it represents how closely three repeated scan measurements agree to each other.

The **Dewaterability** of the sludge was measured with a **Capillary Suction Time (CST)** supplied by *HeGo Biotec GmbH*. A unit that measures the time (caused by applying sludge). A waterfront needs to travel a distance defined by two data points (1a, b and 2) on a special filter paper. The time is a measure for the ability of the sludge to release water. The higher the CST value, the stronger the water is bound to the solid particles contained in the sludge. A slurry with a high CST value can only be dewatered successfully after pre-treatment for example using a polyelectrolyte. Organic flocculants have a very broad market as conditioning agents of the sludge, for that reason there is need to determine the effectiveness of polymer flocculants and find the ideal polymer from the offered variety. CST then helps, in carrying out laboratory tests for the following the sludge dewatering process: Decanter centrifuge, filter press, band filter or vacuum filter. The CST values will determine what dewatering process might be the optimal.



**Figure 4-3:** Schematic representation of CST unit

#### 4.5. Statistical analysis of data

The data that was processed and had several repetitions was shown with the average and the error bar calculated with the following equation (Eq.4.3). The data was represented through *Excel* and *Matlab*.

$$Error = \frac{SD(n)}{\sqrt{n}} \quad (4.3)$$

Being,

SD: Standard deviation

n: Number of samples

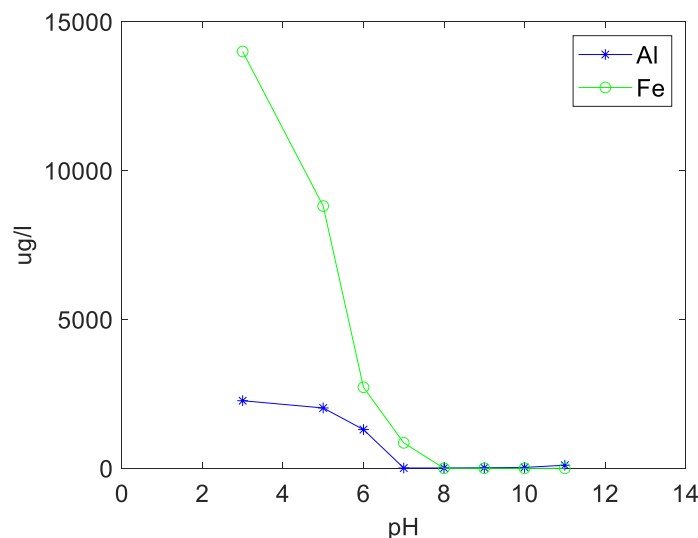
## 5. Results and discussion

The data of the findings of both study I and II will be presented, explained and evaluated. Most of the findings will be represented based in quantitative research, using figures to give an overview and better insight into what has been done. In addition, the chapter will contain some empirically based analysis with pictures and observations done during the experiment protocol that will reinforce the quantitative ones.

### 5.1. Study I: Solubility of metals in Killingdal's mine water

The samples, taken from the inlet of the pilot, were scanned for 8 elements: Iron, Aluminium, Chromium, Nickel, Cadmium, Lead, Zinc, Copper. All results are reported with three significant digits, and all the raw data from ICP-MS is presented in appendix B. Figure results in this section are separated in groups of different order of magnitude to depict better the variation in concentration along the different pH.

The analysis of iron and aluminium content was selected to be scanned based on the considerable amounts that showed previous results. In addition, Fe can cause potential clogging to the treatment plant and therefore it is important to know the levels that we are treating. As it can be seen in Fig. 5.1 in the raw water, the initial concentration of Fe and Al is very high, being 14001  $\mu\text{g}$  and 2272  $\mu\text{g}$  respectively. In both metals the concentration of both ions dissolved in the water decreases with the pH increasing. In the case of Al, the optimal pH seems to be between 7 and 10, and for Fe is between 8 and 10. Al and Fe do not show limit neither condition classes for the Norwegian water, for that reason the limits levels are not shown in the figure.



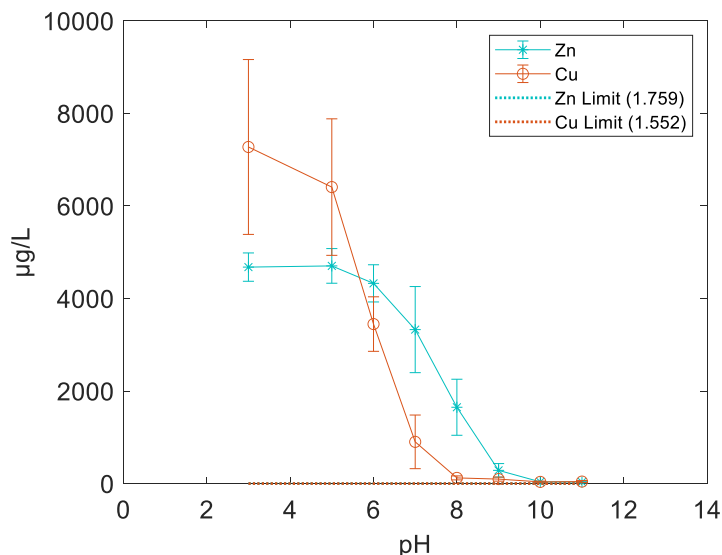
**Figure 5-1:** Represents the residual concentration of Aluminium and Iron dissolve in water at different pH.

Pyrite ( $\text{FeS}_2$ ), Chalcopyrite ( $\text{CuFeS}_2$ ) and Sphalerite ( $\text{ZnS}$ ) are the main ore minerals being S, Fe and Zn, Cu the main elements of the Killingdal facility. It is to expect that those are found in the sediments and in the waters that drain through the site. However, the speciation and solubility of those elements will be affected by some others and the pH conditions as it is seen

in the figure. The fact that Fe has such big concentrations in the acidic water is due to previous formation of AMD in the site. The oxidation of the sulphide mineral turns into iron, sulphate ( $\text{SO}_4$ ) $_2^-$  and protons that create the acidic environment that dissolve other metals ions like aluminium (Akcil and Koldas, 2006). Other metals will be influenced by this phenomenon as it will be seen in the rest of the figures.

Regarding the iron and aluminium behaviour it has been found in the literature that when the pH in the solutions is low, the metal-sulphate ionic complexes are the dominant dissolved forms.  $\text{Fe}^{2+}$  / $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  are present such as  $\text{FeSO}_4^+$ ,  $\text{Fe}(\text{SO}_4)_2^-$ ,  $\text{AlSO}_4^+$ , and  $\text{Al}(\text{SO}_4)_2^+$ . The pH increases and sulphates start to be less abundant and are progressively replaced by the hydroxide forms (e.g.,  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}_3(\text{OH})_4^{5+}$ ), which become the most common at neutral conditions (Sánchez España et al., 2006). These hydroxide forms precipitate in solid forms and that is why the ions do not show as dissolved in the alkaline water. As seen in section 3.1.1, the oxo and hydroxy complexes start to be more dominant after pH 5. Since the AMD contains many other minerals and compositions, the precipitation of new minerals from AMD also called secondary minerals, those may also precipitate. Schwertmannite ( $(\text{Fe}_8\text{O}_8(\text{SO}_4)(\text{OH})_6)$ ) or the Basaluminate ( $\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 12 - 36\text{H}_2\text{O}$ ) are examples (Hedrich and Johnson, 2014). Those are known to attract other metals like Cr, Zn, Cu, among others, from aqueous environments (Letcher, 2007).

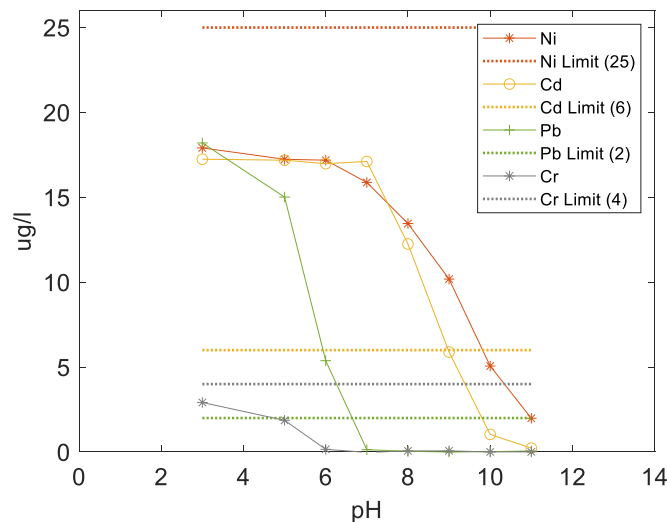
After the initial concentrations of Fe and Al, the next elements to have high concentrations of ions dissolved in the water are Zinc and Copper. Both have initial concentrations in the raw water classified as class V. As it is seen in Fig. 5.2 none of the elements achieve the concentration limits for the Trondheim fjord at any pH. Being the limit concentration 1.759  $\mu\text{g}$  for Zn and 1.552  $\mu\text{g}$  for Cu, the lowest values are 34.49  $\mu\text{g}$  for Zn at pH 11 (class IV) and 37.61  $\mu\text{g}$  for Cu at pH 10(class V), therefore not acceptable.



**Figure 5-2:** Represents the residual concentration and its limit levels of concentration in the Trondheimsfjord of Zinc and Copper dissolved in water at different pH.

Despite not finding the limits neither a good class condition for Zn and Cu, the increase in the pH decreases drastically concentration of ions of Zn and Cu in the water. It seems in Fig. 5.2 that above pH 9 the concentrations of both metals seem to stabilize at minimal concentrations.

In the case of the concentration of lead ions in the initial raw water it appears to be in class IV. Cadmium, Chromium and Nickel fall in Class III. Ni and Cr are actually all the time within limits required to achieve in the Trondheimfjord. After pursuing the neutralization, all elements meet the required limits. Pb and Cr both precipitate at lower pH and are able to reach class I (at pH 9-11), whereas Cd and Ni need higher pH to precipitate and they only reach Class II (pH 10-11), not going further into class I (Fig. 5.3)



**Figure 5-3:** Represents the residual concentration and its limit levels of concentration in the *Trondheimfjord* of Nickel, Cadmium, Lead and Chromium dissolved in water at different pH.

As it suggested the literature in **multimetal solution**, other than the precipitation of hydroxides, the removal of Zn and Cu can be also attributed to the effect of co-precipitation or adsorption onto amorphous Fe and Al hydroxides, since those precipitate at a more acidic pH. Multimetal solution, as it is the case investigated, the precipitation order of metals, discovered by (Hedrich and Johnson, 2014), is Fe-Al-Cu-Zn or Ni. Having previously explained the precipitation mechanisms of Fe and Al, copper probably forms brochantite ( $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ ) in the pH range from 5.0 to 6.6 and transforms to tenorite ( $\text{CuO}$ ) above a pH of 6.6. Precipitation of nickel normally starts at pH 7 and it hardly never reaches the complete precipitation. Nickel precipitates most likely first as  $\text{NiCO}_3$  because only at pH 10 starts to precipitate as  $\text{Ni}(\text{OH})_2$ . Zinc probably precipitates as hydrozincite  $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ . (Petronijević *et al.*, 2020). Cadmium seems to precipitate at the same range as Ni. It seems to be that until pH 8.5 there is  $\text{Cd}^{2+}$  and, then after small progression to  $\text{CdOH}^+$  between pH 8-10, in then starts to precipitate as  $\text{Cd}(\text{OH})_2$  from pH 8.5 until 13 (Matis, Zouboulis and Lazaridis, 1998). At pH values between 6 and 7, the precipitation of Lead in the form of carbonate mineral cerussite ( $\text{PbCO}_3$ ) since  $\text{Pb}(\text{OH})_2$  precipitates at higher pH values between 9 and 10; as a result, 98% of lead precipitated at a pH value of approximately 4.8 (Petronijević *et al.*, 2020). Chromium is mostly present in particular form as  $\text{Cr}_3\text{OH}$  and adsorbed to particles. Cr(VI) occurs in dissolved form as  $\text{CrO}_4^{2-}$  (Stumm and J.Morgan, 2013).

For these set of experiments, it is concluded that **the adequate optimal pH is between 9 and 10** in order to find a small enough concentration of scanned metals dissolved in the water. This pH is adequate considering that the more neutralizing agent the more expensive is the treatment.

The results represented in the figures of Study I match the searched literature that is mentioned in section 3.1.1. It is also possible that many secondary minerals are being formed due to the addition of chemical agents and the change of pH. These secondary minerals might precipitate and help to drag down others. The precipitation of these metals lead to the formation of microflocs that settle, but very slowly. Most of those have neutral charge, but in the water there are still some colloids which normally have negative charges. The addition of a cationic polymer will help bridge the microflocs, attract the suspended colloids and settle faster in order to promote the SSR.

## 5.2. Study II: Suspended solids removal (SSR) and sludge quality

The pH selected to be the optimal for the precipitation of the metals is 9.5. The next step is to explore the flocculation and how this one is affected by the polymer type and the dosage. Many other factors can contribute such as the mixing speed and time and temperatures, but those are not going to be investigated in this study. The flocculation efficiency will be at first determined by the clarity of the water and the amount of heavy metals present in the solvent. The flocculation efficiency will be determinant to explore how the effluent behaved in two techniques of SSR: Sedimentation and Flotation. Afterwards it will be investigated how the polymer type and dosage and SSR have influenced in the sludge conditioning and dewatering.

Regarding the **polymer type** effect on flocculation, in the first set of experiments it was explored both polymers EPIDMA and PAM for the flocculation step of both solid removal techniques, however, as the supplier advised (section 4.2), it was rapidly seen that EPIDMA was a good flotation depressant (sedimentation) and that PAM had good surface load for flotation.

During all the set of experiments it was also analysed how the polymer addition would influence the pH of the water. Both polymers showed good stability and not altering much the pH. As it can be seen in table 5.1 both show reliability at least in the range of pH that the experiments were conducted (9.5). Nevertheless, we do not know how those behave at lower or higher pH. It is possible that those are affected since in the some of the firsts trials we could see some variations experimenting with EPIDMA at pH 6 and at pH 10. This should be studied further if it was convenient for other studies.

**Table 5-1:** Adjusted initial pH, pH after 5 min of adding the polymer and pH after 30 min in different dosages for A) EPIDMA and B) PAM in their respective solid separation methods

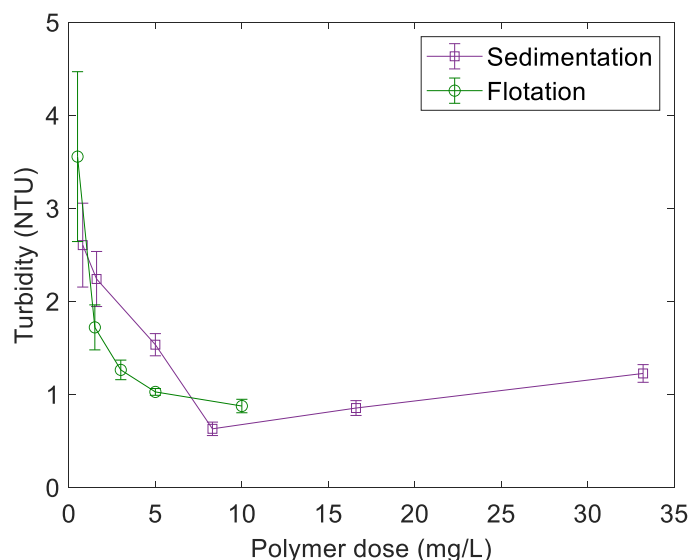
A)	Sedimentation (EPIDMA)	Adjusted pH	After 5'	After 30'
	pH	9.691	9.668	9.600
	Error	0.046	0.045	0.051
B)	Flotation (PAM)	Adjusted pH	After 5'	After 30'
	pH	9.678	9.660	9.251
	Error	0.020	0.020	0.041

In order to see the efficiency of the flocculation at **different polymer dosages** and the consequent removal of suspended solids in the results of the treated water. This one was analysed in terms of turbidity and also metal ions concentration dissolved in the water.

**Table 5-2:** Initial conditions of the raw water in the set of experiments of Study II

Variables	Data
Day of batch	27.05.2020
initial pH	3.65
Adjusted Ph	9.5
initial turbidity	98 NTU
Temperature	6.7-7.1 °c

Both cationic polymers have a huge effect in decreasing **the turbidity** from the water even at low dosages. It goes from 98 NTU of initial turbidity to an average of 3.4 NTU in 0.5 mg/L of EPIDMA in sedimentation and 5.5 NTU in 0.5 mg/L of PAM in flotation. Flotation shows better and faster results in the removal efficiency of suspended solids. Turbidity goes closer to 1 NTU at dosages lower than 5 mg/L. 10 mg/L of PAM, the last tried dosage gives 0.96 NTU. In the case of the sedimentation, reaching the lower turbidity level requires more polymer dosage, even though the lowest turbidity (0.55 NTU) required less polymer dosage (5 mg/L) than in flotation (10 mg/L of EPIDMA). In PAM-flotation the change in turbidity resembles the behaviour of a power function. The equation of the power curve was calculated with Excel and it is  $y=2.3025x^{-0.473}$  and it appears to have an  $R^2=0.963$ . It is possible then to say that there is clearly a relation with both parameters. EPIDMA shows a curve with an increase of turbidity when we add excessive polymer dose.



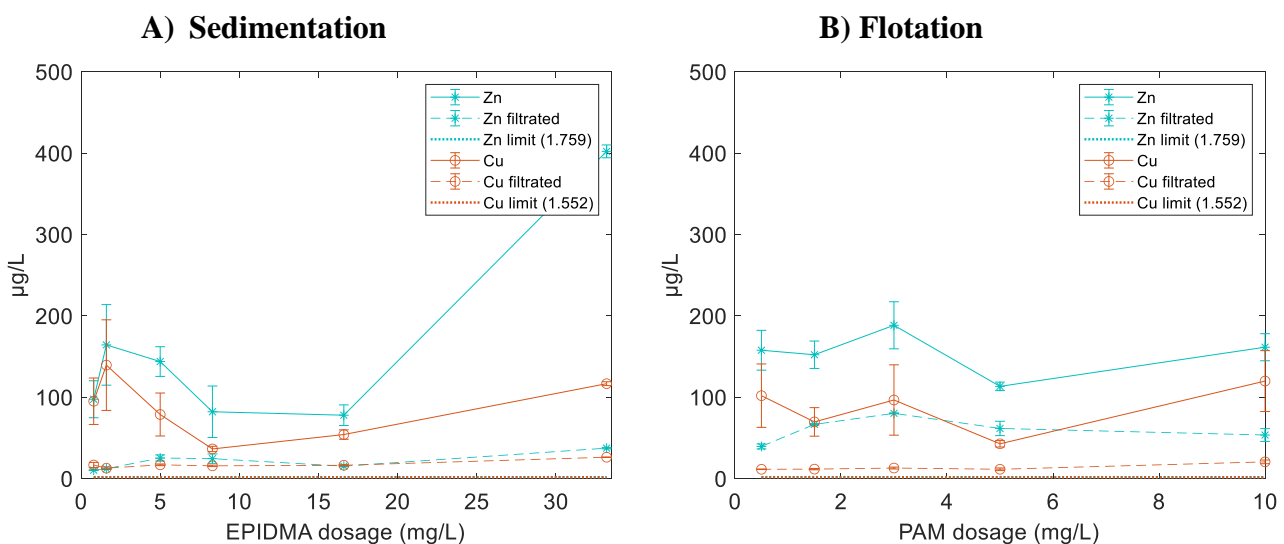
**Figure 5-4:** Comparison curve of turbidity (NTU) versus polymer dosage curve (mg/L) for Sedimentation (EPIDMA) and flotation (PAM).

As it is shown in section 4, material and methods, the optimal working pH suggested by the supplier is between 4 and 7 for EPIDMA and between 3 and 11 for PAM. The working pH is 9.5 which is out of the range of the optimal range conditions for EPIDMA. Also, this increase of turbidity when adding more than 10 mg/L of EPIDMA can be related to the concept of



overdosing, which it has been studied in (Roland Christensen *et al.*, 1993) and it only happens when adding organic polymers as flocculants. **Overdosing** happens when dosages exceed the optimal dosage and it performs returning to the initial values. Saturation of the colloidal surface with polymer is usually accompanied by a reversal of the surface charge. Overdosing normally has been reported to occur at enormous values of dosage (Roland Christensen *et al.*, 1993), which it does not seem to be the case here. The optimal polymer dosage is commonly associated with partial coverage of the colloidal surface accompanied by minimum surface charge. It seems in the case of turbidity that the **optimal dosage for PAM and EPDIMA is between 5 and 10 mg/L**.

Regarding the effect of the polymer and the SSR in the **dissolved metals removal**, Zn and Cu are less present dissolved in the water at lower concentrations of polymer in both sedimentation and flotation and then they go up after overdosing with polymer (at 33 mg/L in sedimentation and 10 mg/L in flotation). The levels of Cu and Zn (filtrated) are bit under the ones of Study I (pH 9). Those values would be the initial conditions for the water to treat in SSR, but in this figure it is not represented the 0 dose of polymer. Both polyelectrolytes perform neutralization and bridging unless there is too much dose, as it is said before. For sedimentation (Fig.5.5A) the dosage to have the least amount of Zn and Cu and therefore the **optimal dosage is 8 mg/L of EPIDMA**, above it seems to be overdose and below it is not sufficient. In polymer dose of 0.8 mg/L the values of both Zn and Cu look good too. In the case of the flotation (Fig.5.5B), it seems to show a peak of high concentration of those elements when the dosage of PAM is 3 mg/L. The optimal dosage seems to be **5 mg/L of PAM**. At 10 mg/L shows a similar overdosing effect as in fig.5.5A that it does not show in that case in the turbidity in the flotation (fig.5.5B)

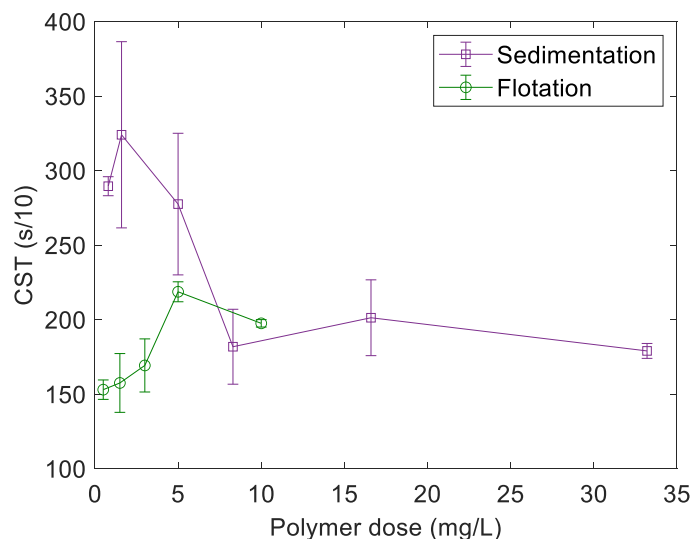


**Figure 5-5:** Comparison curve of residual concentration of Zn and Cu ions in the treated water with different Polymer dosages after A) sedimentation and B) flotation. Comparison with treated water filtrated (45 μm).

After the SSR, the amount of Zn and Cu dissolved in the treated water seems to still not fulfil the limit requirements for the Trondheim fjord (fig.A1). Despite the values seem to approach, even with the filtration of the treated water, which would be the theoretical values, it does not go underneath the limits of requirement to discharge the water. It does prove though that the

water needs final step before being discharged, which could be filtering. Another observation is that based on this (Engebretsen, 2017) study the SS content is directly proportional to the Zn and Cu concentration. This affirmation depicts exactly the correlation of the curve of figure 5.4 and figure 5.5. The amount of SS removed from the water is directly proportional to the turbidity and the removal of dissolved metals Cu and Zn in the water.

To evaluate the **polymer conditioned sludge** the optimal polymer dosage is based on the minimum CST. Both CST in sedimentation and flotation show a curve that is not associated to the typical CST curve versus polymer addition. According to literature, the curve should be a parabola with a positive curvature. As it can be seen in Fig. 5.6, in Sedimentation optimal sludge dewaterability determined in the CST test is at 8.3 mg/L of EPIDMA. And for flotation it seems to be 0.5 mg/L of PAM. Overall, flotation shows better results of dewaterability and both polymers seem to encounter good dewaterability values at dosages between 5 and 10 mg/L. There is no literature found for the CST curve of flotation for that reason is not possible to compare.

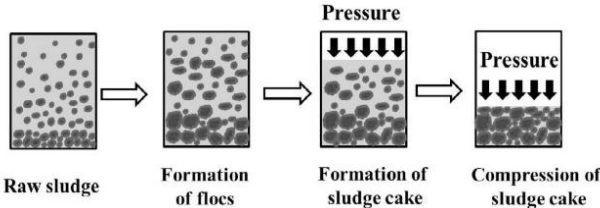


**Figure 5-6:** Comparison curve of dewaterability (CST) versus polymer dosage curve (mg/L) for Sedimentation (EPIDMA) and flotation (PAM).

CST was measured from the sludge in the sedimentation and the flotation. Sludge cake is formed by the aggregation of flocs in raw water, which consists of various colloidal solids, including the Extra Polymeric Substance (EPS) (Polymers with high molecular weight, which is the case). Floc properties, like the size and the compactness, affect the characteristics of the sludge cake and also the dewatering performance. It has been found that a large floc size equates to high removal in sedimentation, but it has been seen that small flocs with high compactness serve as skeleton builders to aid dewatering in the pressure process. Floc compactness might play a greater role in sludge dewatering compared to the floc size.

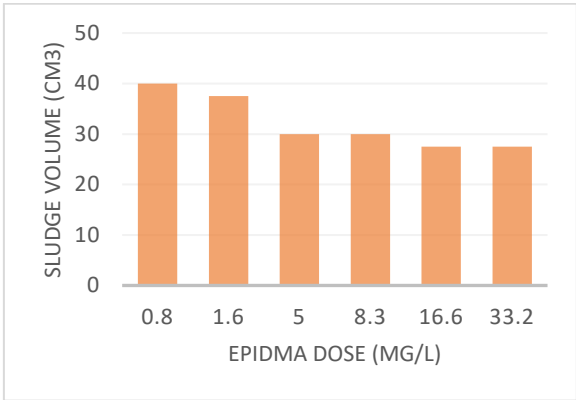
Comparisons show that the floc structure resulting from bridging flocculation is loosest because of the polymer molecules connecting the particles. Thus, large but loose flocs form due to the bridging effect only, and sludge conditioned with PAM alone cannot achieve ideal dewatering

performance (Wei *et al.*, 2018). It is possible that for that reason the dewatering performance of PAM in flotation is not the expected because there is no process of compression of sludge cake (fig.5.7).



**Figure 5-7:** The process of sludge dewatering accompanied with the formation of sludge cake

The **volume of the sludge** of the Sedimentation method was easier to measure due to the laboratory equipment and the amount of sludge generated compared to the one in flotation. As it can be seen in Fig. 5.8 the volume generated through sedimentation process seems to be much at lower dosages, but then it seems to have a stable amount of volume as the polymer dose increase.



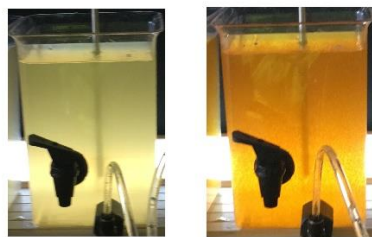
**Figure 5-8:** Bar graph relation between sludge volume and polymer dosages

In the case of flotation it was not possible to measure the volume, the only data that we could extract is that the sludge cake in the jar was on average of 0.5 cm approximately similar in all the different dosages of polymer. According to the dimensions of the top jar this would be 12cmx12cm meaning that the total value, without being compressed as it is in sedimentation, is of 74cm<sup>3</sup>. In the case of sedimentation we see that the more polymer we put it seems to compress better the sludge volume in the funnel.

### 5.3. Qualitative results

Finally, to bring up the qualitative approach of both studies some pictures were taken to have an idea and provide to the reader a better understanding of how the process and the outcome looked like during the precipitation-sedimentation with EPIDMA and the precipitation-flotation with PAM.

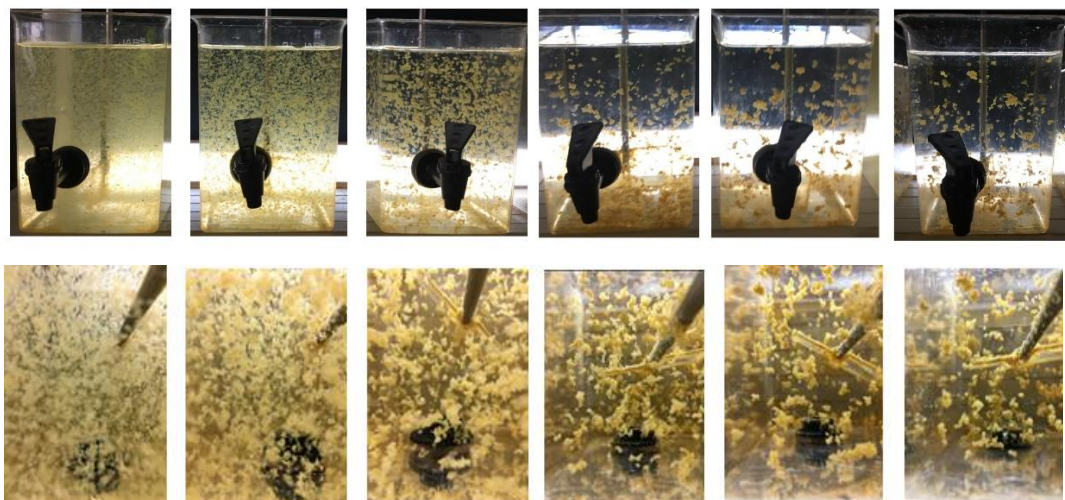
The first step is the **precipitation**, Study I. By adding neutralizing agent the iron oxihydroxides, commonly referred to as ochre, or yellow boy start to appear. Metals and secondary minerals start to precipitate in form of microflocs. The average size of those seem to be around 1mm microflocs and are formed within 10 min. Those precipitate to the bottom of the jar within 30 min. The jar has approximetly a length of 16 cm.



**Figure 5-9:** Raw water (Left), Water after being adjusted to pH 9.5 (Right)

Flocculation is the next step, in where the polymer is added to help settle the particles faster. The settling time is estimated to be less than 5 min until they reach the bottom of the jar. As it can be seen in both Polymers: EPIDMA (Fig. 5.10) and PAM (Fig. 5.11), the more polymer dose we add, the more the flocs are agglomerated and consistent.

In EPIDMA the first two doses (0.8 and 1.6 mg/L) do not seem to have consistent flocs. However, in the following ones the flocs seem well bridged. The results correlate with the quantitative data, nevertheless we do not see any difference in the image with polymer dose of 33.3 mg/L of EPIDMA, that in the quantitative data show overdosing.



**Figure 5-10:** Qualitative result of the flocculation at different polymer dosage (0.8, 1.6, 5, 8.3, 16.6, 33.3 mg/L of EPIDMA). Frontal view (Above), Plan view (Below).



The following figure 5.11 shows the qualitative results of flocculation process of different doses of PAM. We see that the more polymer, the more floc aggregation and compactness. It is difficult to see, but the flocs are smaller and less dense than the ones EPIDMA flocculation.

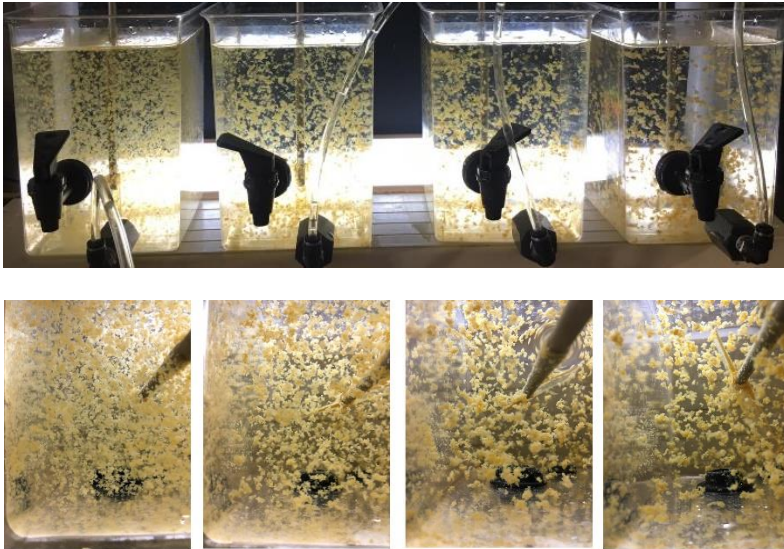


Figure 5-11: Qualitative result of the flocculation for different polymer dosage (0.5, 1, 3, 5 mg/L of PAM) Frontal view (Above), Plan view (Below).

Proper flocculation is, perhaps, the most important factor affecting DAF performance. If destabilized floc particles (low particle charge and fairly hydrophobic) are not produced, then floc particle attachment to air bubbles will be poor. Flotation is more suitable for a small and low-density floc that is able to withstand high shear forces without disintegration and that have (Critten *et al.*, 2004)

In the case of **Sedimentation**, Figure 5.12 it shows the water turbidity and the volume of sludge. We see, as well the filter papers after the CST measurement of the taken samples of sludge of each polymer dose. In here it is possible to see the sludge quality. The more polymer dose the more flocs and the more open bed with larger pore spaces through which the liquid can drain faster (Gray, 2015). The image with more unaggregated sludge cake and more compact flocs (doses 8.3, 16.6, 33.3 mg/L of EPIDMA) match with the CST results in Fig., that the CST is lower and therefore the dewatering is better.

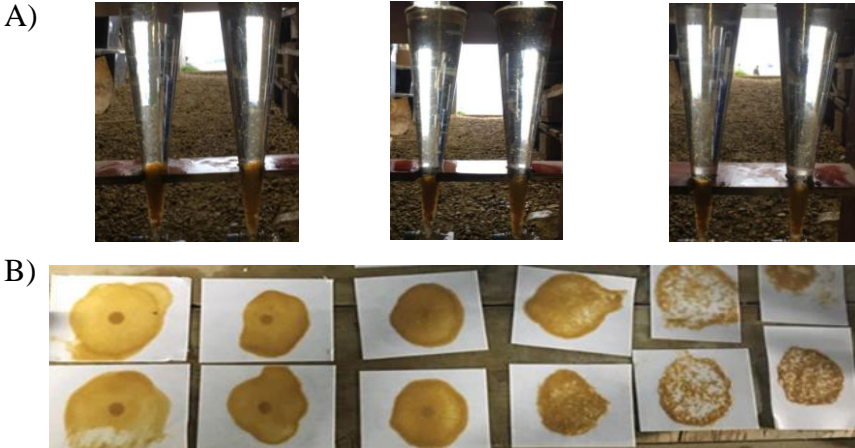
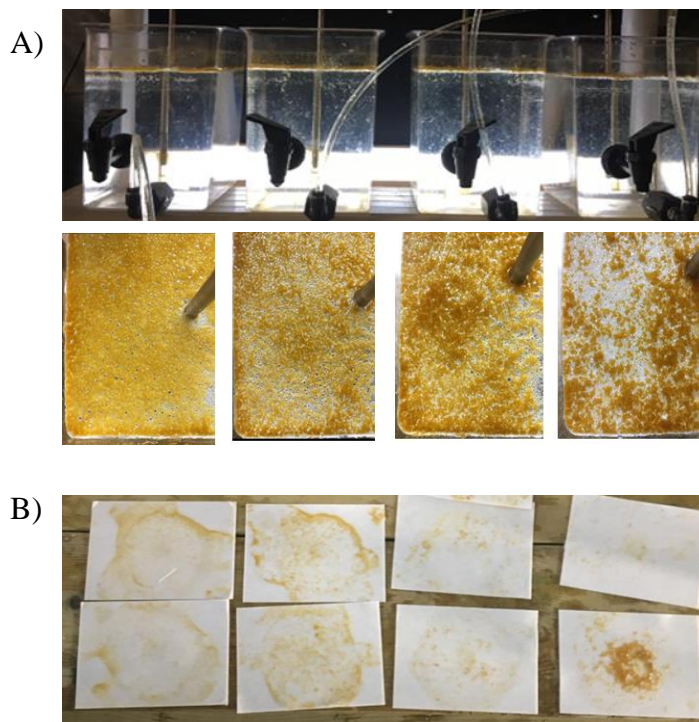


Figure 5-12: Qualitative result of the A) sedimentation and B) dewatering method. For different polymer dosage (0.8, 1.6, 5, 8.3, 16.6, 33.3 mg/L of EPIDMA)

The following figure 5.13 shows the qualitative results of the flotation process of different doses of PAM. We see also in figure A) that the more floc aggregation and compactness drives to better SSR and therefore the turbidity is improved. In addition to floc compactness, floc surface characteristics, including surface charges (hydrophobicity/hydrophilicity) are very important in flotation (Wei *et al.*, 2018). Not only for the floc aggregation and dewatering performance, but it is needed that the flocs have high hydrophobicity to promote flocculation and aggregation to air bubbles to float and form a sludge cake on top (Fig. 5.13 A). The selected PAM, as the supplier advice, shows good surface load for the flotation characteristics it seems to have a very good SSR rate.



**Figure 5-13:** Qualitative result of the A) flotation, Frontal and plant view and B) dewatering method. For different polymer dosage (0.5, 1, 3, 5 mg/L of PAM)

In the case of figure 5.13B. it shows the measurement filter of the CST taken samples. It shows little amount of sludge because as well as the measurement of the volume of the sludge cake on top, the sampling of the foam was not easy. We see that there is much more aggregated particle bed in the small dosages than in the bigger dosages that the flocs are more compact and the particle bed is more unaggregated. However, this qualitative results of figure 5.13 B do not match the ones of the CST, that shows the contrary. This can be perfectly correlated with the sampling of the CST in the flotation sludge, that there was not previous step of compressing cake as in sedimentation, or that CST is not possible to measure in the sludge cake after SSR by flotation.

## 6. Conclusions

There are many technological solutions to treat Acid Mine Drainage and those have been investigated with different approaches and adapted to the site conditions. The efficiency, the cost and especially the dimensions of treatment units are the main constraints to decide what is the best option for the Killingdal area. In this context, the usage of chemical treatment (precipitation), conditioning (flocculation) and the SSR (sedimentation) were identified and selected as a good choice by Trondheim Kommune for the provisional treatment plant. Literature related to the chemical treatment and the SSR units has been researched to investigate how to treat AMD. Based on the case study, the obtained results and the read bibliography, many variables and treatment units take part in this treatment train and in order to be effective and adequate to the needs of the site, some parameters and treatment units can be modified or replaced. The results of this project are merely in a lab scale. The selected method needs to be standardized to then scale it to the pilot.

Regarding the results of Study I, it can be confirmed that from the selected and scanned metals all have very different constants of solubility and precipitate at different pH affecting each other precipitation since it is a multi-metal solution. Hypothesis of Study I can be accepted. The literature corresponds with the empirical results of the samples tested. The pH that should be applied in order to have the smallest concentration of dissolved metals present in the Killingdal water should be above 9. In this case it has been found that between 9 and 10 it is adequate. Applying too much neutralizing agent would imply more expenses, and possibly, poorer sludge quality. After fulfilling the objective of Study I, it was possible to proceed with the Study II which consisted in the flocculation and the SSR.

Study II consisted in the flocculation optimization and the improvement of the sludge conditioning quality depending on the SSR selection (Sedimentation or flotation). In this study it was observed during that the chosen polymer type is definitive for the efficiency of the SSR process. Meaning that the polymer properties need to be adapted to it and this information is normally provided by the supplier. After several trials with PAM and EPIDMA polymers both in sedimentation and flotation it was seen that EPIDMA suited better sedimentation and PAM flotation. Regarding the results from Study II in EPIDMA polymer optimization, 8.3 mg/L is recommended as a good dosage either in flocculation for the SSR (sedimentation) and in the sludge conditioning for better sludge dewatering. Sludge volume at 8.3 mg/L of EPIDMA seems correct compared to the other values. In the case of PAM the optimal dosage seems to be between 5 and 10 mg/L for the flocculation and SSR. Sludge conditioning seems to not follow the pattern that the literature suggests, which should be a concave parabola with a positive curvature when comparing CST in the y axes and polymer dosage in the x axes. For that reason and the impossibility to measure the sludge volume it is not possible to compare with quantitative results. Nevertheless, qualitative results show us a very good sludge quality with low volume.

After obtaining results from Study II, it consisted in the comparison of the SSR units (Sedimentation-Flotation). Hypothesis of Study II was accepted as well. Flotation shows good results in SSR. The turbidity results of flotation showed especially good removal at low polymer

dosages, and similar removal of metals as the ones from the sedimentation unit. Quantitative results of flotation units regarding the sludge quality cannot be compared, since they are not certain, but qualitative results seem to show a more positive outcome in the sludge appearance. In the literature, flotation is contemplated as a thickening method for sludge as far as it was seen in experimental process, flotation sludge was so little, that this did not give enough samples to measure and give representative values. Most likely a better experimental procedure, more time and advice in the measurement would have given better results to provide a good comparison.

The results of this study support the efficiency precipitation and sedimentation, and of flotation as an alternative method for the SSR despite more quantitative results could provide more scientifically evidence. The next step for the future research should be scaling the dosing into the treatment pilot and designing the adequate size of the unit treatment of sedimentation and of flotation. The hydraulics of sedimentation are very important and most of the time require big tanks for a proper solid-liquid separation. This might be a problem that flotation can solve since the tank would be smaller than the one of sedimentation. Sludge handling and thickening is, according to the literature, easier in the flotation, which would be convenient for the Killingdal plant. It would be also interesting to do the same set of experiments by taking the water from the pilot, after the lime tank, and just add the rest of the needed sodium hydroxide to arrive to the studied optimum pH. With it would be possible to see the influence in the sludge quality when adding Lime. This have not been reflected in our results and Lime is a problem in terms of sludge creation.

Even if these treatment trains alternatives work none of them accomplishes the requirements of the Environmental Directorate of Norway. A treatment step should be added to the train to reduce the metals dissolved in the water. More research should be focus into that. Chemical treatment is a conventional technology and a safe option since it has been quite researched. But once the limits are fulfilled it could be interesting to find methods that do not produce metal-rich solid products that require disposal in designated landfill sites and they are more expensive the more toxic the product is. Metals like copper or zinc have commercial value and are by an active biological treatment those would be recovered and recycled. This can have high constructing and operating costs so it can be more complicated as full-scale system, but at least is could remove some amount of metal and maybe it could be complementary as a first stage of the actual chemical treatment, so the final results of metals dissolved in the water fulfill the limits of the Trondheim fjord.



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## Appendix A – Theory

Table A1: Coastal water classification limits in Norway and Trondheimfjord limits.

$\mu\text{g/L}$	Coast water classification					Limits to Trondheim fjord
<b>Cu</b>	0-0.3	0.3-2.6	2.6-5.2	>5.2		<b>1.552</b>
<b>Zn</b>	0-1.5	1.5-3.4	3.4_6	6_60	>60	<b>1.759</b>
<b>Pb</b>	0-0.02	0.02-1.3	1.3_14	14-57	>57	<b>2</b>
<b>Cd</b>	0-0.03	0.03-0.2				<b>6</b>
<b>Cr</b>	0-0.1	0.1-3.4	3.4_36	36-358	>358	<b>4</b>
<b>As</b>	0-0.15	0.15-0.6	0.6-8.5	8.5_85	>85	<b>2</b>
<b>Ni</b>	0-0.5	0.5-8.6	8.6_34	34-67	>67	<b>25</b>

Table A2: Sediments classification limit in Norway

$\text{mg/kg TS}$	Sediments classification				
<b>Cu</b>	0-20	20-84	84-147	>147	
<b>Zn</b>	0-90	90-139	139-750	750-6690	>6690
<b>Pb</b>	0-25	25-150	150-1480	1480-2000	2000-2500
<b>Cd</b>	0-0.2	0.2-2.5	2.5_16	16-157	>157
<b>Cr</b>	0-60	60-660	660-6000	6000-15500	15500-25000
<b>As</b>	0-15	15-18	18-71	71-580	>580
<b>Ni</b>	0-30	30-42	42-271	271-533	>533

## Appendix B – Materials and Methods

Table B1: Characteristics of EPIDMA Polymer

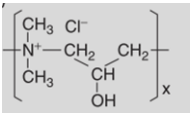
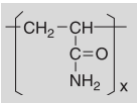
Superfloc C-577	EPIDMA
	Cationic Epichlorohydrin-diamethylamine copolymer 48-52 %. Aqueous solution of Polymeric Quarternary Amine. C5H12ONCl
<b>Commercial form:</b>	Solid
<b>Charge density:</b>	~ 7.3 meq/g
<b>Molecular weight:</b>	Medium-High
<b>Specific gravity:</b>	~1.14-1.18
<b>Density:</b>	1100-1200 kg/m <sup>3</sup>
<b>Viscosity:</b>	550-750 mPas
<b>Optimal working pH</b>	4-7, but does not influence pH of water
<b>Supplier:</b>	Kemira Oyj
<b>Toxicity:</b>	Chronic aquatic toxicity category 3; Harmful to aquatic life with long lasting effects, harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. This substance contains no components considered to be bioaccumulative, toxic, persistent at levels of 0.1% or higher.
<b>Prevention:</b>	Avoid release to the environment. Dispose of contents as special waste in compliance with local and national regulations
<b>Disposal:</b>	Dispose of contents/container as special waste in compliance with local and national regulations
<b>Comments:</b>	Good flotation depressant, gland water clarification, slimes handling. Tailings filtration, paste thickening, wastewater treatment. For maximum efficiency, add dilution water up to achieve a ratio equal to or greater than 10: 1. Disperse the product in the feed stream and promote big turbulences. Residence time must be optimized.

Table B2: Characteristics of PAM Polymer

N-SEP438	PAM
	Cationic polyacrylamide (PAM)
<b>Commercial form:</b>	Solid
<b>Charge density:</b>	~5.2 meq/g
<b>Molecular weight:</b>	-
<b>Specific gravity:</b>	-
<b>Density:</b>	700 kg/m <sup>3</sup>
<b>Viscosity:</b>	-
<b>Optimal working pH:</b>	3-11, but does not influence pH of water
<b>Supplier:</b>	Norwegian technology
<b>Toxicity:</b>	Not readily biodegradable. Not expected to be accumulated in organisms. Acute toxicity on aquatic organisms
<b>Prevention:</b>	Prevent entry to sewers and public water
<b>Disposal:</b>	In accordance with national, state and local regulations
<b>Comments:</b>	Short reaction time (5-10 sec), large and stable flocs, good separation of SS, and high surface load for the flotation characteristics Reduce sludge production results Reduce the plant size (no need for coagulation and flocculation pools) Stable in water >70% (28d)(pH value> 6). In contact with water the substance will hydrolyse rapidly Removal efficiency of SS is 90%

## Appendix C - Results Study I

Table C1: Set of titration experiments at different days (6.03.20, 10.03.20, 3.05.20)

06.03.2020 6.7 °C								
	PH	0.1M NaOH (mL)	1M NaOH (mL)	0.1M HCl (mL)	1M HCl (mL)	pH adjusted	PH end	Sampling
Raw water (1)	3.66							F/NF
Raw water (2)	5.21							F/NF
5(1)		17		0,7		5.01		F
6(1)			2.1			6		F
7(1)						7.05		F
8(1)						8.02		F
9(1)						9		F
10(2)						10.13		F
11(2)						11.03		F

10.03.2020 6.5°C								
	PH	0.1M NaOH (mL)	1M NaOH (mL)	0.1M HCl (mL)	1M HCl (mL)	pH adjusted	PH end	Sampling
Raw water	3.34							F/NF
5	3.33		3.4			5.10	5.22	F
6	3.32		5.1			6.02	5.97	F
7	3.36		6.5			7.18	6.53	F
8	3.34		8			8.01	7.68	F
9	3.32		9	0.6		9.03	8.45	F
10	3.34		9.4			10.01	9.92	F
11	3.34		12.2			11.00	10.35	F

03.04.2020 6.5°C								
	PH	0.1M NaOH (mL)	1M NaOH (mL)	0.1M HCl (mL)	1M HCl (mL)	pH adjusted	PH end	Sampling
Raw water	3.03							F/NF
5	3.06	20				5.00	5.22	F
6	3.11	31.5				6.04	5.96	F
7	3.03	40				7	6.8	F
8	2.98	4.25				8.25	8.6	F
9	3.05	50	3			9.13	8.52	F
10	2.97		6			10.25	10.22	F
11	2.98		7			11.06	11	F

27.05.2020 7.1°C								
	PH	0.1M NaOH (mL)	1M NaOH (mL)	0.1M HCl (mL)	1M HCl (mL)	pH adjusted	PH end	Sampling
Raw water	3.79							F/NF
5	3.96	2.2				5.04	5.29	F
6	3.77	4.6				6.04	5.95	F
7	3.77	5.6				7.06	6.56	F
8	3.77	7.5				8.25	8.2	F
9	3.77	8.2				9.19	8.96	F
10	3.75	8.8				10.08	10.08	F
11	3.77	11.5				11.00	10.98	F

Table C2: Results of concentration ions of Al, S, Ca, Cr, Fe, Ni, Mo, Cd, Pb in the water after the titration experiments of day 27.05.20

pH	Al [ ug/l ]	S [ ug/l ]	Ca [ ug/l ]	Cr [ ug/l ]	Fe [ ug/l ]	Ni [ ug/l ]	Mo [ ug/l ]	Cd. [ ug/l ]	Pb [ ug/l ]
3.00	2 272	123 367	116 937	2.92	14 001	17.91	0.09	17.24	18.20
5.00	2 029	123 167	118 486	1.86	8 810	17.24	0.00	17.19	15.01
6.00	1 303	119 294	113 701	0.16	2 723	17.19	0.01	16.98	5.38
7.00	11.98	123 182	117 447	-0.02	857.25	15.88	0.05	17.11	0.14
8.00	12.44	122 760	118 444	0.07	2.38	13.46	0.05	12.25	0.04
9.00	20.66	122 052	116 070	0.07	3.74	10.18	0.04	5.89	0.00
10.00	32.40	120 134	114 404	0.01	0.78	5.06	0.09	1.04	0.02
11.00	104.55	121 071	113 160	0.01	1.25	1.99	0.10	0.23	0.06

Table C3: Results of concentration ions of Zn in the water after the titration experiments of days 10.03.20, 03.04.20 and 27.05.20.

pH	10. March Zn [ ug/l ]	3. April Zn [ ug/l ]	27. May Zn [ ug/l ]	Average Zn [ ug/l ]	SD Zn
3.00	4544.11	4229.48	5 264	4679.25	306.24
5.00	4355.51	4306.54	5 454	4705.28	374.52
6.00	3839.64	4019.05	5 125	4328.04	402.04
7.00	2479.96	2318.65	5 187	3328.66	930.52
8.00	1300.29	821.48	2 830	1650.48	605.58
9.00	122.25	158.47	579.35	286.69	146.70
10.00	30.95	49.28	35.69	38.64	5.49
11.00	23.00	66.89	13.59	34.49	16.42

Table C4: Results of concentration ions of Cu in the water after the titration experiments of days 10.03.20, 03.04.20 and 27.05.20.

pH	10. March Cu [ ug/l ]	3. April Cu [ ug/l ]	27. May Cu [ ug/l ]	Average Cu [ ug/l ]	SD Cu
3.00	10896.16	6402.26	4527.31	7275.24	1889.63
5.00	9262.45	5628.75	4333.86	6408.36	1475.19
6.00	3929.47	2276.42	4138.79	3448.23	589.01
7.00	313.57	333.38	2061.95	902.96	579.52
8.00	90.03	209.65	71.95	123.88	43.20
9.00	92.98	177.29	23.59	97.96	44.44
10.00	33.23	69.70	9.91	37.61	17.40
11.00	43.17	82.71	7.17	44.35	21.81

## Appendix D - Results Study II

Table D1: Flocculation and sedimentation treatment of raw water from 27.05.20 with EPIDMA polymer. Adjustment of pH at 9.5 with (0.1 and 1M of NaOH and HCl). Results of initial and final turbidity (NTU) of the water. Results of sludge dewaterability (CST) and Volume (cm<sup>3</sup>). Sample uptake which is Filtered (F) and non-filtered (NF).

Polymer dose (mg/L)	Polymer dose (mL)	pHi	NTUi	0.1M NaOH (mL)	1M NaOH (mL)	0.1M HCl (mL)	pH adjusted	NTUf	CST	Vol (cm <sup>3</sup> )	Sample
0	0	3.69	89.22				9.53		155		NF/F
0.8	0.33	3.65	88.3		5		9.58	3.40	293	40	NF/F
								3.33			
								3.74	88.5	4.5	9.52
1.6	0.66	3.67	89.7		5		9.55	2.87	494	35	NF/F
								2.75	341		
								2.81			
		3.69	88.1		3.2		9.66	1.23	239	40	NF/F
								1.54	222		
								1.84			
5	2	3.66	90.2		5		9.55	1.63	230	30	NF/F
								1.45	325		
								2.02			
		3.68	87.5		3,4		9.48	1.33		25	NF/F
								1.24			
8.3	3.33	3.70	92.2		5		9.48	0.41	191	30	NF/F
								0.50	218		
								0.73	209		
		3.68	87		3,6		9.45	0.81	108	25	NF/F
								0.70	183		
								0.86			
16.6	6.66	3.78	91.5		5		9.51	0.80	200	30	NF/F
								1.01	240		
								0.75			
		3.79	87.3		3,6		9.59		140	25	NF/F
									225		
33.2	13.3	3.69	91.5		3,6		9.4	1.32	184	25	NF/F
								1.13	174		

Table D2: Flocculation and flotation treatment of raw water from 27.05.20 with PAM polymer. Adjustment of pH at 9.5 with (0.1 and 1M of NaOH and HCl). Results of initial and final turbidity (NTU) of the water. Results of sludge dewaterability (CST) and Volume (cm<sup>3</sup>). Sample uptake which is Filtered (F) and non-filtered (NF).

Polymer dose (mg/L)	Polymer dose (mL)	pHi	NTUi	0.1M NaOH (mL)	1M NaOH (mL)	0.1M HCl (mL)	pH adjusted	NTUf	CST	Sample
0	0	3.65	98.92				9.54	155		NF/F
0.5	1	3.72	94.1		4	2.5	9.61	6.55	135	NF/F
								5.48	152	
								4.45		
		3.64		1.3	3.5	1.5	9.62	1.87	164	NF/F
								1.22	161	
								1.76		
1.5	3	3.69	92.3	1	3.5		9.52	2.70	183	NF/F
								2.03	191	
								1.75		
		3.65		1.3	3.5	1.5	9.54	1.53	152	NF/F
								1.26	104	
								1.05		
3	6	3.67	92.2	1	3.5		9.49	1.74	207	NF/F
								1.35	143	
								1.09	125	
		3.66		1.3	3.5	1.5	9.46	1.07	202	NF/F
								1.24	208	
								1.09		
5	10	3.66	92	1	3.5		9.63	1.06	208	NF/F
								0.95	217	
								0.89		
		3.65		1.3	3.5	1.5	9.53	1.05	231	NF/F
								1.08		
								1.13		
10	20	3.55	124	13	2		9.49	0.99	200	NF/F
								1.00	195	
								0.98		
		3.56	125	12.5	2		9.49	0.6		NF/F
								0.7		
								0.98		



Table D3: Set of results from Zn and Cu concentration ions in the treated water after flocculation and sedimentation or flotation treatment of raw water from 27.05.20. Results of the Filtered (F) and non-filtered (NF) samples. Average and error calculated.

<b>Sedimentation 1</b>	<b>Filtered (ug/l)</b>						<b>Not Filtered (ug/l)</b>					
<b>Polymer Dose (mg/L)</b>	<b>Cu1</b>	<b>Cu1</b>	<b>Cu2</b>	<b>Cu2</b>	<b>CuA (ug/L)</b>	<b>CuE</b>	<b>Cu1</b>	<b>Cu1</b>	<b>Cu2</b>	<b>Cu3</b>	<b>CuA (ug/L)</b>	<b>CuE</b>
<b>0.5</b>	22.8	21.7	11.1	11.1	16.7	3.22	139.5	149.2	46.3	45.2	95.1	28.54
<b>1</b>	15.8	15.2	10.6	9.6	12.8	1.58	219.2	251.3	43.4	44.0	139.5	55.69
<b>3</b>	18.6	17.5	17.7	13.9	16.9	1.04	119.2	129.5	32.2	34.2	78.8	26.40
<b>5</b>	14.5	18.1	15.8	14.3	15.7	0.87	32.4	29.9	44.4	39.0	36.4	3.28
<b>10</b>	17.9		15.5	15.7	16.4	0.78	47.8	41.2	65.6	61.9	54.1	5.77
<b>20</b>			26.6	26.0	26.3	0.30			119.0	114.3	116.7	2.38

<b>Sedimentation 2</b>	<b>Filtered (ug/l)</b>						<b>Not Filtered (ug/l)</b>					
<b>Polymer Dose (mg/L)</b>	<b>Zn1</b>	<b>Zn1</b>	<b>Zn2</b>	<b>Zn2</b>	<b>ZnA (ug/L)</b>	<b>ZnE</b>	<b>Zn1</b>	<b>Zn1</b>	<b>Zn2</b>	<b>Zn2</b>	<b>ZnA (ug/L)</b>	<b>ZnE</b>
<b>0.5</b>	9.9	9.8	11.0	10.7	10.3	0.30	131.2	142.2	59.6	57.1	97.5	22.74
<b>1</b>	12.6	11.6	12.2	11.9	12.1	0.21	235.6	263.4	77.7	80.6	164.3	49.52
<b>3</b>	19.1	18.6	33.7	29.9	25.3	3.82	169.4	181.0	112.0	113.0	143.9	18.26
<b>5</b>	12.3	17.0	34.5	34.1	24.5	5.75	28.5	26.3	140.3	133.5	82.1	31.65
<b>10</b>	15.6		16.4	13.7	15.3	0.80	60.7	51.7	101.2	98.0	77.9	12.69
<b>20</b>			38.4	36.5	37.4	0.94			410.1	394.3	402.2	7.90

<b>Flotation1</b>	<b>Filtered (ug/l)</b>						<b>Not Filtered (ug/l)</b>					
<b>Polymer Dose (mg/L)</b>	<b>Cu1</b>	<b>Cu1</b>	<b>Cu2</b>	<b>Cu2</b>	<b>CuA (ug/L)</b>	<b>CuE</b>	<b>Cu1</b>	<b>Cu1</b>	<b>Cu2</b>	<b>Cu3</b>	<b>CuA (ug/L)</b>	<b>CuE</b>
<b>0.5</b>	12.4	11.5	11.0	10.9	11.5	0.34	169.0	169.8	33.7	35.3	101.9	38.96
<b>1.5</b>	9.8	10.7	13.5	12.5	11.6	0.83	107.2	92.0	41.2	38.3	69.7	17.55
<b>3</b>	10.7	11.3	14.6	15.3	13.0	1.17	83.3	222.6	39.2	41.3	96.6	43.22
<b>5</b>	8.2	9.1	14.6	14.0	11.5	1.63	54.5	39.4	37.7	39.4	42.8	3.94
<b>10</b>	26.7	18.2	16.3	21.2	20.6	2.27	183.0	185.4	44.3	66.8	119.9	37.43

<b>Flotation2</b>	<b>Filtered (ug/l)</b>						<b>Not Filtered (ug/l)</b>					
<b>Polymer Dose (mg/L)</b>	<b>Zn1</b>	<b>Zn1</b>	<b>Zn2</b>	<b>Zn2</b>	<b>ZnA (ug/L)</b>	<b>ZnE</b>	<b>Zn1</b>	<b>Zn1</b>	<b>Zn2</b>	<b>Zn2</b>	<b>ZnA (ug/L)</b>	<b>ZnE</b>
<b>0.5</b>	35.6	33.1	45.2	44.3	39.5	3.04	243.2	241.6	70.7	75.4	157.8	24.45
<b>1.5</b>	65.1	66.2	69.5	65.7	66.6	0.99	220.9	199.2	96.4	92.4	152.2	16.84
<b>3</b>	79.8	79.6	81.7	79.8	80.2	0.49	205.0	345.8	100.8	102.1	188.4	28.93
<b>5</b>	44.1	48.7	76.6	77.1	61.6	8.83	140.4	118.8	95.4	98.8	113.4	5.19
<b>10</b>	43.6	37.2	63.1	70.3	53.6	7.85	213.8	223.2	93.8	115.2	161.5	16.62