

LUT UNIVERSITY

LUT School of Engineering Science

Master's Degree in Chemical and Process Engineering

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**SOLIDS AND SULFATE IONS REMOVAL  
FROM MINE WATER BY DISSOLVED AIR  
FLOTATION**

Examiners: Professor Antti Häkkinen

M. Sc. Marina Ängeslevä

Instructors: Dr. Eija Saari

M. Sc. Janne Kauppi

## **Abstract**

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Environmental and acceptance risks related to water discharge together with raw water scarcity at mineral processing plants and their surroundings demand the implementation of correct measurements to reduce water consumption. However, recycling mine water by closing water loops in the plant may result in efficiency and selectivity problems in other parts of the process, particularly in froth flotation.

Some of the parameters present in mine waters that can affect the efficiency of the process are colloids, ions, residual reagents, microorganism, pH, redox potential and temperature. In this work, the focus has been set to remove colloidal matter and sulfate ions. Colloids, measured as suspended solids, is one of the main parameters to determine water quality. Moreover, sulfates, mainly produced by the treatment of sulfide ores, can cause environmental discharge problems such as acid mine drainage apart from imperiling flotation.

Therefore, this master's thesis focuses on study of laboratory scale Dissolved Air Flotation (DAF) for water clarification of two different mine waters. In addition, sulfate removal via ettringite precipitation prior to DAF is tested. The results show that DAF can reduce water turbidity to under 10 NTU for all cases. Ettringite precipitation followed by DAF can effectively decrease the content of  $\text{SO}_4^{2-}$ , along with Mg, Ca, V, Mn, As, Sb, and U in the water.

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## List of symbols and abbreviations

### Abbreviations

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AMD	Acid Mine Drainage
DAF	Dissolved Air Flotation
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EC	Electric Conductivity
EDL	Electrical Double Layer
EWT	Electrochemical Water Treatment
ICP	Induced Coupled Plasma
ORP	Oxidation Reduction Potential
PSD	Particle Size Distribution
pzc	Point Zero of Charge
ROM	Run-Of-Mine
SHE	Standard Hydrogen Electrode
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorous
TSF	Tailings Storage Facility

### Equation Symbols

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A/S	Air-to-Solids ratio	[kg air/kg solids]
$A_b$	Bubble radius	[m]
$A_p$	Particle radius	[m]
$A_s$	Chamber surface area	[m <sup>2</sup> ]
$A_t$	Rise rate of solids	[m/s]
C	Concentration of gas dissolved	[mol/m <sup>3</sup> ]
$C_s$	Air solubility at 1 atm and operating temperature	[kg/ m <sup>3</sup> ]
D	Tank depth	[m]
EC	Electric Conductivity at 25 °C	[S/m]

Eh	Redox potential	[V]
f	Fraction of air dissolved	[-]
H	Henry's constant	[mol/(m <sup>3</sup> ·Pa)]
k <sub>e</sub>	Correlation factor between EC and TDS	[(kg·m)/(S·m <sup>3</sup> )]
ORP	Oxidation Reduction Potential	[V]
Pa	Absolute saturation pressure	[Pa]
P <sub>gas</sub>	Gas partial pressure	[Pa]
Q	Feed flow rate	[m <sup>3</sup> /s]
R	Recycle flow rate	[m <sup>3</sup> /s]
T	Turbidity	[NTU]
TDS	Total Dissolved Solids	[kg/m <sup>3</sup> ]
TS	Total Solids	[kg/m <sup>3</sup> ]
TSS	Total Suspended Solids	[kg/m <sup>3</sup> ]
x <sub>c</sub>	Bubble-particle critical distance	[m]
X <sub>f</sub>	Feed solids concentration	[kg/m <sup>3</sup> ]
α <sub>bp</sub>	Collision efficiency factor	[-]
η <sub>T</sub>	Efficiency based on turbidity	[%]

### Subscripts

---

e	Effluent
f	Feed

## **Introduction**

At the end of 2017, the government of the South African city of Cape Town declared that Day Zero, the day when water would stop running from the taps, would take place in March of 2018. Fortunately, after the significant efforts of residents and farmers in the city, Day Zero has been indefinitely postponed (York, 2018; Browdie, 2019). However, water scarcity is still an issue, not only in Cape Town but also in other cities, such as Sao Paulo, Bangalore, Beijing, Cairo, Jakarta and many others. (BBC, 2018). The United Nations claimed that 1.8 billion people would not have any access to fresh water and two thirds of the world population would suffer from water stress by 2025 (United Nations, 2019). Therefore, the challenge is to find solutions for the correct administration and preservation of water resources.

Minerals processing is one of the industries demanding the implementation or improvement of water management. Water discharge in minerals processing operations entails environmental and acceptance risks. Moreover, many mines are located in areas with little or no water availability. To tackle these problems, water consumption and discharge in mineral processing plants can be drastically reduced by a correct administration of tailings disposal and subsequent closing of water loops (ITERAMS, 2017; Hagnäs and Suvio, 2018).

Tailings are waste products generated in the concentration of ores, typically discharged in dams, where the greatest losses in water take place due to seepage and evaporation. The water recovered from clarification at the tailings impoundment is called long or external recycle (Slatter *et al.*, 2009). This recycle is associated with high footprint and environmental risks, such as failures in the tailings dam (Benito *et al.*, 2007). Dewatering tailings before their disposal enables the recycling of water in earlier stages in a circuit. Hence, shorter water recycle loops are possible, which can generate raw water savings up to 90 – 95% (Gunson *et al.*, 2012). Recovering the water from thickeners overflow or other clarification operations before the tailings pond is an option to save costs, to improve water quality, to minimize contaminants discharge and to reduce tailings footprint (Palmer, 2018). Water in short or internal water recycle loops spend less time in the circuit. Thus, valuable reagents do not have enough time to decompose, so they can be reused in froth flotation (Slatter *et al.*, 2009).

Nevertheless, the implementation of closed water loops faces some obstacles that need to be handled. Water recycle results in accumulation of impurities and suspended matter that can

compromise froth flotation efficiency and selectivity (Rao and Finch, 1989). In addition, complete closed loops are more sensitive to fluctuations in water quality and quantity that can appear as a result of seasonal variations (Muzinda and Schreithofer, 2018). Therefore, adequate water treatment is needed before water reuse in other parts of the mineral process to compensate for these deficiencies. It is not essential that water recirculated back to the process is thoroughly purified; only the minimum requirements for successful froth flotation need to be fulfilled.

Countless water treatment methods can be used for water clarification. In particular, Dissolved Air Flotation (DAF) is a widespread technique used in wastewater and water treatment plants, which is currently gaining attention for its application in recycling and effluent treatment of waters in mineral processing plants (Haarhoff and Edzwald, 2012). DAF generates microbubbles that can successfully remove colloids, fine and ultrafine particles, microorganisms, metal ions, or even oils and greases from water (Rodrigues and Rubio, 2007). It is a competitive alternative to conventional water treatment techniques, such as filtration, sedimentation or precipitation. Improved water quality, quick start-up, production of thicker sludge and small space demand are some of its benefits (Zabel, 1985; Rodrigues and Rubio, 2007).

Many studies have been conducted to evaluate the influence of different water compositions and properties in conventional froth flotation (Rao and Finch, 1989; Farrokhpay and Zanin, 2012; Liu, Moran and Vink, 2013). However, the effect of water quality on the efficiency of dissolved air flotation is barely documented. Evaluating the impact of the water quality factors affecting DAF performance can constitute an advantageous tool to improve the response and control of disturbances in the mineral process.

The research in this thesis focuses on the study of the impact of different water quality parameters on DAF performance. Additionally, the suitability of DAF to reach the required quality levels for the water treatment of recycling waters in a mineral processing plant is verified. A DAF laboratory scale unit is applied to four different water samples originated in two different minerals processing plants, taken at different points of the process.

The current work is divided into 8 chapters. In Chapter 1 the mineral process is addressed together with the use of water and the different forms of tailings management in a mineral processing plant. In Chapter 2 the main parameters affecting water quality and monitoring

techniques are described. Chapter 3 describes different techniques of sulfate removal in mine waters, including ettringite precipitation. Chapter 4 includes the basis of DAF process including process description, principle, design parameters and mention of the possible applications of DAF in water treatment. Following, Chapters 5, 6 and 7 are reserved for the experimental part, where the objectives, methods and results of the work are discussed. Finally, in Chapter 8 the main conclusions from the research and possible future lines of investigation are presented.

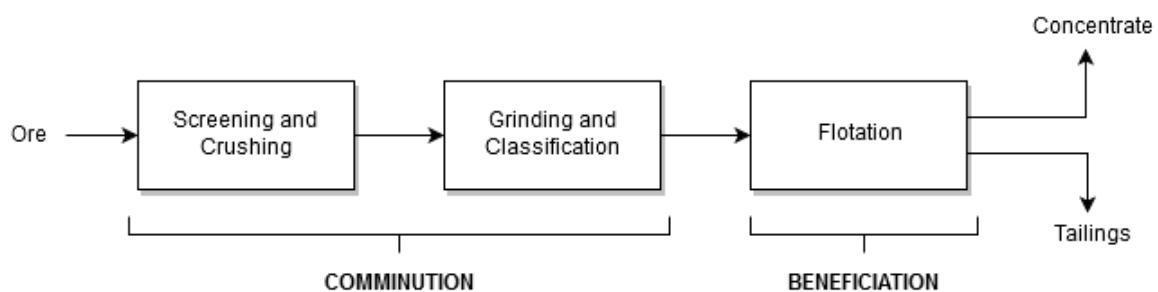
# LITERATURE REVIEW

## Chapter 1. Minerals Processing

### 1.1. The mineral process

Minerals are inorganic compounds which exist in nature with a crystal structure. They usually appear surrounded or mixed with a worthless fraction of a material called gangue. This composition of gangue and mineral is called ore (AngloAmerican, 2019). The commercial product is obtained through a series of operations to produce a material rich in the valuable fraction of the ore. This process is known as a mineral process, ore dressing or mineral dressing (Wills, 2006).

The process of extracting valuable minerals from ores comprises two main operations. First, initial mechanical processing called comminution, where the ore is reduced to relatively fine particles. The second process is enrichment or beneficiation, where physical or chemical methods are used to extract a valuable metal from the gangue. This last stage is also known as concentration. (Wills, 2006). **Figure 1** shows a simplified block diagram with common operations in a mining process plant.



**Figure 1** Simplified block diagram of operations in mining process plant (Wills, 2006).

The run-of-mine (ROM) ore is subjected to a comminution step after being collected. In this step, the aim is to liberate the mineral from the gangue by reducing particle size. For that purpose, the ore enters the system and is exposed to a series of crushers for preliminary size diminution. The crushing step is followed by screening, where the particles, which do not achieve the required size are recycled back to the crushers. Then, in grinding, particles are reduced to a finer fraction. Likewise in the crushing stage, the coarser particles are returned to be ground again (Bustillo Revuelta, 2018). Grinding is a very energy consuming process;

hence it is of high importance to achieve an optimum particle size. Too fine particles can result in high energy costs and mineral losses due to the difficulty of treating them in subsequent stages. On the contrary, too coarse particle can produce low-grade concentrate materials (Wills, 2006).

Following comminution, the ground ore passes through a beneficiation stage, where the gangue waste (tailings) is separated from the valuable mineral (concentrate). Beneficiation can be performed by physical or chemical treatment. Examples of physical methods are magnetic, electrostatic or gravitational enrichment. Regarding chemical treatment, froth flotation is considered one of the most essential techniques for ore beneficiation in mineral processing for sulfide ores. Finally, the froth containing the mineral is further concentrated by dewatering processes, usually by concentrate thickeners followed by filters. The tailings from flotation are transferred to tailings thickeners. The final thickened tailings product is then disposed of in, for example, dams or ponds. (Wills, 2006)

## **1.2. Use of water in a mineral process**

In the mining industry, water can be obtained from superficial bodies of water, from aquifers or directly from the process in the form of recycling waters (Lottermoser, 2010). The use of water in mineral processing only accounts for less than 3% of the total of water consumed in both industry and households in 2015 in northern Europe (EEA, 2018). Nonetheless, most of the mining operations are located in undeveloped, non-industrialized countries where the difficulty to access to water sources is considerably higher than in developed countries. Thus, the search for proper and more efficient water management in the sector is needed. Wastewater disposal regulations are increasing, and fresh water is a scarce resource in some mines due to their location.

Some of the operations previously mentioned, such as grinding and froth flotation, have associated enormous water consumptions. The amount of water used is related to the type of ore to be concentrated. For example, the average demand for water in Kevitsa mine in Finland from 2012 to 2015 is 104 m<sup>3</sup>/h of raw water and 2,500 m<sup>3</sup>/h of process water. Kevitsa mine produces per year 130,000 tons of Ni concentrate with 11% of nickel content and 115,000 tons of Cu concentrate with 25% of copper (Gray, Cameron and Briggs, 2016).

### ***1.2.1. Long and short recycle waters***

Recycled waters can proceed from several sources in a mineral processing plant. It is of high importance to distinguish between long and short recycle waters. Long recycle waters generated in clarification ponds or tailings dams, are also called external recycle waters. On the contrary, the waters from internal recycle are recirculated from the dewatering units directly connected to beneficiation (Slatter *et al.*, 2009).

Apart from their origin, the characteristics and composition of these waters differ on account of the time it takes for the water to return. Shorter periods in the internal recycle result in better preservation of chemicals, such as reagents, allowing their reuse. On the other hand, shorter cycles also promote the accrual of suspended matter to the detriment of flotation (Slatter *et al.*, 2009).

External recycles from tailings also contain several types of contaminants and tend to have higher composition of organic matter than shorter recycles. Evaporation or seepage in dams are principal causes of water loss and are subject to environmental risks because of the percolation of chemicals into the earth. Tailings disposal is also associated with higher costs in infrastructure related to the civil constructions or dam walls. Consequently, shortening external recycle loop is an interesting option to save costs, improve water quality and to minimize contaminants discharge. Reduction in long water recycling can be accomplished by the correct management of tailings disposal (Palmer, 2018). In densified tailings, water can be recovered directly from thickeners overflow and/or filtrates instead of from clarification at the tailings pond.

## **1.3. Tailings management**

Tailings disposal is one of the most significant sources for water losses in a mineral process. Increasing the density of tailings is one of the measures addressed by mining companies to increment water recovery and save space for impoundment, in addition to reduce possible accidents in the tailings storage facility (TSF) (Palmer, 2018). Failures in the TSF can cause major environmental and health-related issues by polluting close water bodies. In this section, conventional tailings along with three densified tailings methods are depicted.

### ***1.3.1. Conventional tailings***

Conventional tailings or tailings dam is the most extended method for tailings disposal nowadays (Wills and Finch, 2016). It consists of slurry with the moderately low percentage of solids (35-50 %) that is pumped to the TSF (Breitenbach, 2010). It is an inexpensive technique if there is the availability of place near the mine site for the sludge pond. The tailings are left to settle for long times, thus a clear overflow can be recovered. Tailings can be constructed in river valleys or valley sides. In some cases, walls are also needed to surround the tailings dam in flat surfaces (Wills and Finch, 2016).

Tailings dams are associated with higher water losses than other types of tailings due to evaporation and seepage. Hence, raw water consumption in plants with tailings dams is higher than in the process using densified tailings. In addition, seasonal rain and snow variations can incur in risks to the volume of the pond. Several cases of failure have been registered over the years with severe consequences to the environment (Benito *et al.*, 2007). Moreover, the increment in fine concentration with modern minerals processing techniques reduces the settleability and therefore requires even larger tailings ponds for sedimentation (Cadena Moreno, 2016).

### ***1.3.2. Thickened tailings***

Thickened tailings are tailings, whose solids density has been increased by high rate thickeners before disposal in the TSF. The sludge produced has a solids content ranging 50 – 70 % (Wills and Finch, 2016). The lower water content considerably reduces the space requirements and failure risks due to the higher homogeneity and less flowability of the sludge. Likewise, seepage and evaporation volumes decrease. Furthermore, water from the thickener overflow can be recovered, meaning lower water consumption in the plant than in conventional tailings (Wills and Finch, 2016).

Nonetheless, this method still has some disadvantages. Even the risks are reduced due to the higher solids density, the use of dams still entails risks necessary to manage, including the issues related to changes in climate conditions, equally to conventional tailings (Kuisma, 2018). Moreover, the use of thickeners increases operational costs compared to tailings dam management (Bustillo Revuelta, 2018).

### ***1.3.3. Paste tailings***

In paste tailings, paste thickeners are used to dewater the sludge to 70 - 85% of solids (Wills and Finch, 2016). The material is disposed in layers in the TSF. Thus, no dam is required resulting in lower space requirements and almost zero failure risks. Dryer material disposal is more sustainable, reducing not only raw water consumption but also the TSF footprint (Wills and Finch, 2016).

However, the use of extra equipment for dewatering the tailings and the difficulties to pump paste materials have associated increments in operational costs. Another challenge with this type of tailings is the accumulation of impurities as more water is circulating in short recycle, therefore water treatment is needed (Kuisma, 2018).

### ***1.3.4. Filtered tailings or dry stacking***

The last method to increase the density of tailings is filtered tailings, also called dry stacking. This method obtains tailings with more than 85% of solids by thickening and filtering. After filtration, the dry tailings are discharged by trucks or conveyors at the TSF (Wills and Finch, 2016). Freshwater consumption is drastically reduced due to high solids content and the possibility of recirculation from thickeners overflow and filtration. It is the most sustainable technique from all the previously mentioned, with the smallest operational and environmental risks (Kuisma, 2018).

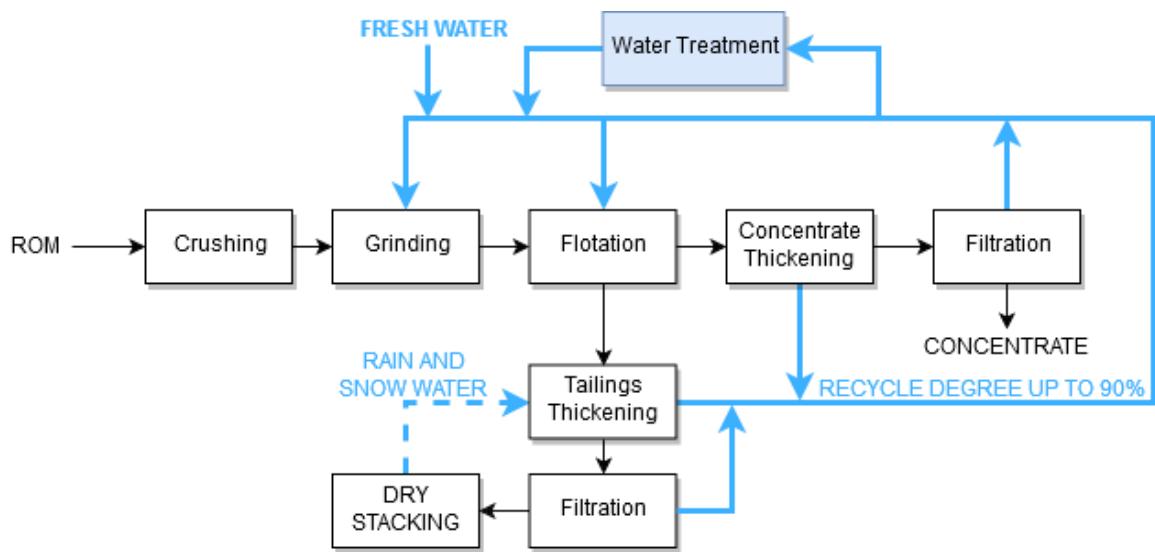
As in paste tailings, the downsides of this technology are high costs and water management in short circulation recycles (Kuisma, 2018).

## **1.4. Water treatment in the mineral process**

Recycle degrees up to 90-95% could be relatively easy to achieve by using paste tailings or dry stacking (Gunson *et al.*, 2012). In addition, some extra water make-up could be recovered from rain and snow water. Nevertheless, this high percentage of water recirculation can have a negative effect on previous flotation stages due to the accumulation of impurities or residual chemicals (Rao and Finch, 1989). Therefore, water treatment is required to avoid the necessity of adding raw water to compensate for quality deficiencies.

One example of a configuration to increase the rate of water recycled without compromising the efficiency of the flotation process is presented in **Figure 2**. In this figure, a combination

of dry stacking with water treatment is used to attain water recycle up to 90%. It is important to emphasize that the goal of the water treatment is to obtain water of the right quality. That is water with the minimum quality requirements to perform successful flotation (Hagnäs and Suvio, 2018). For that purpose, a portion of the overflow from concentrate and tailings thickeners, as well as the clarified liquid from filtration can be treated and mixed with non-treated process water till the right quality is acquired.



**Figure 2** Use of water treatment and dry stacking to increase water recycle in mineral process.

Currently, there is a myriad of water treatment techniques available. The selection of the water treatment depends mainly on the particle size, density and concentration. Three examples of techniques for water treatment are electrochemical water treatment (EWT), polishing filtration and DAF.

#### 1.4.1. *Electrochemical water treatment (EWT)*

Electrochemical water treatment (EWT) is a group of physical-chemical methods that use the potential difference from redox reactions generated between two electrodes in the electrolysis process (Sillanpää and Shestakova, 2017). The electrolytic reactions in the solution allow the removal of contaminants by three different means:

- (1) Conversion of the impurities to modify their properties in the wastewater. Electrocoagulation, electroreduction and electrooxidation are examples of conversion methods;

- (2) Separation without considerable changes in physical-chemical properties. Examples of separation are electroflootation or electrodialysis, where electric fields attract charged particles in the water;
- (3) Combination of conversion and separation.

In general, EWT are environmentally friendly methods with high performance and little residual impurities. The most used method in the mining industry is electrocoagulation or electrocoagulation followed by electroflootation, which are good and versatile alternatives that produce smaller amounts of sludge compared with common coagulation technologies (Feng *et al.*, 2016). In particular, electrocoagulation shows high efficiency for the removal of surfactants, used as reagents in froth flotation, or heavy metals (Liu, Zhao and Qu, 2010). On the other hand, side effects of EWT are the problems related to continuous operation due to anode passivation or accumulation of sludge in the electrode. Also, the effluent can be polluted with high amounts of aluminum and iron (Feng *et al.*, 2016).

#### ***1.4.2. Polishing filtration***

Water polishing refers to the removal of fine particles in low concentration from waters, such as biological oxygen demand (BOD) or remaining suspended solids from primary and secondary treatments (Chokhavatia, 2019). There are many types of polishing filters available, one particular case is the Outotec Larox® LSF filter (Outotec, 2019), which uses adsorptive filtration to remove solids from process waters. Other options could be sand filtration (Hamoda, Al-Ghusain and Al-Mutairi, 2004) and filtration with ceramic membranes (Farsi *et al.*, 2014).

Polishing filtration yields very high filtrate qualities with low operating costs. However, fluctuations in solids content in the feed can lead to problems in the filter. For instance, very high solids concentrations are prone to produce thicker and more compact cakes that would lead to exceptionally short filtration times and cleaning difficulties. Polishing filters are typically placed after pressure filtration or dissolved air flotation units. (Holliday, 2010)

#### ***1.4.3. Dissolved Air Flotation***

Dissolved Air Flotation (DAF) is a particle separation process where air microbubbles generated by a pressurized air stream attach to the particulate matter in suspension. The

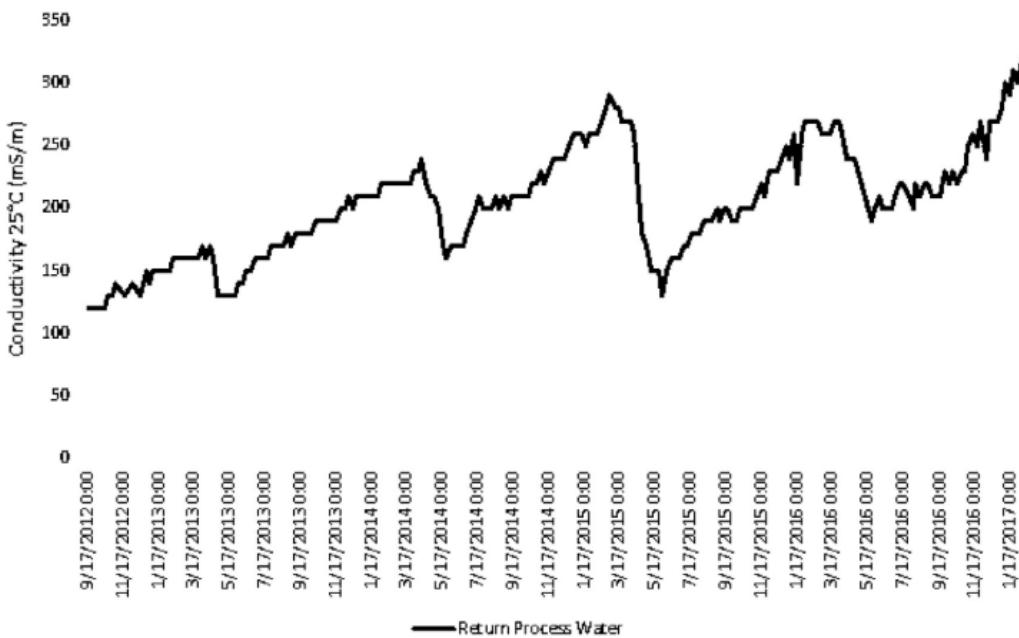
particles together with the bubbles float to the top of the flotation tank where they are withdrawn (Haarhoff and Edzwald, 2012).

This method can be used as a primary, secondary or tertiary treatment of waters containing colloids, fine and ultrafine particles, microorganisms, metal ions, or even oils and greases (Rodrigues and Rubio, 2007). DAF has a fast start-up and can operate at high loading rates. Hence the space demand is low compared with other clarification methods (Zabel, 1985). Additionally, DAF units produce thicker sludge. This technique can treat larger water volumes per unit of time than with filtration (Ferguson, Logsdon and Curley, 1995). The drawbacks of this technology are energy and chemical consumption and operational costs due to the need of air saturation. In addition, high turbidity waters are difficult to treat with DAF (HDR, 2002; Khiadani (Hajian) *et al.*, 2014).

## 1.5. Quality variations in mining waters

The properties and composition of the feed in a water treatment application have a significant impact on choosing setup and design parameters. In that sense, the treatment of waters in mineral processing faces bigger challenges related to variations in water quality. Water fluctuations should be avoided or counteracted due to the sensitivity of the mining process to them (Muzenda, 2010).

These variations are caused by several reasons, such as differences in the mineralogy of the mined ores, accumulation of impurities or merely by seasonal changes (Punkkinen *et al.*, 2016). Seasonal differences in the conductivity of process waters in Boliden Kevitsa plant can be observed in **Figure 3**. The highest conductivity has been recorded every year around February-March, after that the snowmelt season drops the conductivity by dilution (Westerstrand and Öhlander, 2011; Muzinda and Schreithofer, 2018). Besides, the graph shows a tendency of conductivity to increase over time due to the accumulation of ionic compounds generated in mining activities and flotation reagents.



**Figure 3** Conductivity of process water in Kevitsa from 2012 to 2017 (Muzinda and Schreithofer, 2018).

During winter, metal recoveries are worse because of the effect of low temperatures in flotation kinetics (Sousa, 1984; Hagnäs and Suvio, 2018). Therefore, more reagents are needed to compensate for poor recoveries and conductivity starts to increase. In addition, froth stability problems can appear. Other sources of disturbances are the presence of humic substances, blooming of algae and microbial activity or evaporation and precipitation phenomena (Hagnäs and Suvio, 2018).

Management of recycling waters influences water quality fluctuations in addition to the impact of accumulation of contaminants. Earlier in section 1.2.1 two types of recycles in the plant were introduced. In this regard, tailings management plays an important role where the water loop is closing with increasing tailings density disposal. Closing the water loops results in higher accumulation of chemicals and impurities in the water circuit, meaning stronger disturbances in the mineral process. Without water treatment, the properties of the water eventually change, including pH, redox potential, temperature or conductivity (Hagnäs and Suvio, 2018).

## **Chapter 2. Water Quality in Mineral Processing**

### **2.1. Water composition and properties**

The composition of wastewater produced in mining operations depends mainly on the process. Different ores, equipment, chemicals dosage in flotation results in different water compositions and properties. Substances in mining waters can include colloidal matter, ions, residual reagents and microorganisms (Hagnäs and Suvio, 2018). Eh and pH water conditions are also considered in this chapter due to their importance in the mineral process (Wills *et al.*, 2016).

#### **2.1.1. Colloidal matter**

Colloids are suspensions consisting of dispersed particles or aggregates. These particles are fine particulate matter with size smaller than 10 µm or even 1 µm in some cases (Boily, 2018). Fines are undesired species in froth flotation because of their high surface area, which results in higher consumption of chemicals (Hagnäs and Suvio, 2018). Colloids do not settle or float to the surface when they are stable. Therefore, it is necessary to add coagulants to destabilize the matter in suspension and generate agglomerates that can be removed through water treatment methods (Boily, 2018).

One particular type of colloidal or fine particles are clay minerals. They are crystalline minerals comprised of layers of tetrahedral silicon and octahedral aluminum. Typical clay minerals are categorized in the kaolin group, mica group, smectite group and chlorite group (Wimpenny, 2018). Since they affect pH and viscosity, the presence of clay minerals in water can compromise froth flotation efficiency. Moreover, the coating of the metal surfaces by clay slimes can reduce the selectivity of flotation significantly (Chen and Peng, 2018). No evidence of a negative effect of clay particles on DAF for wastewater treatment has been found in the literature.

The quantity of colloidal particles in suspension is expressed as Total Suspended Solids (TSS), typically in mg/L or ppm. In laboratory tests, TSS is measured as the solid portion weighted after filtrating the water sample with a 1.5 µm glass fiber filter (Missouri State University and OEWRI, 2007). Suspended particles are also the cause of turbidity in water, which is one common parameter to assess DAF efficiency. One method to determine turbidity by quantifying the amount of light reflected in a water sample with a nephelometer

(measured in Nephelometric Turbidity Units, NTU) (Dharmappa, Sivakumar and Singh, 1998). Turbidity and TSS are physical characteristics of water that can be seen by the naked eye.

### ***2.1.2. Ions***

Some of the ions that can be found in mineral processing waters are  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , cyanides, sulfates, thiosulfates, nitrates or different heavy metal ions depending on the mining process (Dharmappa, Sivakumar and Singh, 1998).

Metal ions are precipitated as hydroxides when they are under conditions of alkaline pH. These hydroxides can generate hydrophilic surfaces that hinder the attachment to bubbles in flotation (see chapter 4.2). Particle-bubble or particle-particle attachment can also be reduced if the surface charge of the particles is modified by the presence of metal ions (Liu, Moran and Vink, 2013). On the other hand, the hydroxides of multivalent cations, such as  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  or  $\text{Mg}^{2+}$ , can contribute to the formation of positively charged bubbles in DAF making unnecessary the use of coagulants (Han, Kim and Shin, 2006; Mun, Park and Han, 2006).

Total Dissolved Solids (TDS), in mg/L or ppm, is an indicative measurement of the number of cations and anions dissolved in water. Dissolved solids are those whose size is smaller than 2  $\mu\text{m}$ . They are mainly comprised of inorganic matter, accounting to approximately 95 % of the TDS. This inorganic matter, in turn, is composed of cations and anions which dictate the salinity or conductivity of the solution. Therefore, the conductivity of water can be used as an indicator of the TDS, which is easier and faster than directly to measure the TDS with the aid of a conductivity meter (Boyd, 2015). An estimation of the relationship between the TDS and conductivity is given by the equation (Atekwana *et al.*, 2004):

$$\text{TDS} = k_e \cdot EC \quad (1)$$

where TDS is Total Dissolved Solids ( $\text{kg}/\text{m}^3$ );  $EC$  is the electrical conductivity at 25 °C ( $\text{S}/\text{m}$ );  $k_e$  is a correlation factor, whose values can vary from 5.5 to 8 ( $(\text{kg}\cdot\text{m})/(\text{S}\cdot\text{m}^3)$ ) (Atekwana *et al.*, 2004; Hubert and Wolkersdorfer, 2015).

### ***2.1.3. Residual reagents***

The use of collectors, frothers and regulators is typical practice in froth flotation for the concentration of minerals. Collectors are surfactants used to induce hydrophobicity in the particles in suspension, thus bubbles can attach to them. Frothers are also surfactants but

used to improve the stability of the froth and to reduce bubble size. Finally, regulators are substances that modify the action of the collectors. Regulators are, in turn, divided into (Wills *et al.*, 2016):

- *Activators*: react with certain species to increase their hydrophobicity and, thus, improving their selectivity.
- *Depressants*: increase selectivity by acting the opposite of activators. They inhibit the attachment of some undesired particles to bubbles.
- *Dispersants*: prevent particles from forming aggregates. Usually, depressants are also dispersants. The most used one is sodium silicate.
- *pH modifiers*: alkaline conditions are usually more appropriate for flotation. In most cases, pH is regulated by the addition of lime or sodium carbonate.

These reagents can be reused in froth flotation together with the water carrying them, resulting in chemicals savings. Nevertheless, residual reagents in process waters may cause bulk flotation, which can reduce selectivity (Hagnäs and Suvio, 2018). Furthermore, some particular regulators, such as the natural depressant carboxymethylcellulose, are related to the growth of microbiological activity (Hagnäs and Suvio, 2018). In contrast, the aim of the DAF process is to remove all the possible impurities in water till the quality is good enough for froth flotation performance. Therefore, the presence of residual depressants can negatively influence efficiency by preventing determined compounds from being collected by bubbles.

#### **2.1.4. Microorganisms**

The microbiological activity in the water of some mineral processing plants can reach relatively high levels. Levay, Smart and Skinner (2001) determined that the concentrated pulp produced in froth flotation under conventional process parameters can contain 1.5 billion colony-forming units (cfu) per mL. The recycle of some treated effluents, such as sewage, or the presence of flotation reagents contribute to biological growth (Slatter *et al.*, 2009).

Microorganisms may cause negative consequences in froth flotation. Total Organic Carbon (TOC) in high quantities is related to issues with the froth (Slatter *et al.*, 2009; Liu, Moran and Vink, 2013). Surface hydrophobicity of particles in flotation can be reduced as well by the existence of bacteria in the water. A positive aspect of bacteria in recycling waters is that

they can act as a depressant, which can increase the selectivity of froth flotation (Liu, Moran and Vink, 2013). However, as mentioned in the previous section, depressants may be counter-productive in DAF treatment.

### **2.1.5. pH**

Monitoring and controlling pH is a must in a mineral processing plant. Alkalinity needs to be adjusted, amongst other things, to avoid the corrosion of the equipment and pipes that occurs at low pH values (typically below 6.5). Moreover, alkaline conditions are frequently chosen in mineral plants to favor the stability of collectors in froth flotation. Lime or sodium carbonate are added in most cases to raise pH, but sodium hydroxide or ammonia can also be used. On the contrary, sulfuric or sulfurous acids are added when acidic conditions are needed (Wills *et al.*, 2016).

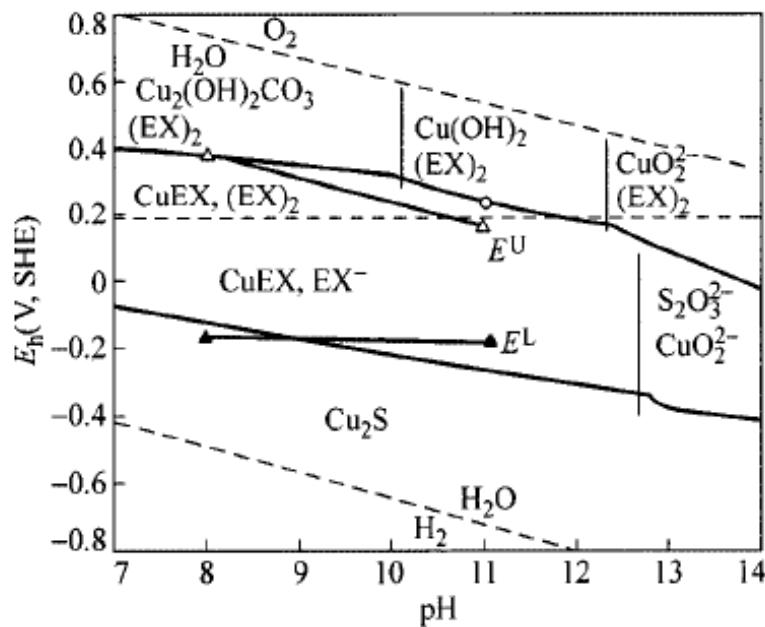
pH plays a significant role in the speciation of collectors and metals ions in water. While the range of low pH is related to higher solubility of the species, higher pH values can cause the precipitation of metal oxides, sulfates or carbonates (Dharmappa, Sivakumar and Singh, 1998; Liu, Moran and Vink, 2013). Furthermore, pH also has a direct effect on the surface charge of the particles in a solution. For the majority of the particles, the higher the pH, the more negative its surface charge is. Hence, pH affects coagulation and flocculation and bubble-particle attachment (see chapter 4.2.1) (Haarhoff and Edzwald, 2012).

### **2.1.6. Redox potential**

The reduction potential (Eh), also called redox potential or oxidation reduction potential (ORP), is defined as the predisposition of a chemical compound to capture electrons. Eh units are volts relatives to the standard hydrogen electrode (SHE). A substance with high positive ORP has higher capability to oxidize another substance and hence, to be reduced. The potential together with pH are two variables of great importance in the froth flotation of mineral species. The complexity of the reactions involved in froth flotation makes it very difficult to control and measure pulp potential in real life (Woods, 2003). Although, knowledge about alkalinity and potential conditions is the key to understand species involved in the flotation process (Ralston, 1991). In plants with closed water loops, the potential of water recycled to flotation can influence the potential of the pulp and, thus, affecting the flotation.

Reduction-oxidation potential affects not only the chemistry of the minerals dissolved in the pulp but also their interactions with collectors. Xanthates are one of the most common collectors used in sulfide minerals flotation. The adsorption of xanthate on the surface of a mineral is characterized for being an anodic reaction. In that sense, an excessively low potential is not suitable for xanthate-mineral reactions to occur, making the mineral floatable (Wills *et al.*, 2016). Collectorless flotation is an example of the influence of pulp potential in flotation. Moderately oxidizing environments can produce self-induced flotation of some sulfide minerals (Ralston, 1991; Hu, Sun and Wang, 2009b).

Redox potential is strongly dependent on pH and oxygen concentration in the pulp. Pourbaix or predominance diagrams are used to predict the predominant species in the equilibrium of the system. This diagram is the representation of the most probable species in solution in dependency of pH and Eh. Nevertheless, equilibrium potentials are calculated based on thermodynamics, which confers limitations to the applicability of this method to predict the flotation behavior. A thermodynamically stable reaction may not occur due to slow kinetics (Bennett, 1996). **Figure 4** shows the Eh-pH diagram in the case of chalcocite flotation for the extraction of copper. Higher recoveries are obtained in the area where the hydrophobic cuprous ethyl xanthate is the predominant species (Hu, Sun and Wang, 2009a).



**Figure 4** Eh-pH predominant phase diagram of chalcocite/ethyl xanthate (EX)/oxygen system.  $E^U$  and  $E^L$  are the upper and lower potentials, between which the flotation recovery is higher than 50% (SHE: standard hydrogen electrode) (Hu, Sun and Wang, 2009a).

### ***2.1.7. Temperature***

Flotation of sulfide ores is carried out at ambient temperature in most cases. Nevertheless, it is well-known that temperature has a notable effect on reaction rates, thus froth flotation can be affected by temperature changes (Wills *et al.*, 2016). Moreover, high water temperatures in the plant can lead to microbiological and bacterial growth. One of the disturbances related to closing the water loops in minerals processing plants is the possible rise of temperature (ITERAMS, 2017).

## **2.2. Quality monitoring**

The analysis of water quality throughout the mineral process is essential for proper water management. Many mineral plants only focus on the monitoring of crucial sites of the process, such as downstream discharge. However, knowing the composition and characteristics of water with more detailed monitoring can help to predict and prevent quality fluctuations and, thus, disturbances in the process. In a mineral processing plant, different types of tests are performed to determine water quality and quantity. Depending on where and how they are carried out, these tests can be classified as onsite (or on the field), laboratory and online analysis. The ore and process characteristics, environmental conditions, as well as possible site legislation dictate which parameters would provide meaningful information to monitor the mineral process.

Onsite monitoring is performed on the field with portable equipment right after the sample is collected. It is used when parameters that may be unsteady with time are involved. These parameters include temperature, pH, electric conductivity (EC), Eh, dissolved oxygen (DO) and turbidity. The information obtained from the field monitoring can also be compared with those obtained from laboratory tests. Apart from already listed parameters, other possible measurements performed at laboratory are TDS, TSS, chemical oxygen demand (COD), total organic carbon (TOC), dissolved organic carbon (DOC), total phosphorous (TP), phosphate phosphorous, soluble phosphorus, total nitrogen (TN), toxicity, bacteria or characterization of metal ions. Chloride and sulfate ions measurements are also recommended to assess water quality (Punkkinen *et al.*, 2016).

Online monitoring is the continuous real-time monitoring at the site with subsequent storage of the information obtained. These data can be used to create models to predict and quickly react to process disturbances. At present applications, online monitoring focuses mainly on

monitoring of water volume and flow and, in some cases, electrical conductivity, pH and turbidity. Further analysis can be performed if water quality variations are detected by changes in these parameters (Punkkinen *et al.*, 2016).

Nowadays, the online measurement of more parameters is gaining in popularity. Although, the minerals industry still presents reservations about this issue. Firstly, because online sensors have a short lifespan and require frequent maintenance by mine workers. It would be more economical if the personnel take onsite samples since they must go to check the sensor in any case. Secondly, because online sensors are expensive and sensitive equipment. Finally, some parameters are difficult to test by online sensors due to lack of development of the equipment. In addition, sensors may present problems at mines placed in cold climate areas. Water freezing during winter causes changes in the flow which results in calibration difficulties (Punkkinen *et al.*, 2016).

Nonetheless, advances in the field of the online measurements are on a stage to be improved and to create new techniques and equipment. One example is the online characterization of cations and anions through capillary electrophoresis. Moreover, currently, almost 50 different quality parameters and metals can be determined by sensor analysis. In some cases, online measurements could be more reliable and generate savings up to 30 % of the investment and maintenance costs in comparison to manual sampling and testing (Punkkinen *et al.*, 2016).

## **Chapter 3. Sulfate removal in mine waters**

Mining industry is a big contributor to the release of anthropogenic sulfates to water, mainly as a result of the treatment of sulfide ores (Runtti *et al.*, 2018). When sulfide minerals are oxidized, acidic water rich in sulfate and metals is produced. This phenomenon is a critical environmental issue in mine effluent discharge called acid mine drainage (AMD) (Hanrahan, 2012).

Although sulfates are not considered toxic or particularly harmful for the environment when released in water effluents under certain levels, high levels of sulfate in waters are related to corrosive and purgative problems and may cause scaling. Moreover, the accumulation of sulfate over the time induces water quality problems for mining processes (Bowell, 2004).

This chapter discusses different water treatment alternatives to remove sulfates from mining waters with focus on precipitation via ettringite formation. Several technologies are available to remove sulfate from the water in mining industry including ion exchange, membrane filtration, biological treatment and precipitation (Lorax Environmental, 2003).

### **3.1. Ion exchange**

Ion exchange bases its principle on the substitution of the ions present in an ion-exchange resin with the undesired ions of a solution (Cobzaru and Inglezakis, 2015). A technique to remove calcium and sulfate from water via ion exchange is the GYP-CIX process. GYP-CIX uses lime and sulfuric acid to regenerate the resin, producing gypsum as solid waste (Lorax Environmental, 2003).

The GYP-CIX process can reduce TDS and sulfate content from 2000 – 4500 mg/L and 1200 – 2800 mg/L to under 240 mg/L and 50 mg/L (Lorax Environmental, 2003). However, the main disadvantages of this method are the production of sludges and that, although GYP-CIX counts with a low-cost resin, it is an expensive technology. Moreover, ion exchange would probably require a preliminary chemical precipitation step due to selectivity and capacity limitations (Runtti *et al.*, 2018).

### **3.2. Membrane technology**

Membrane technologies for the reduction of sulfate in mine waters are electrodialysis (ED) and reverse osmosis (RO). ED uses electric potential difference to force the pass of ions

through the membrane, while in RO uses high pressure to move the pure water through a semipermeable membrane (Strathmann, 2000).

RO presents problems with waters containing high levels of Ca and  $\text{SO}_4^{2-}$ , or even Al ad Fe. Slurry Precipitation and Recycle Reverse Osmosis (SPARRO) where seed crystals of gypsum are added to the feed to foster the precipitation and crystallization of gypsum to avoid scaling in the membrane. SPARRO process could remove sulfate from 6639 mg/L to 159 mg/L with 95 % recovery. Despite this, the membranes have short membrane life and high salt rejection rates caused by failing and fouling. Similar problems apply to ED where also drinking water qualities can be produced, but scaling causes reduced life of the membrane. (Lorax Environmental, 2003)

### **3.3. Biological sulfate removal**

Sulfate reducing bacteria (SRB) take sulfate as oxidant and reduce it to  $\text{HS}^-$ . Then the hydrogen sulfide is finally reduced to elemental S by chemotrophs or phototrophs bacteria. Biological sulfate removal is a cost-effective method to reduce sulfate from water (Lorax Environmental, 2003). Biological removal systems are categorized into active or passive processes. Passive systems are run without human intervention, while active biological system require control over chemicals and process parameters (Runtti *et al.*, 2018).

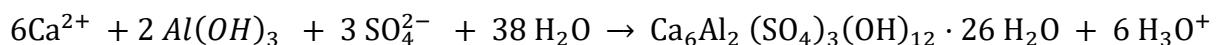
Apart from sulfate reduction, SRB can also remove trace metals with very small waste generation (Lorax Environmental, 2003). Levels of sulfate under 100 mg/L can be reached but the high hydraulic retention times difficult the treatment of greater feed rates without arranging more than one reactor in parallel (Runtti *et al.*, 2018).

### **3.4. Ettringite Precipitation**

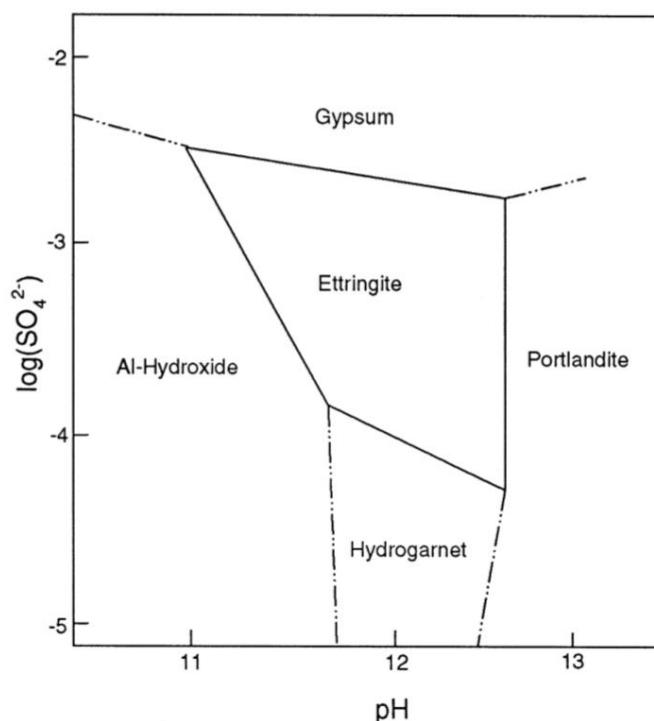
Typically, sulfate in mine water is reduced by precipitation with lime or limestone as gypsum. The problem of this process is that it is limited by the solubility of  $\text{CaSO}_4$  ( $K_{\text{sp}} = 3.14 \times 10^{-5}$ ) (Liang, Tamburini and Johns, 2015). Hence, precipitation with ettringite has been suggested due to its lower solubility ( $K_{\text{sp}} = 1.26 \times 10^{-45}$ ) (Perkins and Palmer, 1999).

Ettringite  $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26 \text{H}_2\text{O}]$  is a sulfate mineral present in cements and concrete. Toxic metals attach to the crystalline structure of ettringite. In particular, ions inside the ettringite structure can be replaced via diodochic (with ions of similar size and

charge) or isomorphic substitution (ions with similar size and different charge). In addition, isomorphic substitution leads to a change of charge in the ettringite structure that can allow the entrapment of more toxic metals (Hossein, 2000). The reaction for the formation of ettringite occurs as follows (Müller Cadorin, 2008):



To ensure the formation of ettringite, it is very important to keep the pH near 12, the region of stability of ettringite according to **Figure 5**.



**Figure 5** Stability of ettringite at high pH region (Myneni, Traina and Logan, 1998).

SAVMIN and CESR (cost effective sulfate removal) are two processes which use precipitation of ettringite to remove sulfates from water, leaving concentrations of 100 mg/L or lower of SO<sub>4</sub><sup>2-</sup> in the treated water (Lorax Environmental, 2003). SAVMIN method consists on several steps where:

- 1) Metals are precipitated as hydroxides with lime at pH 12
- 2) Gypsum is precipitated by the addition of gypsum crystals as catalyst
- 3) Precipitation of ettringite through the addition of aluminum hydroxide
- 4) pH reduction with CO<sub>2</sub>

Finally, the aluminum is recycled back to the process after being recovered by thickening and filtration. CESR process is similar to SAVMIN but an aluminum salt reagent is used instead of aluminum hydroxide and this reagent is not recycled. The main stages of the process are (Reinsel, 1999):

- 1) Gypsum precipitation with hydrated lime at relatively low pH
- 2) pH adjustment to 10.5 with extra lime to precipitate metals as hydroxides
- 3) Addition of more lime, to rise pH to 11.5, and an aluminum reagent for ettringite precipitation
- 4) pH reduction with CO<sub>2</sub>

## **Chapter 4.      Dissolved Air Flotation (DAF)**

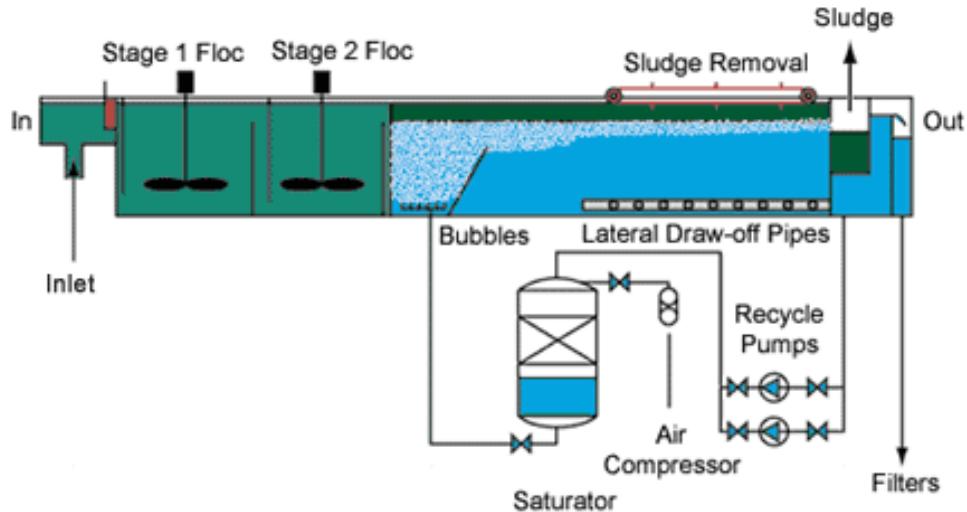
The technology proposed for the treatment of process waters in mineral processing industry is Dissolved Air Flotation, better known as DAF. Dissolved air flotation is a solid-liquid separation method, where the particles in the liquid are separated through the dissolution of pressurized air in a flotation tank injected by a nozzle. This pressurized air forms micro-sized bubbles where the suspended matter is attached and subsequently floated to the surface to be removed when the pressure is released (Shammas and Bennett, 2010).

DAF should not be confused with froth flotation, even if both methods are based on the separation of particles through the injection of bubbles. Froth flotation is a conventional technique for the concentration of minerals in ore beneficiation. Larger bubbles are involved in froth flotation (600 – 2000  $\mu\text{m}$ ), providing higher efficiency to remove coarser particles (Rubio, Souza and Smith, 2002). In contrast, dissolved air flotation produces microbubbles with a size comprised between 30 – 100  $\mu\text{m}$ . These microbubbles make it especially suitable in water treatment applications to eliminate aggregate colloids, fine and ultrafine particles, microorganisms, ions, or even oils from water (Rodrigues and Rubio, 2007). Furthermore, froth flotation requires the addition of reagents to increase the selectivity of the desired mineral products. DAF, however, often employs coagulants and flocculants to improve the overall floatability of the suspended matter.

### **4.1. Process description**

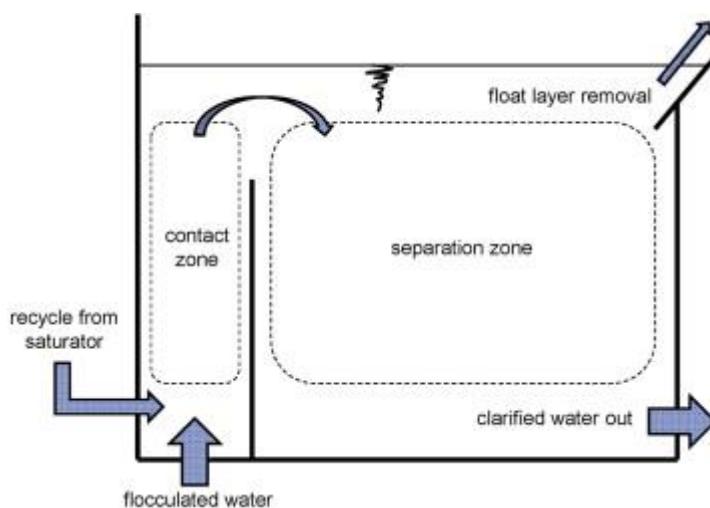
The typical gas used for bubble generation is air. Although nitrogen, methane or carbon dioxide can be used for the process (Shammas and Bennett, 2010). In the DAF process, bubbles are generated by dissolving air in the pressurized wastewater inflow. A pressurizing pump saturates the feed to approximately between 2 and 6 atm, and then this stream is liberated at the base of the flotation basin after passing across a press-release valve (Shammas and Bennett, 2010). As a result of the pressure drop after the valve, microbubbles with a diameter range from 30 to 100  $\mu\text{m}$  are released. These microbubbles form agglomerates with the particles in suspension and float to the top of the flotation chamber. Finally, the floated sludge formed at the surface is removed by scrapers and the effluent, or clarified liquid is then recovered from the bottom (Wang, Fahey and Wu, 2005). In most cases, there is also a pretreatment stage where chemicals are added to the inlet flow to

improve hydrophobicity of the suspended solids and foster floc formation (Shammas and Bennett, 2010).



**Figure 6** Typical DAF process schematic diagram (Shivam Water Treatment, 2010).

There are two defined zones inside of the flotation tank: the contact or reaction zone and the separation zone, as shown in **Figure 7**. In the contact zone, air bubbles are introduced and the flocs form aggregates with bubbles due to bubble-particle collisions. After that, the bubble-floc aggregates, including some free bubbles and flocs, flow to the separation zone where they rise. Finally, they accumulate in a floating layer at the surface that would be later removed (Edzwald, 2010).

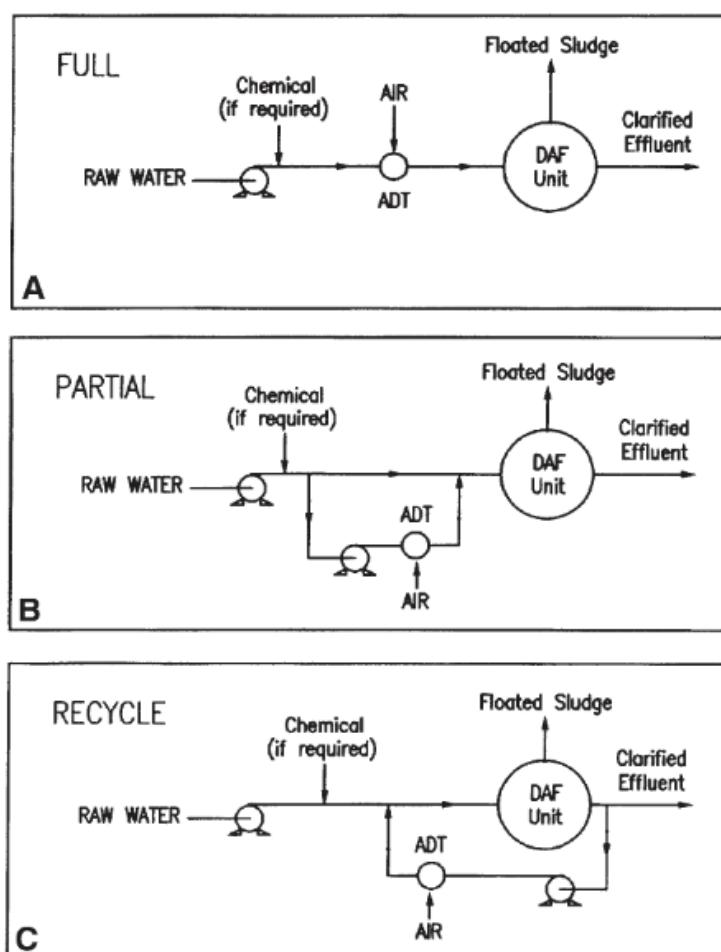


**Figure 7** Schematic representation of DAF tank zones (Haarhoff and Edzwald, 2013)

#### 4.1.1. Process configurations

There are three different options for the operation of a DAF system depending on the amount of inlet flow that is further pressurized. These three options are full flow, partial or split flow and recycle flow. In full flow, all the influent is pressurized prior to its entrance to the flotation tank. Full flow is especially recommended for applications that do not require flocculation and coagulation. The split flow consists of pressurizing only part of the feed entering the tank. This mode is applied to wastewaters containing particles that can compromise the pumping system. Finally, in recycle flow a percentage of the clarified liquid is pressurized and saturated with air and recycled to the flotation tank (Palaniandy *et al.*, 2017). Recycle ratio is defined as recycling flow divided by effluent flow. As a rule of thumb, its value is typically around 10% (Haarhoff and van Vuuren, 1995; Edzwald, 2010).

**Figure 8** presents the flow diagrams for all three process configurations in DAF.



**Figure 8** Flow diagram of modes of operation in DAF. A: full flow, B: split flow, C: recycle flow (Wang, Fahey and Wu, 2005).

From the mentioned above, only split and recycle flow configurations are suitable for wastewater treatment (Wang, Fahey and Wu, 2005). Furthermore, recycle flow is the most common configuration among all three. It is the preferred option when the addition of chemicals for floc formation is involved.

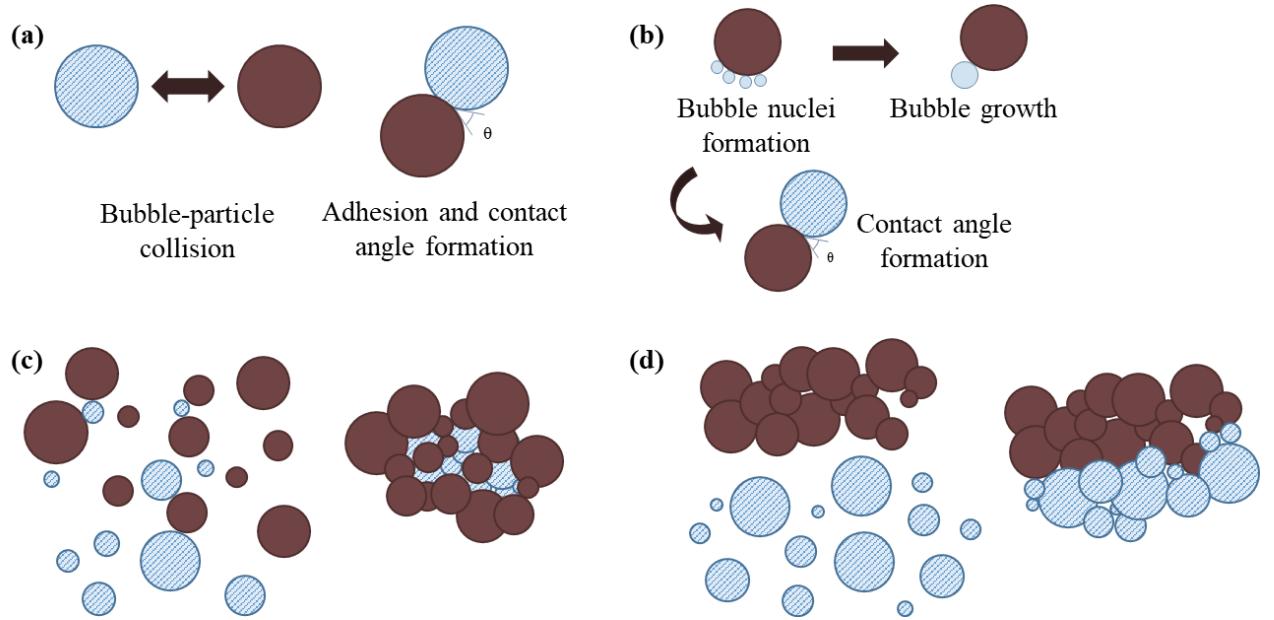
## **4.2. Principle and mechanisms**

For a successful flotation, the attachment between particles and bubbles must take place. This phenomenon occurs when particles fulfill two conditions: surface hydrophobicity and charge neutralization (Edzwald, 1995; Palaniandy *et al.*, 2017). This section depicts the theory and mechanisms behind the interactions of bubbles and particles in flotation related to surface hydrophobicity, charge and particle size.

### ***4.2.1. Bubble-particle interactions***

According to Shammas & Bennett (2010), the general process for removing suspended matter from water in DAF consists of the following steps:

- 1) Microbubble addition to the flotation chamber
- 2) Bubble-particle collisions
- 3) Attachment of small bubbles to the particles in suspension;
- 4) Formation of agglomerates due to collisions between the particles already attached to bubbles
- 5) Capture of more bubbles within the flocs
- 6) Flotation of the flocs with the bubbles to the water surface



**Figure 9** Bubble-particle interactions (bubbles: stripped; particles: plain ): (a) particle-bubble collision and adhesion; (b) bubble formation at particle surface; (c) micro-bubble capture in aggregates; (d) bubbles entrainment by aggregates (Rubio, Souza and Smith, 2002).

A schematic view of the interactions between bubbles and particles is presented in **Figure 9**. The figure introduces an important concept to describe the flotation of the particles produced by the interaction with the bubbles: the contact angle. The contact angle is used as a measurement of the hydrophobicity of the particles. The attachment between the particles and bubbles can occur when both particle and bubble surfaces are put into contact. This contact would only occur if the water between the bubble and the particle is displaced (Jefferson, 1997). As stated by Gochin & Solari (1983), the energy of adhesion of water to the surface of the particle should not be greater than the cohesion between the water molecules. The larger the contact angle, the more hydrophobic the particle is.

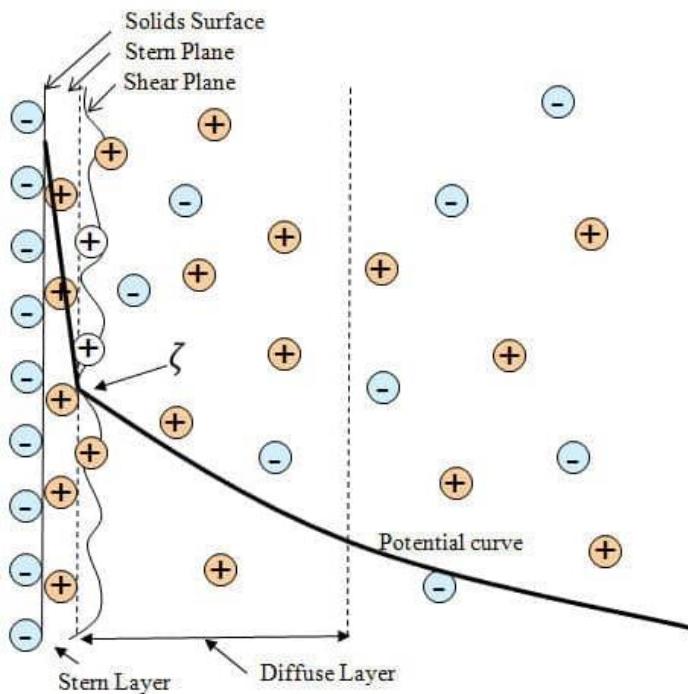
The presence of hydrophobic particles is fundamental in the mechanism of direct bubble-particle collisions and attachment represented in **Figure 9 (a)**. However, hydrophilic particles can also be removed in DAF systems due to the growth of bubble nuclei at the solid surfaces (**Figure 9 (b)**) (Rubio, Souza and Smith, 2002; Rodrigues and Rubio, 2007). **Figure 9 (c)** and **(d)** shows two other possible mechanisms where the presence of hydrophobic particles is not required. In **(c)**, the microbubbles are captured inside of already existing flocs, thus reducing their density and allowing their flotation. In **Figure 9 (d)**, a formation of bubbles raises the particle agglomerates without necessary attachment (Rodrigues and Rubio, 2007). Floc and bubble size are crucial for these two mechanisms.

Among all the four previously discussed mechanisms, the one determining for the formation of particle-bubble aggregates is the adhesion of bubbles to hydrophobic particles or hydrophobic spots on their surface (Edzwald, 1995). The addition of flotation reagents can modify particles which are not naturally hydrophobic.

#### **4.2.2. Electrostatic nature of bubbles and particles**

Along with hydrophobicity, particle charge plays a fundamental role in flotation. Some studies (Han and Dockko, 1998; Han, 2002) pointed out that when bubbles and particles had the opposite charge, the collision efficiency between them could reach its highest value. The surface charge of a particle in suspension is measured as zeta potential (in mV).

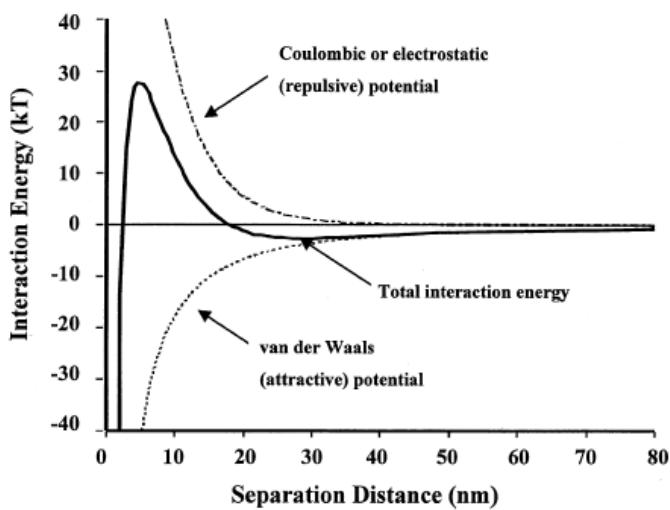
More precisely, zeta potential is defined as the potential difference within the electric double layer (EDL) of a solid-liquid interface. The EDL is divided into the Stern layer and the diffuse layer. The Stern layer is formed by solvent molecules and adsorbed species that are in direct contact with the particle surface. The diffuse layer contains the accumulation of non-adsorbed ions surrounding the particle by the action of the electric field. Both layers are separated by a shear plane. Zeta potential is the potential at the shear plane, whereas the potential at the Stern layer is called Stern or streaming potential. **Figure 10** illustrates the possible allocation of charges around a dispersed particle in a solution. If a particle has a negative charge, a layer of positive ions encircles the particle forming the Stern layer. The diffuse layer is constituted by an equilibrium of positive and negative ions. Positive ions are attracted to the particle charge but repelled by the Stern layer, while negative ions are attracted to the positive charge of the Stern layer but repelled by the particle (Ghernaout, 2017).



**Figure 10** Schematic representation of the electric double layer (EDL) in a particle with a negative charge (C. Schoemaker *et al.*, 2012).

Customarily, the surface charge of microbubbles in aqueous solution is negative (Takahashi, 2005). Bubble zeta potential is highly dependent on pH. As a result, Takahashi suggested in his paper that bubbles had a negative surface charge because water-bubble interface had higher tendency to adsorb OH<sup>-</sup> than H<sup>+</sup> ions. Moreover, the high dielectric constant of water causes particles in suspension to carry a negative charge on their surface (Han, 2002), resulting in electrostatic repulsion that prevents bubbles and particles from coming into contact.

According to DLVO theory (named after Derjaguin, Landau, Verwey and Overbeek), electrostatic forces in the particle EDL coexist with van der Waals forces. For interparticle distances lower than approximately 5 nm, these forces are independent and related to the distance between two particles. For particles to attach, or particles and bubbles, the repulsive electrostatic forces must be overcome, leading to attraction due to van der Waals forces as shown in **Figure 11** (Adair, Suvaci and Sindel, 2001). These phenomena can explain why there is no substantial variation in attachment efficiency with the increase in zeta potential of particles below point zero of charge (pzc). Thus, only neutralization is needed for a favorable flotation (Edzwald, 1995; Han, Kim and Dockko, 2001; Han, 2002).



**Figure 11** Interaction energy between two particles as a function of separation distance. (Adair, Suvaci and Sindel, 2001).

In practice, a standard method to increase the efficiency of the DAF process is to neutralize the charge of the solid matter through the use of coagulants in a pretreatment stage. However, there is the possibility of altering the charge of the bubbles to increase the attraction to the negative particles, hence zero or very low coagulation is needed (Edzwald, 2010). This could be attained by the addition of surfactants (Henderson, Parsons and Jefferson, 2008), similar to froth flotation, with the associated problems of discharging possible hazardous chemicals. On the contrary, the presence of particular metal ions at specific pH and concentration can contribute to the generation of positively charged bubbles (Han, Kim and Shin, 2006).

On the other hand, it is more efficient to neutralize the charge of the particles. Therefore, particles stick together forming flocs where bubbles can be entrapped and reduce their density to make them float.

#### 4.2.3. *Bubble and particle size*

Apart from hydrophobicity and charge, bubble and particle size have also a substantial impact in collision efficiency. Collision efficiency is higher when particles and bubbles have similar size. Finer particles require finer bubbles, likewise bigger particles need bigger bubbles for higher removal efficiency (Han, 2002). Moreover, if particles are larger than bubbles, the efficiency is diminished (Han, Kim and Kim, 2007). From the trajectory analysis perspective, the collision efficiency factor is given by the relationship between the bubble and particle size and the critical distance separating them (Han, 2002):

$$\alpha_{bp} = \frac{x_c^2}{(A_b + A_p)^2} \quad (2)$$

where  $\alpha_{bp}$  is the collision efficiency factor (range 0-1) (-);  $x_c$  is the critical distance that separates the bubble and the particle before the attachment is produced (m);  $A_b$  is the bubble radius (m);  $A_p$  is the particle radius (m).

However, bubble entrapment in the flocs should also be considered for bubble size. In this case, as reported by Leppinen and Dalziel (2004), overly large bubbles (more than 150  $\mu\text{m}$  diameter) can have more difficulties to join the aggregates. Therefore, the air inside the bubbles is not used to increase the floatability of the suspended matter in the tank.

### 4.3. Design considerations

This section comprises a summary of the most critical design parameters determining DAF process performance: air pressure, hydraulic loading and air-to-solids ratio. At the end of this section, some examples of design values collected from the literature are given (see **Table 1**). However, optimization tests should be performed for each particular application.

#### 4.3.1. Air Pressure

To operate DAF process, it is necessary to dissolve air under pressure. Then, the pressurized air forms bubbles that are released when the pressure in the system is reduced. The solubility of a gas in a solution depends on the temperature and initial pressure following Henry's Law, which defines how much gas a solution can dissolve:

$$C = H \cdot P_{gas} \quad (3)$$

where  $C$  is the concentration of gas dissolved ( $\text{mol}/\text{m}^3$ );  $H$  is the Henry's constant ( $\text{mol}/\text{m}^3 \cdot \text{Pa}$ );  $P_{gas}$  is partial pressure of the gas (Pa) (Zumdahl and Zumdahl, 2010).

Air pressure dictates not only the solubility of air in water within the system, but also it regulates the size of the produced bubbles. In addition, the pressure drop through the nozzle, where the air is injected into the system, has a significant effect on the bubble size. Higher pressures are related to smaller bubble diameters and the larger amount of bubbles (Han *et al.*, 2002; Han, Kim and Kim, 2007). The average design pressure recommended by literature is 56 psig (~3.8 atm) (Shammas and Bennett, 2010).

#### **4.3.2. Hydraulic loading**

Hydraulic loading (often in  $\text{m}^3/\text{m}^2\text{d}$  or  $\text{m}/\text{d}$ ) is defined as the flow entering the process per unit of surface area of the flotation chamber. It is strictly correlated with the rise rate and, hence, with the residence time of the suspended solids. For particles to be successfully removed by flotation, they need to have sufficient velocity to travel through the height of the flotation tank. In theory, in the case of an ideal flotation chamber, this is achieved when solids rise rate equals or surpasses to the hydraulic loading (Wang, Fahey and Wu, 2005).

$$A_T = \frac{D}{T} = \frac{Q}{A_s} \quad (4)$$

Equation (4) shows the relationship between the rise rate of solids  $A_T$  ( $\text{m}/\text{s}$ ); depth of the tank  $D$  ( $\text{m}$ ) and retention time  $T$  ( $\text{s}$ ) ratio; and hydraulic ratio defined as inlet flow rate  $Q$  ( $\text{m}^3/\text{s}$ ) by chamber surface area  $A_s$  ( $\text{m}^2$ ).

#### **4.3.3. Air-to-solids ratio (A/S)**

Air-to-solids ratio is the measure of the flow of air introduced to the system. It is defined as the amount of air leaving the solution due to the pressure reduction in the separation zone per unit of mass of solids to be floated (Srinivasan and Viraraghavan, 2009; Shammas and Bennett, 2010). For a system flow configuration, the air-to-solids ratio is expressed as follows:

$$\frac{A}{S} = \frac{RC_s}{QX_f} (fP_a - 1) \quad (5)$$

where  $A/S$  is the air-to-solids ratio ( $\text{kg air/kg solids}$ );  $R$  is the flow rate of recycle stream ( $\text{m}^3/\text{s}$ );  $Q$  feed flow rate ( $\text{m}^3/\text{s}$ );  $C_s$  is the solubility of air at 1 atm and operating temperature ( $\text{kg}/\text{m}^3$ );  $X_f$  the solids concentration in the feed ( $\text{kg}/\text{m}^3$ );  $f$  is the fraction of air dissolved in the flotation chamber (typically 0.8) (-);  $P_a$  is the absolute saturation pressure (Pa) (Shammas and Bennett, 2010).

This parameter should be optimized because very low air masses could not be sufficient to carry out the flotation. Whereas, consuming more air than necessary results in inefficient usage of the energy to pressurize the excess of air. To do so, recycle rate and air pressure should be controlled according to equation (5).

To summarize, typical parameter ranges for DAF design operation is collected in **Table 1**.

**Table 1** Example of parameter range for DAF design operation (Srinivasan and Viraraghavan, 2009).

Parameter	Range	Unit
Air pressure in saturation tank	172-148	kPa
Air to solids ratio	0.01-0.1	kg/kg
Retention time		
Flotation tank	20-60	min
Pressurization tank	0.5-3	min
Hydraulic loading	24.5-39	m <sup>3</sup> /(day·m <sup>2</sup> )
Recycle	5-120	%

#### 4.4. Pretreatment

Pretreatment comprises coagulation and flocculation, which are common operations applied before water treatment processes, such as flotation or sedimentation. The goal in pretreatment stage is to increase the hydrophobicity of the particles in suspension and to neutralize their surface charge (Crittenden *et al.*, 2012). It is not a mandatory step, but generally, it is executed to augment process efficiency by favoring the formation of flocs. The correct application of pretreatment facilitates floc settlement in the case of sedimentation or their floatability by the action of bubbles, as is the case of DAF (Haarhoff and Edzwald, 2012).

Coagulation is a chemical addition step to destabilize particles in the solution. The most common chemicals used for coagulation are inorganic salts of aluminum or iron, habitually aluminum or ferric sulfate, polyaluminum chlorides or ferric chloride. These salts neutralize the electrical charge at the particle surface, hence flocs can be generated as a result of van der Waals attractive forces. In some occasions, cationic polymers with a high density of charge can be added as coagulant aids to enhance the flocculation (Haarhoff and Edzwald, 2012). In the coagulation stage, not only the coagulant conditions are controlled, but also pH.

Flocculation follows coagulation. In this step, the neutralized particles collide and attach forming larger particles or flocs by mixing (Haarhoff and Edzwald, 2012). Flocculation is slower than coagulation. Nonionic or slightly anionic flocculants, or polymers, with high

molecular weight, can be added to improve the rate of flocculation by increasing particle mass (Crittenden *et al.*, 2012).

Pretreatment with coagulation and flocculation is a typical stage in sedimentation applications. In sedimentation, large flocs are desired to improve settleability of the particles. Nevertheless, the desired floc size for DAF should be less than 100 µm to allow good floatability (better in the range of 25-50 µm) (Haarhoff and Edzwald, 2012). Thus, the chemical consumption in DAF is approximately 30% lower than in sedimentation. Determination of the optimal type and dosage of coagulant and flocculants, including the mixing conditions in the flocculation stage, requires pilot-scale testing (Haarhoff and Edzwald, 2012).

#### **4.5. Efficiency of DAF**

The definition of process efficiency depends on the goal of that specific application. For example, Ahmadi, Mostafapour and Bazrafshan (2017) defined process efficiency in terms of aniline and COD removal. Whereas Amaral Filho *et al.* (2016) and Cadena Moreno (2016) used the percentage of sulfate ions or xanthates eliminated from the feed, respectively. For this study, the main parameter selected to determine the efficiency of the DAF process is colloids and fine removal, indirectly measured as turbidity. The same approach was chosen by Couto, França and Barbosa (2014). In their article, DAF was studied as a treatment to reuse the water produced in the production of aluminum from bauxite.

The efficiency based on turbidity,  $\eta_T$  (%), is calculated as:

$$\eta_T(\%) = \left(1 - \frac{T_e}{T_f}\right) \quad (6)$$

where  $T_e$  is the turbidity in the effluent (NTU);  $T_f$  is the turbidity in the feed (NTU).

#### **4.6. Applications of DAF**

Dissolved Air Flotation (DAF) has been in use as a solid-liquid separation method in water and wastewater treatment since its inception in the 1920s (Kiuri, 2001). Moreover, since the 1960s it has increased in popularity over sedimentation, particularly in countries like Sweden or Finland (Haarhoff, 2008). Nevertheless, the use of DAF to reuse process water in the minerals industry is relatively recent. Currently, only Chile counts on DAF treatment plants,

mainly for recycling filter wastewaters or concentrate thickener overflows in the Cu/Mo extraction process (Azevedo, Oliveira and Rubio, 2018).

DAF is used in many applications as seen in **Table 2**. It is an extended technique for the clarification of drinking water where the effluent from the DAF unit is further treated by filters (Haarhoff and Edzwald, 2012). It can also be used as a primary, secondary or tertiary treatment for municipal wastewater. This technique is gaining attention for sewage applications as well (WWT, 2018). In wastewater from industry, it is successfully applied in fields, such as chemical, pulp and paper or food industries, among others (Viitasaari, Jokela and Heinänen, 1995; Jokela and Immonen, 2003).

One can think DAF should possibly have a niche in the mineral processing industry as a replacement of conventional flotation for the concentration of ores. However, the smaller size of the bubbles makes the recovery of coarser minerals difficult because of their higher weight. Entrainment of fine particles of gangue into the product has been observed with the use of microbubbles resulting in selectivity problems (Rodrigues and Rubio, 2007).

Overall, DAF arises as a promising technique for the treatment and recycle of effluent water in the minerals processing industry. The advantages mentioned above make it a particularly interesting alternative over other conventional water treatment methods. Moreover, numerous studies have proven the potential of DAF to remove pollutants from water in mineral dressing plants (Rodrigues and Rubio, 2007; Al-Thyabat and Al-Zoubi, 2012; Couto, França and Barbosa, 2014; Cadena Moreno, 2016; Azevedo, Oliveira and Rubio, 2018). Therefore, the present manuscript is focusing on the study of the validity and efficiency of DAF to treat wastewater produced in sulfide flotation process plants.

**Table 2**

Applications of Dissolved Air Flotation (Haarhoff and Edzwald, 2012)

<b>Drinking Water Treatment</b>
Clarification in a conventional water treatment plant
Clarification in low-pressure membrane treatment plants and nanofiltration-membrane plants
Clarification in reverse osmosis desalination plants
Treatment of spent filter backwash water
<b>Municipal Wastewater Treatment</b>
Primary clarification
Secondary clarification
Tertiary treatment: Suspended solids removal, phosphorous removal following chemical precipitation
Combined sewer water and storm water treatment
Wastewater reclamation
Thickening of waste suspensions
<b>Industrial Water Supply and Industrial Wastewater Treatment</b>
Chemical industry
Food wastes: vegetable wastes, dairies, meat packing, poultry processing, vegetable oil production
Oil production and refineries
Pharmaceutical plants
Pulp and paper mills
Steel mills
Soap manufacturing
<b>Other</b>
Separation of mineral from ores
Fiber separation in the internal process water recovery in pulp and paper industry
Removal of PCBs at hazardous waste sites
In situ treatment of lakes for algae and seawaters for algae and oil spills

## **EXPERIMENTAL PART**

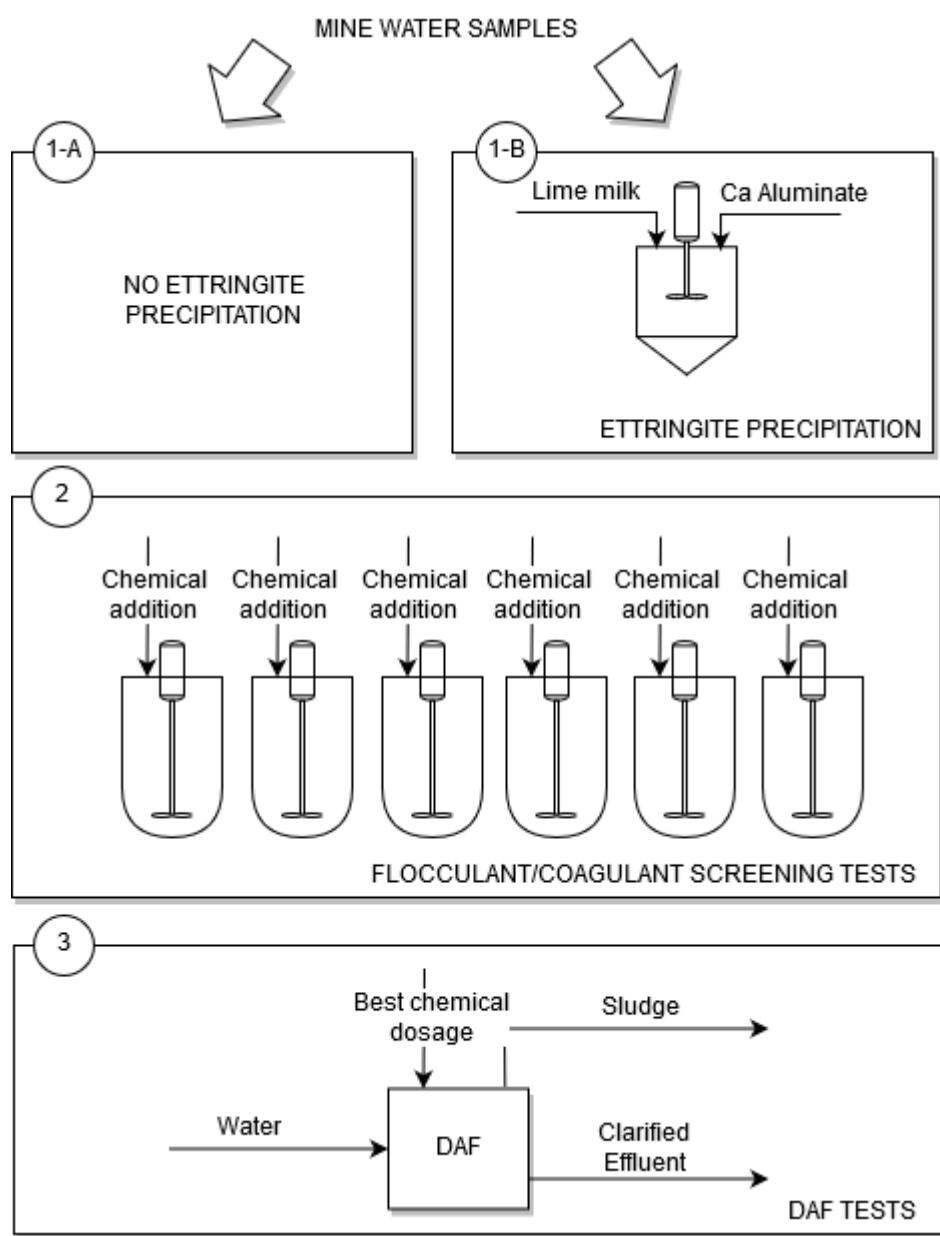
### **Chapter 5. Objectives**

The aim of the present Master's Thesis work is to determine the correlations between the input water quality and the efficiency of DAF process. Moreover, dissolved ions reduction, with special interest on sulfates, is studied by adding a step of ettringite precipitation before DAF separation.

Water samples coming from two minerals processing plants (Mine A and Mine B) are analyzed and tested. From these two mine waters two parallel processes are carried out, which leads to a total of four different experiments to test DAF performance. A diagram is included in **Figure 12** to help the reader to understand the tasks followed during the experimental procedure. As seen in the figure, each mine water goes through either path A, (only DAF) or path B (with preliminary ettringite precipitation step).

Suitable conditions of coagulant and flocculant dosage are found for each sample. In that regard, flocculant/coagulant screening tests are also performed before the flotation tests. The best sedimentation behavior in terms of dosage is replicated to be treated in a DAF laboratory vessel. Finally, the effluent from DAF with lower turbidity for each one of the four water samples is further analyzed to check the performance of the procedure. The characteristics of the input water are analyzed as well.

Furthermore, chemical dosage for ettringite precipitation is also investigated. The amount of aluminate salt added is varied in relation to the molar ratio between lime milk and sulfate content of the sample.



**Figure 12** Diagram of experimental part. Path A: 1) No treatment 2) Flocculant/coagulant screening Tests 3) DAF Tests. Path B: 1) Ettringite precipitation 2) Flocculant/coagulant screening Tests to determine best chemical dosage 3) DAF Tests.

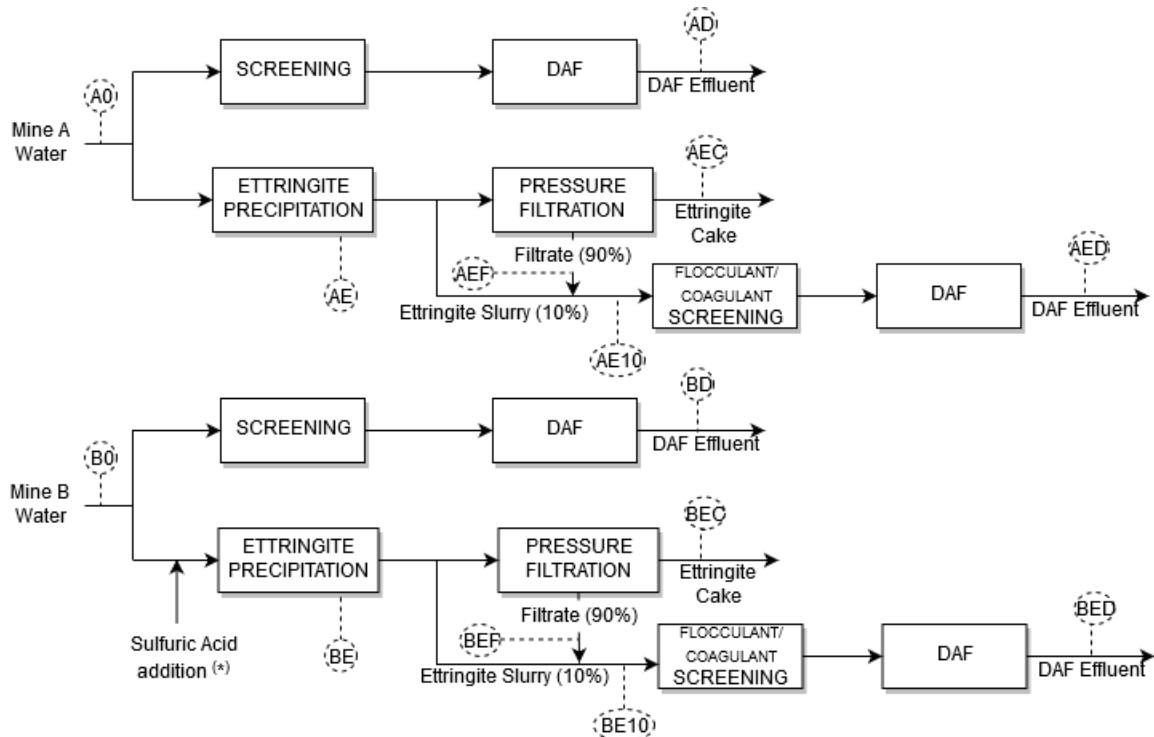
# Chapter 6. Materials and Methods

Experimentation conditions, laboratory equipment, chemicals and materials used are described in this chapter to ensure the repeatability of the research.

The main tests were conducted in Outotec (Finland) Oy Dewatering Technology Center (DTC) facilities in Lappeenranta, while the analyses of water composition were carried out by the laboratory of LUT University.

## 6.1. Testing method and sampling

Both Mine A and Mine B water are treated through two different scenarios. The first one consists of treating the water directly with DAF. The second setup includes ettringite precipitation before solids separation with DAF. In this second situation, a filtration step is also performed after the precipitation to reduce the high solids content produced in ettringite process. The filtrate is used to dilute the original ettringite sludge to 10% and this diluted water is clarified by DAF. Testing method is illustrated in **Figure 13** together with sampling points (described in **Table 3**).



**Figure 13** Detailed testing methodology and sample points. (\*) Addition of sulfuric acid was required due to the low sulfate content of the original Mine B water.

**Table 3** Description of sampling points and parameters analyzed.

Sample Name	Description	Analyzed parameters
A0	Water from Mine A	TSS, TDS, Conductivity, Turbidity, pH, ORP, Dissolved Elements, Sulfate content, Streaming potential
AD	DAF effluent of water from Mine A	Conductivity, Turbidity, pH, ORP, Dissolved Elements, Sulfate content
AE	Ettringite reaction samples every hour from Mine A water	pH, Sulfate content
AEF	Filtrate of ettringite sludge of water from Mine A	Conductivity, pH, ORP, Dissolved Elements
AEC	Filter cake of ettringite sludge of water from Mine A	Solids composition
AE10	Dilution of 10% ettringite sludge with ettringite filtrate of water from Mine A	TSS, TDS, Conductivity, Turbidity, pH, ORP, Dissolved Elements, Sulfate content, Streaming potential
AED	DAF effluent of water from Mine A treated with ettringite precipitation	Conductivity, Turbidity, pH, ORP, Dissolved Elements, Sulfate content
B0	Water from Mine B	TSS, TDS, Conductivity, Turbidity, pH, ORP, Dissolved Elements, Sulfate content, Streaming potential
BD	DAF effluent of water from Mine B	Conductivity, Turbidity, pH, ORP, Dissolved Elements, Sulfate content
BE	Ettringite reaction samples every hour from Mine B water	pH, Sulfate content
BEF	Filtrate of ettringite sludge of water from Mine B	Conductivity, pH, ORP, Dissolved Elements
BE10	Dilution of 10% ettringite sludge with ettringite filtrate of water from Mine B	TSS, TDS, Conductivity, Turbidity, pH, ORP, Dissolved Elements, Sulfate content, Streaming potential
BEC	Filter cake of ettringite sludge of water from Mine B	Solids composition
BED	DAF effluent of water from Mine B treated with ettringite precipitation	Conductivity, Turbidity, pH, ORP, Dissolved Elements, Sulfate content

## 6.2. Chemicals

Chemicals for flocculation and coagulation were used in this work. Flocculant solutions of 2.5 mg/L with tap water were made under constant mixing of 500 rpm during approximately 24 hours. The solutions were kept in cold storage till their use, where they were further diluted up to 0.25 mg/L for easier addition to the water samples. Coagulants were used in liquid form and diluted with tap water to 10% before their addition. The complete lists of coagulants and flocculants used are displayed in **Table 4** and **Table 5**. Other chemicals used are collected in **Table 6**.

**Table 4** List of coagulants

Name	Supplier	Description	Type	Physical State
PIX-105	Kemira	Ferric Sulfate (35-45%)	Inorganic	Liquid
PAX XL-100	Kemira	Polyaluminium Chloride	Inorganic	Liquid

**Table 5** List of flocculants

Name	Supplier	Description	Charge	Molecular Weight	Physical State
Superfloc A120	Kemira	Polyacrylamide	Medium Anionic	Medium	Granular powder
Magnafloc M10	BASF	Polyacrylamide	Low Anionic	Very High	Granular powder
Superfloc N100	Kemira	Polyacrylamide	Nonionic	Medium	Granular powder
Superfloc C491 HMW	Kemira	Polyacrylamide	Very Low Cationic	High	Granular powder
Superfloc C494	Kemira	Polyacrylamide	Medium Cationic	Medium	Granular powder

**Table 6** Other chemicals

Chemical	Composition	Characteristics	Comments
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub> 98% purity		Used to spike Mine B water
Calcium aluminate SRB 710	Al <sub>2</sub> O <sub>3</sub> : 69.6% CaO: 29.5% SiO <sub>2</sub> : 0.4% MgO: <0.5% TiO <sub>2</sub> : <0.4% SO <sub>3</sub> : <0.3% Fe <sub>2</sub> O <sub>3</sub> : 0.2% K <sub>2</sub> O + Na <sub>2</sub> O: <0.5%	Dry powder Size: 38 µm	For ettringite precipitation
Calcium aluminate Makadam	Al: 34.4% Ca: 12.7% Cr: <0.005% SiO <sub>2</sub> : <0.2% Mg: 6.86% Fe: 0.36% Ti: 0.15%	Dry powder Size: 38 µm	For ettringite precipitation
Lime milk	200 g Ca(OH) <sub>2</sub> per L of deionized water	Liquid	

### 6.3. Analysis equipment

The equipment used to characterize the different samples mentioned in section 6.1 is listed in **Table 7**.

**Table 7** Equipment required for water characterization

Measured parameter	Equipment
pH	Thermo Scientific ORION 9107BNMD epoxy body gel-filled triode electrode
ORP	Thermo Scientific ORION 9180BNMD epoxy body gel-filled triode electrode
Conductivity	Thermo Scientific ORION 013005MD conductivity cell
Turbidity	2100P HACH Turbidimeter
Streaming potential	Mütek PCD-05 Travel
Sulfate	Spectrophotometer HACH DR3900 with cuvettes LCK 153 and LCK 353

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Elemental analysis	Inductively Coupled Plasma (ICP) spectroscopy
Solids composition	Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS)

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## 6.4. Total Solids

Total Solids (TS) are the suspended and settleable solids (TSS) together with dissolved solids (TDS). Solids content in water can be determined by gravimetry. A portion of 100 mL of sample is filtered through a 0.45 µm cellulose nitrate filter by vacuum filtration. Then, the retained solids on the filter paper are used to calculate TSS and the filtrate liquid to calculate TDS. Both filter papers with solids and filtrate liquid are dried overnight in the oven at 105 °C ± 2 °C. Finally, the mass of the remaining residue is weighted. For samples with low content of solids, TSS and TDS are compared in terms of turbidity and conductivity respectively.

### 6.4.1. Total Suspended Solids

TSS are measured according to European Standard DIN EN 872:2005 (European Committee for Standardization, 2005). The mass of the filter paper containing the retained solids after filtration minus the mass of the clean filter gives the quantity of suspended solids in 100 mL sample, according to Equation (7). This method has a lower limit of 2 mg/L.

$$TSS = \frac{1000 \cdot (f - f_0)}{V} \quad (7)$$

Where  $TSS$  is the content of suspended solids (mg/L);  $f$  is the mass of dry filter after filtration (mg);  $f_0$  is the mass of filter before filtration (mg);  $V$  is the volume of the sample (mL).

### 6.4.2. Total Dissolved Solids

The filtrate liquid from vacuum filtration with 0.45 µm filter is collected in a beaker to measure TDS. The equation used to calculate TDS is:

$$TDS = \frac{1000 \cdot (b - b_0)}{V} \quad (8)$$

where  $TDS$  is the content of dissolved solids (mg/L);  $b$  is the mass of the beaker after filtration and drying in the oven (mg);  $b_0$  is the mass of the beaker before filtration (mg);  $V$  is the volume of the sample (mL).

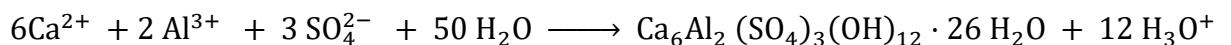
## 6.5. Ettringite tests

Kemira Flocculator 2000 was also used to perform ettringite precipitation tests to maintain rapid mixing speed during the whole experiment. Two different types of calcium aluminates in varying aluminate molar ratios are used. Each vessel contains 1 L of water for the reaction.



**Figure 14** Setup for ettringite precipitation experiments.

The experiments were conducted at ambient temperature and pH above 12 at any case. To calculate the necessary amount of chemicals, ettringite precipitation reaction is considered:



The molar ratio lime:aluminate:sulfate was varied as 6:x:3, keeping lime milk and sulfate constant. However, greater lime milk quantities are added to those tests where the stoichiometric addition is not enough for maintaining the pH at 12 or higher. The amount of chemicals added are calculated according to the following equations:

$$[\text{Al}^{3+}] = \frac{x}{3} \cdot [\text{SO}_4^{2-}] \quad (9)$$

where  $[\text{Al}^{3+}]$  is the required concentration of aluminate (mol/L);  $x$  is the variation coefficient for aluminate addition (values used are 1, 2, 3, 6, 10);  $[\text{SO}_4^{2-}]$  is the concentration of sulfate in the water (mol/L)

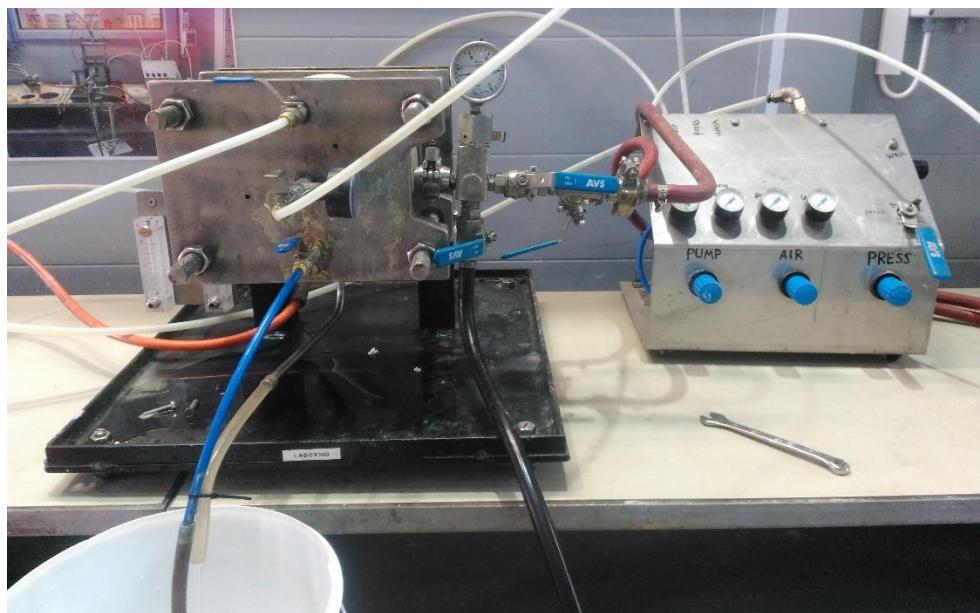
$$\min[Ca(OH)_2] = \frac{6}{3} \cdot [SO_4^{2-}] - [Ca^{2+}]_{aluminate} \quad (10)$$

where  $\min[Ca(OH)_2]$  is the minimum concentration of lime milk added (mol/L); and  $[Ca^{2+}]_{aluminate}$  is the amount of calcium already present in the calcium aluminate powder (mol/L).

The reaction is controlled during approximately 6 hours or till the remaining sulfate concentration is lower than 40 mg/L. Every hour 10 mL sample is collected and filtered with a 0.45 µm Whatman syringe filter to analyze the sulfate content via spectrophotometry. Lime milk is added during the reaction when the pH drops under 12. After the experiments with varying aluminate dosage, the reaction yielding the best performance results is replicated with 35 L sample to be used later for flocculant/coagulant screening and DAF.

## 6.6. Filtration of ettringite slurry

The slurry obtained from ettringite precipitation has a very high content of suspended solids. For DAF tests to work, ettringite sludge is filtered with a pressure filter. The filtrate is then used to dilute the unfiltered ettringite product to 90 % dilution. The equipment used is presented in **Figure 15**, it consists on Outotec® Larox Labox 100 equipped with a 60 mm chamber and polypropylene filter cloth ASKO T54 (air permeability 50 L/dm<sup>2</sup>min).



**Figure 15** Outotec® Larox Labox 100.

## 6.7. Flocculant/coagulant screening tests

In this stage, chemical addition is optimized. Tests with the best performance are selected for treatment with DAF laboratory unit. Preliminary flocculant/coagulant screening is done in beakers with 0.5 L samples and manual agitation. The chemicals with best sedimentation behavior are transferred for jar tests with Kemira Flocculator 2000 equipment, shown in **Figure 16**, in 1 L samples. The speed settings are:

- Rapid mixing for coagulation during 30 s.
- Gentle mixing for flocculation during 10 min.

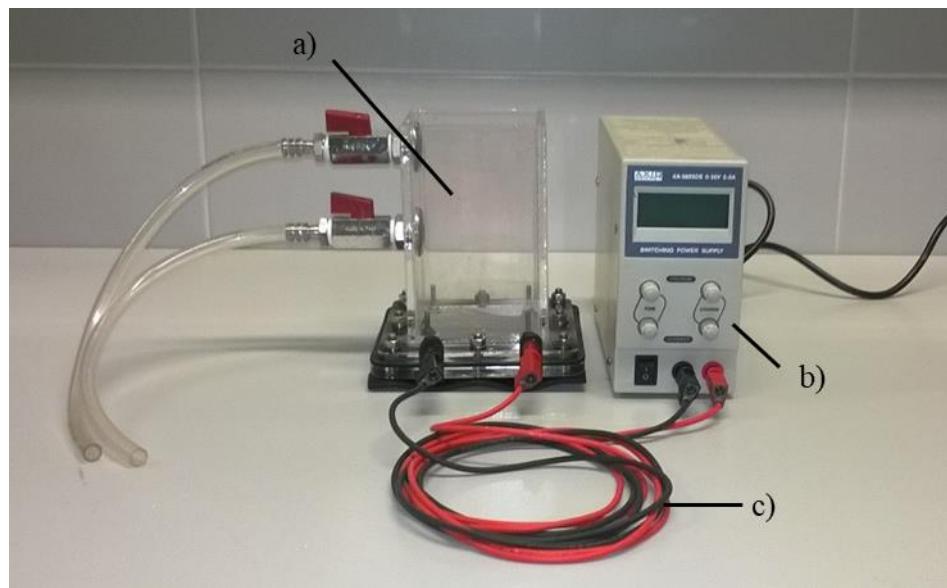


**Figure 16** Kemira Flocculator 2000 equipment.

Best chemical dosage is deduced by qualitative analysis and turbidity measurements of the clarified liquid.

## 6.8. DAF tests

Flotation tests are carried out in a batch DAF electroflotation cell at laboratory scale (see **Figure 17**).



**Figure 17** Laboratory scale DAF. Electroflotation test unit. a) 1 L DAF vessel with electrical and sampling connections b) Power unit c) Electrical cables

The functioning principle is that the electric current generated passes through the electrodes at the bottom of the unit. This electric current breaks some water molecules into H<sub>2</sub> and O<sub>2</sub> gases. The gases produced are released as bubbles of 10 – 50 µm which rise to the surface and drag the suspended solid matter to the top of the vessel forming surface sludge.

Since it is a batch system, the solutions need to be prepared beforehand. For that reason, flocculator is used with the same mixing configuration as in flocculant/coagulant screening tests. The solution is carefully poured in the DAF vessel to prevent floc breakage. Once the solution is in the vessel, the voltage and current of the power unit is slowly increased from minimum. After one minute of bubbling, the power is turned off and the solution is let to float for other five minutes. Extreme bubbling produced by high current values is avoided since it may lead to the rupture of flocs or turbulence inside the vessel. Therefore, the conditions of the test are:

- Voltage: 6 V
- Current: 2 A
- Bubbling time: 1 min
- Floating time: 5 min

Once the test is done, the effluent is collected from the lower valve to be analyzed.

## Chapter 7. Results and Discussions

### 7.1. Characterization of initial samples

The characterized parameters of the two original water samples and the spiked Mine B water are collected in **Table 8**. As it can be seen, the non-spiked water from Mine B contains less solids, both suspended and dissolved, and lower sulfate. Values of turbidity and redox potential are similar in A and B. However, the spiked water presents low pH and higher redox potential values, as expected from the addition of sulfuric acid.

**Table 8** Measured parameters of the initial mine waters

	Mine A (A0 sample)	Mine B (B0 sample)	Mine B (B0 + H <sub>2</sub> SO <sub>4</sub> )
SO <sub>4</sub> <sup>2-</sup> (mg/L)	1716	377.5	1813
Turbidity (NTU)	88.8	62.2	64.0
pH	7.9	8.1	2.0
TSS (mg/L)	126	15	(Below detection limit)
TDS (mg/L)	8300	900	2650
Conductivity (μS/cm)	4190	893	7820
ORP (mV)	153.4	165.5	298.8

In addition, **Table 9** includes the elemental analysis of the aforementioned waters. It is worth mentioning that the increment of the acidity in spiked Mine B by addition of sulfuric acid leads to bigger amounts of some metals, such as aluminum and copper. These metals appear as free ions under low pH conditions (Hong, Duncan and Dietrich, 2010; Albrecht, Addai-Mensah and Fornasiero, 2011). Furthermore, levels of Ca, Na, and K are intrinsically higher in Mine A than Mine B water.

**Table 9** ICP elemental analysis of Mine A, Mine B and Mine B spiked waters.

	Mine A (A0)	Mine B (B0)	Mine B, spiked (B0 + H <sub>2</sub> SO <sub>4</sub> )
<b>Na (ppm)</b>	150.35	46.93	41.88
<b>Mg (ppm)</b>	46.22	14.71	14.58
<b>Al (ppm)</b>	0.13	< 0.0051	0.23
<b>S (ppm)</b>	1007.40	144.20	959.50
<b>K (ppm)</b>	144.57	6.54	6.70
<b>Ca (ppm)</b>	526.85	145.93	206.27
<b>V (ppb)</b>	2.94	0.24	0.30
<b>Cr (ppb)</b>	1.29	1.92	3.14
<b>Mn (ppb)</b>	3.63	1.08	10.10
<b>Fe (ppb)</b>	< 3.22	< 3.22	164.90
<b>Co (ppb)</b>	< 0.11	0.11	< 0.11
<b>Ni (ppb)</b>	< 0.84	0.88	< 0.84
<b>Cu (ppb)</b>	< 0.65	< 0.65	2.43
<b>Zn (ppb)</b>	< 1.04	23.58	12.49
<b>As (ppb)</b>	1.24	1.58	1.51
<b>Se (ppb)</b>	1.74	< 1.17	< 1.17
<b>Mo (ppb)</b>	91.32	11.51	10.47
<b>Ag (ppb)</b>	< 0.0675	< 0.0675	< 0.0675
<b>Cd (ppb)</b>	< 0.078	< 0.078	< 0.078
<b>Sb (ppb)</b>	1.38	1.35	1.35
<b>Te (ppb)</b>	< 2.80	< 2.80	< 2.80
<b>Au (ppb)</b>	6.84	11.99	9.70
<b>Hg (ppb)</b>	4.26	6.08	4.90
<b>Pb (ppb)</b>	< 0.065	< 0.065	1.80
<b>Bi (ppb)</b>	< 0.073	0.10	< 0.073
<b>U (ppb)</b>	15.84	1.67	3.01

## 7.2. Ettringite precipitation tests

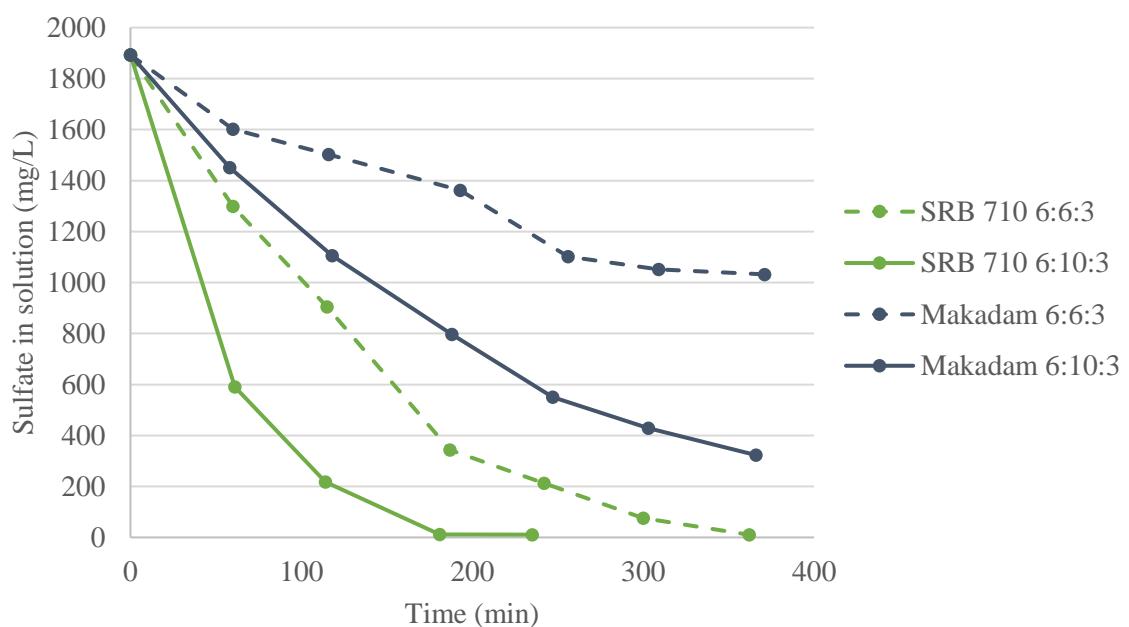
Results for preliminary precipitation tests for Mine A water indicate that stoichiometric calcium aluminate ratios of Ca(OH)<sub>2</sub>:Al:SO<sub>4</sub><sup>2-</sup> are not enough to significantly reduce the amount of sulfate in the water. A summary of the results for molar ratios ranging 6:1:3, 6:2:3 and 6:3:3 is presented in **Table 10**.

**Table 10**

Ettringite precipitation results summary for Mine A (samples AE). Molar ratios 6:1:3, 6:2:3 and 6:3:3

Lime 200g/L (mL/L)	Final pH	Type of Ca-Al	Molar ratio Ca:Al:SO <sub>4</sub> <sup>2-</sup>	Initial SO <sub>4</sub> <sup>2-</sup> (mg/L)	Reaction time (min)	Final SO <sub>4</sub> <sup>2-</sup> (mg/L)	Sulfate reduction
12.7	12.41	SRB 710	6:1:3	1893	361	1356	28%
11.8	12.36	SRB 710	6:2:3	1893	357	1253	34%
11.0	12.30	SRB 710	6:3:3	1893	355	1086	43%
13.0	12.40	Makadam	6:1:3	1893	360	1403	26%
12.5	12.40	Makadam	6:2:3	1893	357	1304	31%
11.9	12.35	Makadam	6:3:3	1893	356	1229	35%

Despite of the elevated final sulfate content, it is clearly seen that higher dosage of calcium aluminate results in greater percentage of reduction. Therefore, tests with increased molar ratio of aluminate reagent are considered. In this case, molar rates of 6:6:3 and 6:10:3 are selected. Sulfate content over time is represented in **Figure 18**, while other parameters of the reaction are depicted in **Table 11**.

**Figure 18**

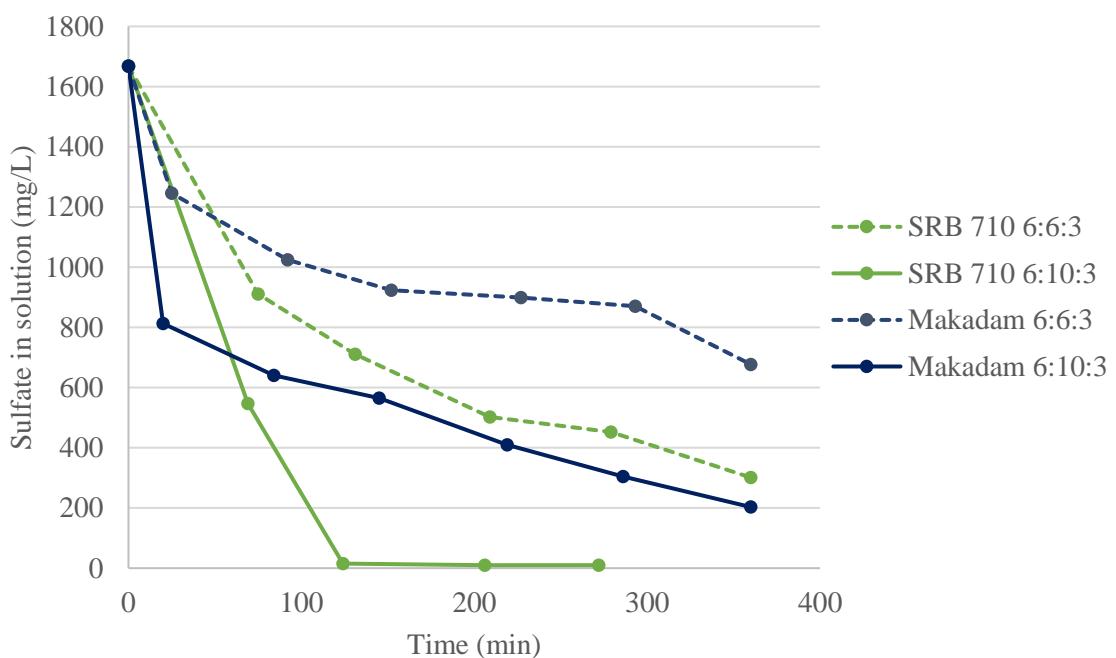
Ettringite precipitation of Mine A water over time for molar ratios 6:6:3 and 6:10:3.

From **Figure 18** it can be appreciated the faster kinetics of the precipitation with SRB 710 reagent over Makadam. One of the reasons for this behavior is the larger content of magnesium in this last one. The presence of  $Mg^{2+}$  ions lessens the removal of sulfates by competing with  $Ca^{2+}$  and  $Al^{3+}$  in the reaction (Dou *et al.*, 2017). In **Table 11** it can be examined in more detail that sulfate concentration after more than 6h of reaction is still greater than 300 mg/L with the addition of Makadam, while SRB 710 reagent achieves reductions over 98%.

**Table 11** Results summary of Mine A ettringite precipitation (samples AE). Molar ratios 6:6:3 and 6:10:3.

Lime 200g/L (mL/L)	Final pH	Type of Ca-Al	Molar ratio Ca:Al: $SO_4^{2-}$	Initial $SO_4^{2-}$ (mg/L)	Reaction time (min)	Final $SO_4^{2-}$ (mg/L)	Sulfate reduction
11.5	12.0	SRB 710	6:6:3	1893	362	<40	>98%
14.7	12.0	SRB 710	6:10:3	1893	235	<40	>98%
10.1	12.1	Makadam	6:6:3	1893	371	1032	45%
9.9	12.0	Makadam	6:10:3	1893	366	323	83%

The results of the ettringite precipitation for the spiked water from Mine B are presented in **Figure 19** and **Table 12**. As well as for Mine A, SRB 710 reagent shows an improved behavior with respect to Makadam. However, the reduction of sulfate is slower than the previous case for all Makadam reagents and SRB 710 with ratio 6:6:3. could be caused by the higher concentrations of Cr, Mn and Fe in B0 +  $H_2SO_4$  sample in relation to sample A0 (Müller Cadorin, 2008). Moreover, it may be also possible that the concentrations of Ca initially in the water and added later to the reaction influence the formation of ettringite. The addition of lime milk to the samples can be compared by looking at **Table 11** and **Table 12**. Ettringite formation in Mine B water required larger quantities of  $Ca(OH)_2$  to maintain pH over time. The extra addition of lime could be produced as a result of the very acidic starting pH and the lower initial levels of Ca in the spiked water from Mine B (see **Table 9**). Also, the lower concentration of Ca in the starting water of Mine B (**Table 9**) may suggest the influence of Ca concentration in ettringite reaction.



**Figure 19** Ettringite precipitation of spiked Mine B water over time for molar ratios 6:6:3 and 6:10:3.

**Table 12** Results summary of Mine B ettringite precipitation (samples BE). For molar ratios 6:6:3 and 6:10:3

Lime 200g/L (mL/L)	Final pH	Type of Ca-Al	Molar ratio Ca:Al:SO <sub>4</sub> <sup>2-</sup>	Initial SO <sub>4</sub> <sup>2-</sup> (mg/L)	Reaction time (min)	Final SO <sub>4</sub> <sup>2-</sup> (mg/L)	Sulfate reduction
17.5	12.0	SRB 710	6:6:3	1668.5	362	302	82%
24	12.0	SRB 710	6:10:3	1668.5	235	<40	>99%
12.3	12.1	Makadam	6:6:3	1668.5	371	680	59%
16.1	12.0	Makadam	6:10:3	1668.5	366	204	88%

The reagent SRB 710 proved to be effective for the elimination of sulfate ions. The proportion 6:6:3 is chosen as the most efficient for achieving acceptable levels of sulfate removal. Therefore, SRB 710 reagent at a proportion 6:6:3 is selected for further analysis and treatment with DAF. The ICP analysis of ettringite reaction performed for both mine waters is included in **Table 13**. In the table, sulfate content and elemental composition of the filtrate from pressure filtration after precipitation is featured along with the data from **Table 9** for better comparison.

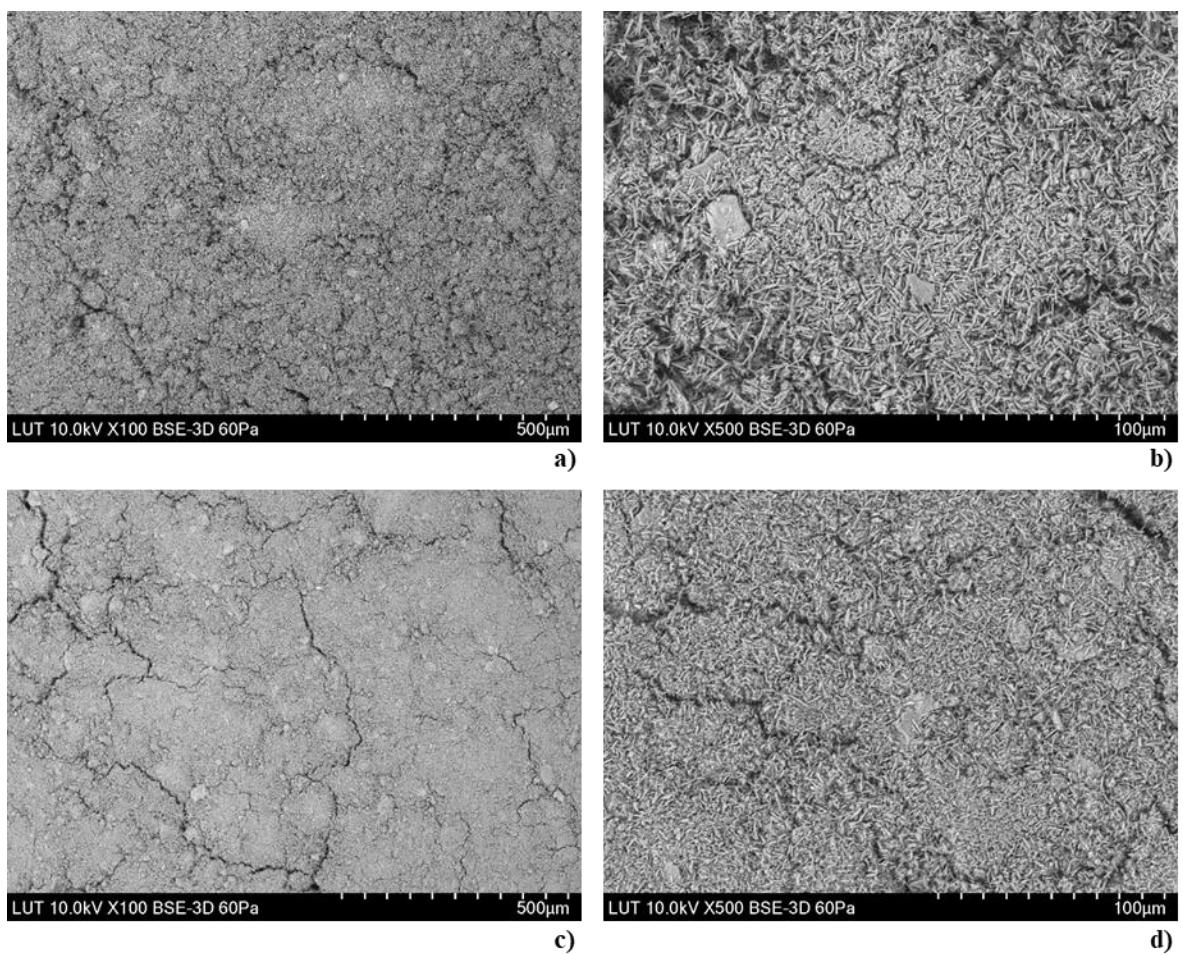
**Table 13** Sulfate content and elemental composition of ettringite filtrates from Mine A and B.

<b>Sample</b>	<b>Mine A (A0)</b>	<b>Mine A Ettringite filtrate (AEF)</b>	<b>Mine B. spiked (B0 + H<sub>2</sub>SO<sub>4</sub>)</b>	<b>Mine B Ettringite filtrate (BEF)</b>
<b>SO<sub>4</sub><sup>2-</sup> (ppm)</b>	1716	<40	1813	<40
<b>S from SO<sub>4</sub><sup>2-</sup> (ppm)</b>	573	<13	605	<13
<b>ICP Elemental composition</b>				
<b>S (ppm)</b>	1007.40	< 58.75	959.50	186.90
<b>Na (ppm)</b>	150.35	183.23	41.88	50.95
<b>Mg (ppm)</b>	46.22	0.18	14.58	0.22
<b>Al (ppm)</b>	0.13	73.96	0.23	164.81
<b>K (ppm)</b>	144.57	133.63	6.70	7.44
<b>Ca (ppm)</b>	526.85	127.72	206.27	148.26
<b>V (ppb)</b>	2.94	1.06	0.30	0.54
<b>Cr (ppb)</b>	1.29	5.52	3.14	252.42
<b>Mn (ppb)</b>	3.63	< 0.52	10.10	147.36
<b>Fe (ppb)</b>	< 3.22	< 3.22	164.90	5.43
<b>Co (ppb)</b>	< 0.11	< 0.11	< 0.11	6.19
<b>Ni (ppb)</b>	< 0.84	< 0.84	< 0.84	174.93
<b>Cu (ppb)</b>	< 0.65	5.28	2.43	< 0.65
<b>Zn (ppb)</b>	< 1.04	12.57	12.49	27.26
<b>As (ppb)</b>	1.24	< 0.122	1.51	0.50
<b>Se (ppb)</b>	1.74	< 1.17	< 1.17	< 1.17
<b>Mo (ppb)</b>	91.33	40.12	10.47	22.68
<b>Ag (ppb)</b>	< 0.0675	< 0.0675	< 0.0675	< 0.0675
<b>Cd (ppb)</b>	< 0.078	< 0.078	< 0.078	0.08
<b>Sb (ppb)</b>	1.38	0.15	1.35	0.39
<b>Te (ppb)</b>	< 2.80	< 2.80	< 2.80	< 2.80
<b>Au (ppb)</b>	6.84	6.53	9.70	5.82
<b>Hg (ppb)</b>	4.26	3.92	4.90	3.34
<b>Pb (ppb)</b>	< 0.065	0.16	1.80	< 0.065
<b>Bi (ppb)</b>	< 0.073	< 0.073	< 0.073	< 0.073
<b>U (ppb)</b>	15.84	0.07	3.01	0.07

As observed in the table, the values of sulfur, together with sulfates were substantially decreased. From the calculations of sulfur present in sulfate by molar stoichiometry, sulfates

in the samples accounted for more than half of the content of sulfur determined by ICP analysis. In addition, other metals amounts have declined, such as magnesium, calcium, vanadium, iron (in Mine B), arsenic, antimony and uranium. However, the samples are richer in aluminum, zinc, chromium and sodium, as well as manganese and nickel for Mine B. The higher Al amounts indicate that not all the Al was eliminated as ettringite after its precipitation.

Finally, the solids cake produced after pressure filtration was characterized by SEM. The SEM microscope images are illustrated in **Figure 20**. In the images, needle-shaped crystals can be appreciated, proving that the main component of the solids is ettringite (Walker, Lane and Stutzman, 2006). Moreover, the size of the crystals formed from the ettringite precipitation of Mine A water are larger than those produced from Mine B water. One of the reasons for that is the lower thermodynamic stability of smaller crystals. Small crystals tend to recrystallize into larger and more stable ones (Baur *et al.*, 2004). Sample AEC was collected few days before performing ettringite precipitation of Mine B water. Hence, crystals of sample AEC had more time to recrystallize and increase their stability than sample BEC.



**Figure 20** SEM images of sample AEC at 100x, a), and x500, b); and sample BEC at 100x, c), and 500x, d).

In addition to the SEM images, the gathered information obtained from the SEM-EDS spectra is prompted in **Table 14**. From the results, the main elements forming ettringite appear: Ca, S, Al and O. Also, some traces of Mg, Si and Cl. The presence of carbon in relatively high proportion can denote the presence of organic compounds in the sample or decomposition of the ettringite by carbonation. The exposure of atmospheric CO<sub>2</sub>, together with the heat used to dry the samples as pretreatment before SEM, could have degraded the ettringite to calcium carbonate, gypsum and aluminum hydroxide (Grounds, Midgley and Novell, 1988). Furthermore, if CO<sub>2</sub> levels are high and there is low presence of H<sub>2</sub>O, ettringite can decompose to aragonite with intermediate phase of vaterite (crystal forms of CaCO<sub>3</sub>) (Myneni, Traina and Logan, 1998).

Theoretical elemental composition of ettringite by weight has been calculated to compare it with the data from SEM-EDS spectra. Molecular formula of ettringite  $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26 H_2O$  excluding hydrogen has been used for the calculations.

Molecular weights: O = 15.9994 g/mol, S = 32.065 g/mol, Ca = 40.078 g/mol and Al = 26.9815 g/mol (NIST, 2018).

**Table 14** EDS of solids filter cake for Mine A and B at 20 kV.

	Mine A (AEC) (Weight%)	Mine B (BEC) (Weight%)	Theoretical Ettringite (Weight%)
<b>C K</b>	3.7	4.2	
<b>O K</b>	53.7	52.0	67
<b>Mg K</b>	0.5	0.3	
<b>Al K</b>	9.1	6.4	5
<b>Si K</b>	0.2	0.4	
<b>S K</b>	8.0	8.7	8
<b>Cl K</b>	0.3	-	
<b>Ca K</b>	24.6	28.1	20
<b>Total</b>	100.0	100.0	100.0

Despite of the similar values for some elements, such as S or Al for Mine B case, the weight percentages of Ca and O are rather far from the theoretical values for pure ettringite. Thus, it is possible that compounds other than ettringite have formed at the precipitation. More studies are needed to determine the existence and type of other precipitates.

### 7.3. Flocculant/coagulant screening and DAF

The best test samples from ettringite precipitation tests (SRB 710 with molar ratio 6:6:3) were selected for flocculant/coagulant screening and DAF tests, where ettringite sludge at 10% dilution was used (samples AE10 and BE10). Screening experiments with the original water samples from each mine, A0 and B0, were also performed.

Ettringite slurry samples (AE and BE) were screened as well, however, the results were deficient due to the high content of solids and the poor settleability of the ettringite product. The thin layer of clarified liquid generated after settling of a non-diluted sample of ettringite slurry is illustrated in **Figure 21**.



**Figure 21** Flocculant/coagulant screening of sample AE. Mine A ettringite slurry without dilution.

The measured values of streaming potential for the four samples A0, B0, AE10 and BE10 are collected in **Table 15**. These values suggest that a cationic coagulant would be appropriate to neutralize the charge of the solids in the liquid.

**Table 15** Streaming potential and titrant consumption of samples A0, B0, AE10 and BE10

	Mine A water (A0)	Mine B water (B0)	Mine A ettringite 10% dil. (AE10)	Mine B ettringite 10% dil. (BE10)
<b>Streaming potential (mV)</b>	-45.5	-30	-121.5	-213
<b>Titrant consumption (μeq/L)</b>	-3.85	-1.93	-1.6	-3.575

The most meaningful results obtained after flocculant/coagulant screening and DAF tests are depicted in **Table 16**, **Table 17**, **Table 18** and **Table 19**. Looking at the data, high removal efficiencies are achievable for every case with the right dosage of coagulant and flocculant. Furthermore, even without chemical addition it is possible to meet a turbidity removal over 50% for the initial mine samples A0 and B0 and over 75% for ettringite samples AE10 and BE10.

Coagulants alone did not show any improvement. Particularly PAX XL-100 proves to be inefficient also with the addition of flocculants for all cases. Nevertheless, PIX-105 did

present enhanced turbidity removal efficiency with the action of flocculants. The samples A0 and B0 presented better behavior by the addition of PIX coagulant together with cationic or non-ionic flocculant, respectively. Regarding ettringite samples, AE10 and BE10, better quality flocs and clearer supernatant liquid was produced with slightly negatively charged flocculant. Sample AE10 required very low dosage of flocculant without coagulation.

It is also worth to mention that those samples where the titrant consumption was higher (see **Table 15**) provided less turbid effluents after flotation tests. Nonetheless, more experiments would be needed to prove a relationship between titrant consumption and final clarity of the effluent.

**Table 16** Flocculant/coagulant screening and DAF main results for sample A0.

		CHEMICALS				ANALYSIS		EFFECT
Run	Equipment	Coagulant		Flocculant		Turbidity (NTU)		Turbidity removal
		ppm	type	ppm	type	in	out	
1	Beaker	-	No coagulant	1;2	Superfloc C491 HMW	88.8	4.0	96%
2	Beaker	-	No coagulant	1;2	Superfloc C494	88.8	5.4	94%
3	Beaker	50	PIX-105	2	Superfloc C494	88.8	4.9	94.5%
4	Beaker	100	PIX-105	2	Superfloc C494	88.8	4.1	95.4%
5	DAF	50	PIX-105	2	Superfloc C494	88.8	2.5	97.2%
6	DAF	25	PIX-105	1	Superfloc C494	88.8	1.8	97.9%
7	DAF	-	No coagulant	-	No flocculant	88.8	42.1	53%

**Table 17** Flocculant/coagulant screening and DAF main results for sample B0.

		CHEMICALS				ANALYSIS		EFFECT
Run	Equipment	Coagulant		Flocculant		Turbidity (NTU)		Turbidity removal
		ppm	type	ppm	type	in	out	
1	Beaker	-	No coagulant	1;2;4;6	Magnafloc M10	62.2	20.7	67%
2	Beaker	-	No coagulant	1;2;4;6	Superfloc N100	62.2	21.0	66%
3	Beaker	50	PIX-105	4	Magnafloc M10	62.2	13.0	79%
4	Beaker	50	PIX-105	4	Superfloc N100	62.2	9.8	84%
5	DAF	50	PIX-105	2	Magnafloc M10	62.2	8.9	86%
6	DAF	50	PIX-105	2	Superfloc N100	62.2	7.2	88.5%
7	DAF	-	No coagulant	-	No flocculant	62.2	19.1	69%

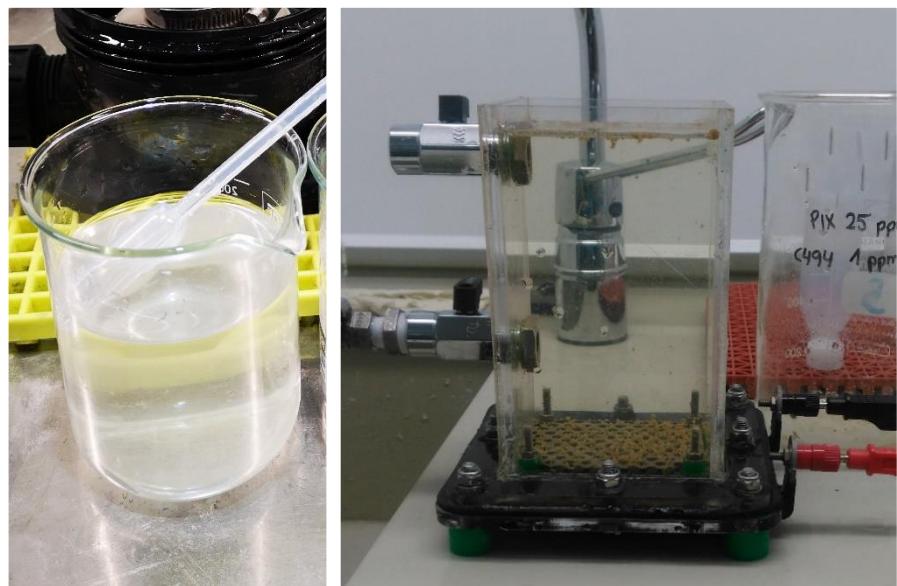
**Table 18** Flocculant/coagulant screening and DAF main results for sample AE10.

		CHEMICALS				ANALYSIS		EFFECT
Run	Equipment	Coagulant		Flocculant		Turbidity NTU		Turbidity removal
		ppm	type	ppm	type	in	out	
1	Flocculator			0.5	Magnafloc M10	715	8.6	98.8%
2	Flocculator			1	Magnafloc M10	715	10.3	98.6%
3	Flocculator			2	Magnafloc M10	715	9.4	98.7%
4	DAF	-	No coagulant	-	No flocculant	715	113.0	84.2%
5	DAF			0.5	Magnafloc M10	715	5.9	99.2%

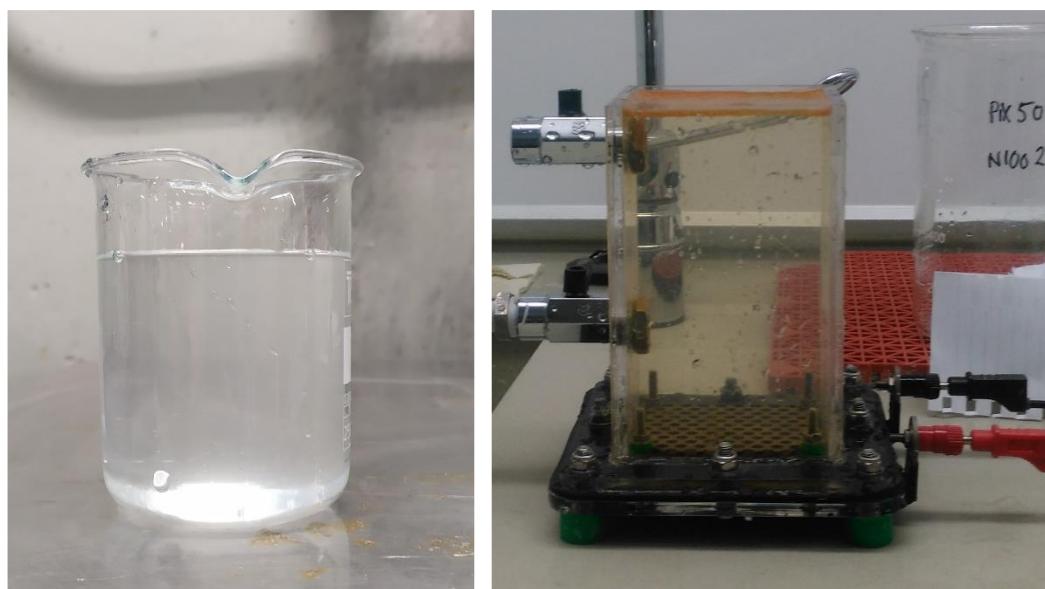
**Table 19** Flocculant/coagulant screening and DAF main results for sample BE10.

		CHEMICALS				ANALYSIS		EFFECT
Run	Equipment	Coagulant		Flocculant		Turbidity (NTU)		Turbidity removal
		ppm	type	ppm	type	in	out	
1	Flocculator	-	No coagulant	1;2;4;6	Magnafloc M10	487	6.0	98.8%
2	Flocculator	-	No coagulant	1;2;4;6	Superfoc N100	487	8.0	98.4%
3	Flocculator	100	PIX-105	2	Magnafloc M10	487	1.6	99.7%
4	Flocculator	100	PIX-105	2	Superfoc N100	487	1.5	99.7%
6	DAF	100	PIX-105	1	Magnafloc M10	487	3.3	99.3%
7	DAF	-	No coagulant	-	No flocculant	487	120.0	75.4%

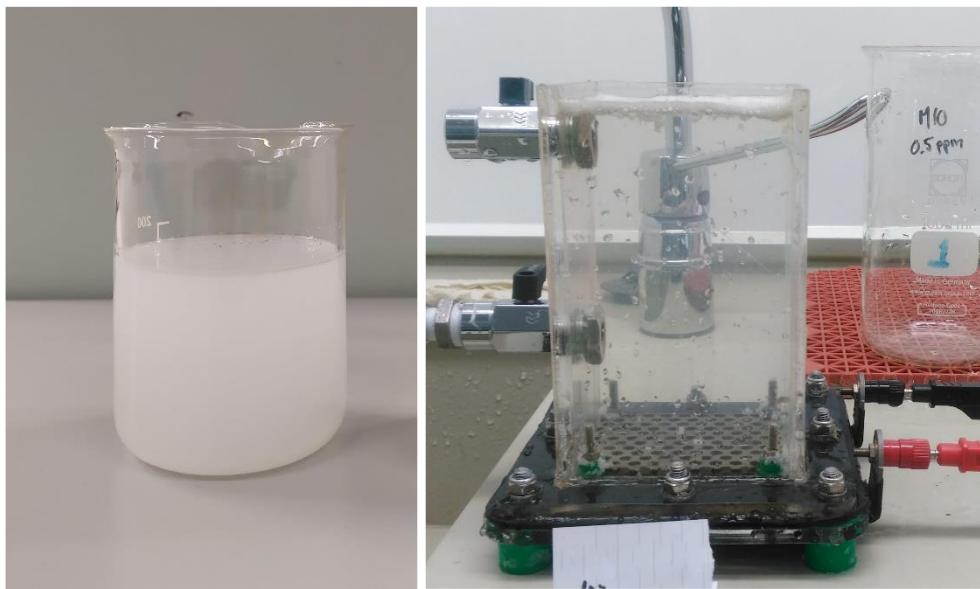
Apart from the information detailed in the previous tables, the flotation experiments with DAF laboratory scale unit that produced effluent of lowest turbidity are displayed in **Figure 22** to **Figure 25** for qualitative examination.



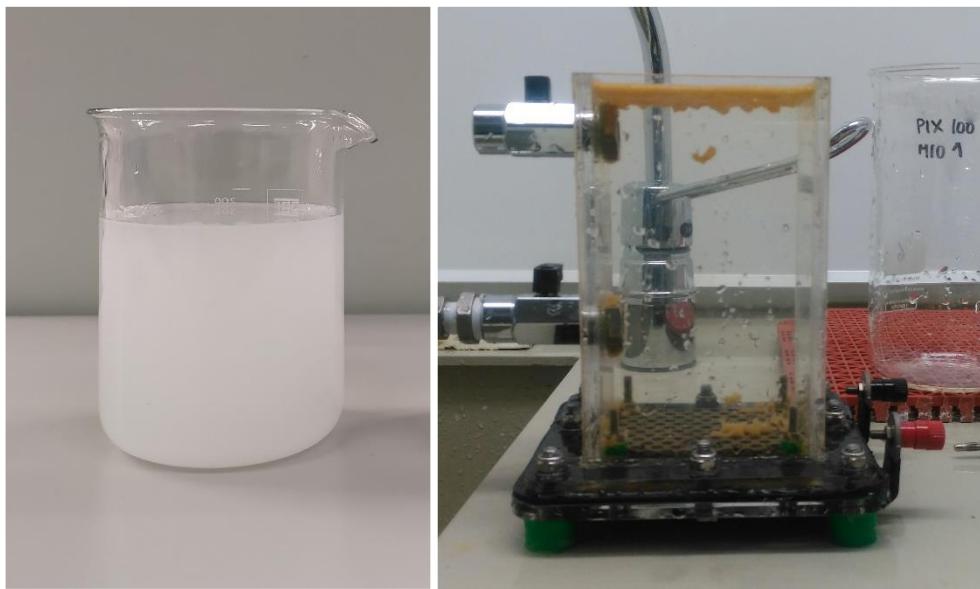
**Figure 22** Left: original Mine A water, sample A0. Right: picture of DAF flotation test after 1 min bubbling and 5 min flotation of sample A0 (the clarified effluent is sample AD).



**Figure 23** Left: original Mine B water, sample B0. Right: picture of DAF flotation test after 1 min bubbling and 5 min flotation of sample B0 (the clarified effluent is sample BD).



**Figure 24** Left: Mine A water after ettringite formation at 10% dilution, sample AE10. Right: DAF flotation test after 1 min bubbling and 5 min flotation of sample AE10 (the clarified effluent is sample AED).

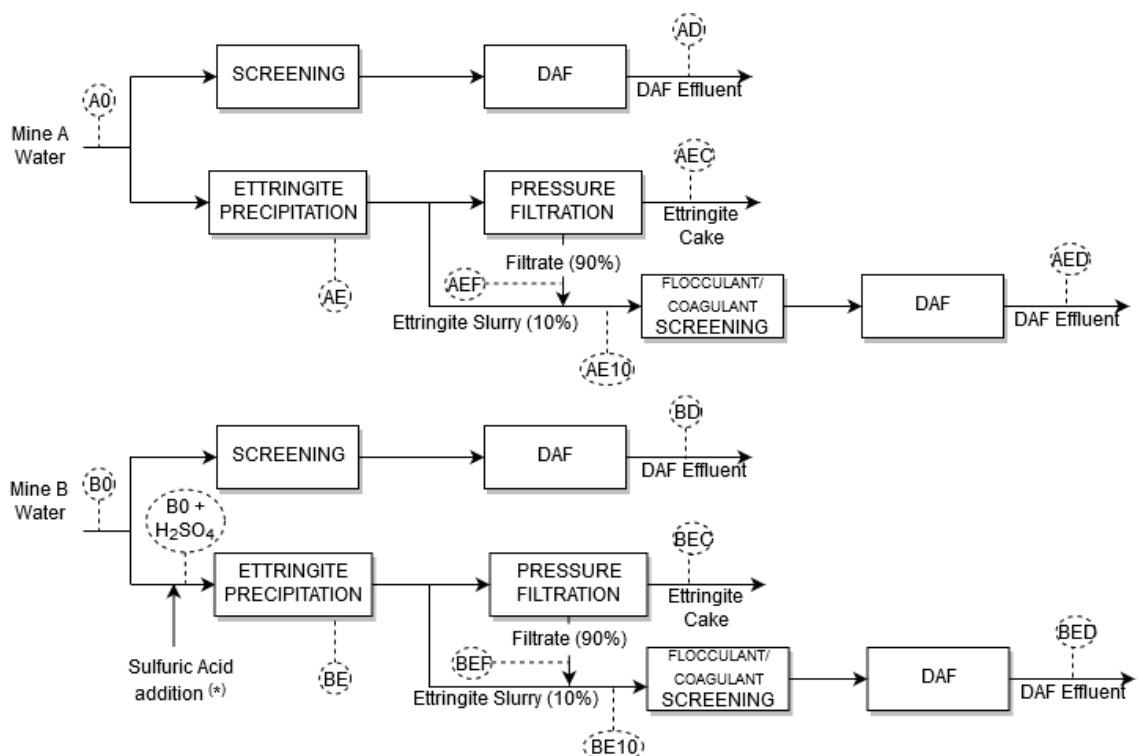


**Figure 25** Left: Mine B water after ettringite formation at 10% dilution, sample BE10. Right: DAF flotation test after 1 min bubbling and 5 min flotation of sample BE10 (the clarified effluent is sample BED).

The pictures show residual flocs settling on the bottom of the vessel which can be related to the nature of the tests performed. Since the DAF unit uses electric current to generate bubbles, some of them are not big enough to carry the flocs or even slightly charged particles can be attracted to the metallic bottom. In addition, bubbling is only turned on during 1 min which can also cause a lack of bubbles to transport all the solids to the surface.

## 7.4. Final sample analysis

Water parameters of the effluents from the best-performance DAF tests and results, together with sulfate amounts, of every stream involved in the process are included in the process diagram illustrated in **Figure 26**. The values of conductivity in the table demonstrate that the process with ettringite precipitation step is able to remove from the water high quantities of dissolved solids together with the suspended solids eliminated via DAF. In addition, the DAF product previously treated by ettringite precipitation presents substantially lower ORP values. Lower redox potential in the water may result in complications to froth flotation after the water is recirculated (Wills *et al.*, 2016).



	A0	AD	AE (final point)	AEF	AE10	AED	
<b>SO<sub>4</sub><sup>2-</sup> (mg/L)</b>	1716	1990	<40	<40	<40	<40	
<b>Turbidity (NTU)</b>	88.8	1.8	>1000	8.0	715.0	5.9	
<b>pH</b>	7.9	7.6	11.4	11.5	11.4	11.3	
<b>Conductivity (μS/cm)</b>	4190	4410	2518	2445	2250	2140	
<b>ORP (mV)</b>	153.4	159.8	80.9	82.1	85.5	-113.1	
	B0	BD	B0+H2SO4	BE (final point)	BEF	BE10	BED
<b>SO<sub>4</sub><sup>2-</sup> (mg/L)</b>	377.5	433	1813	85.1	<40	<40	<40
<b>Turbidity (NTU)</b>	62.2	7.2	64.0	>1000	6.5	487.0	3.3
<b>pH</b>	8.1	7.1	2.0	11.5	11.1	11.0	11.1
<b>Conductivity (μS/cm)</b>	893	933	7820	1499	857	688	886
<b>ORP (mV)</b>	165.5	155.1	298.8	101.7	111.3	107.1	106.2

**Figure 26** Water parameters and sulfate mass balance of the streams.

Lastly, **Table 20** details ICP spectroscopy analysis results and measured sulfates in the treated waters. Also, a summary of the removal efficiencies can be seen in **Table 21**. The process comprised by ettringite plus DAF is proven to be effective in decreasing the content of  $\text{SO}_4^{2-}$  and metals such as Mg, Ca, V, Mn, As, Sb, and U. In addition, Cu, Zn and Fe in Mine B show high removal percentages compared to sample B0 with sulfuric acid. Higher Cr amounts in samples AED and BED than in the original samples has been detected due to the pH of the samples. In this regard, Ben Maaouia, et al. (2018) reported the highest content of Cr (VI) in the leachate of concrete aggregates at pH range 10.2–11.8.

Whereas, the process only involving treatment with DAF does not show lower concentrations of metals. Instead, the sole use of DAF in the process as treatment appears to increase Mg, Ca, Cr and Co quantities, which could be caused by the slightly more acidic values of pH produced after the addition of coagulants. The lower pH could favor the dissolution of metals in the water that cannot be removed by flotation.

**Table 20** Sulfate content and elemental composition of DAF treated samples and initial mine waters.

	A0	AD	AED	B0	BD	B0 + H <sub>2</sub> SO <sub>4</sub>	BED
<b>SO<sub>4</sub><sup>2-</sup> (ppm)</b>	1716	1990	<40	378	433	1813	<40
<b>S from SO<sub>4</sub><sup>2-</sup> (ppm)</b>	573	664	<13	126	145	605	<13
<b>ICP Elemental composition</b>							
<b>S (ppm)</b>	1007.40	1061.30	< 58.75	144.20	< 58.75	959.50	< 58.75
<b>Na (ppm)</b>	150.35	171.22	262.31	46.93	44.81	41.88	49.17
<b>Mg (ppm)</b>	46.22	48.60	0.20	14.71	15.14	14.58	0.16
<b>Al (ppm)</b>	0.13	0.24	76.73	< 0.0051	0.23	0.23	62.04
<b>K (ppm)</b>	144.57	149.49	130.95	6.54	6.48	6.70	7.85
<b>Ca (ppm)</b>	526.85	554.80	103.24	145.93	168.58	206.27	89.90
<b>V (ppb)</b>	2.94	0.60	1.31	0.24	0.69	0.30	< 0.134
<b>Cr (ppb)</b>	1.29	349.62	85.23	1.92	4.98	3.14	55.01
<b>Mn (ppb)</b>	3.63	54.72	< 0.52	1.08	< 0.52	10.10	< 0.52
<b>Fe (ppb)</b>	< 3.22	< 3.22	< 3.22	< 3.22	< 3.22	164.90	4.40
<b>Co (ppb)</b>	< 0.11	4.22	< 0.11	0.11	1.08	< 0.11	< 0.11
<b>Ni (ppb)</b>	< 0.84	222.76	< 0.84	0.88	< 0.84	< 0.84	< 0.84
<b>Cu (ppb)</b>	< 0.65	< 0.65	< 0.65	< 0.65	< 0.65	2.43	< 0.65
<b>Zn (ppb)</b>	< 1.04	4.61	< 1.04	23.58	0.78	12.49	< 1.04
<b>As (ppb)</b>	1.23	0.23	< 0.122	1.58	0.57	1.51	0.47
<b>Se (ppb)</b>	1.74	1.74	< 1.17	< 1.17	< 1.17	< 1.17	< 1.17
<b>Mo (ppb)</b>	91.32	123.49	50.57	11.51	7.72	10.47	15.32
<b>Ag (ppb)</b>	< 0.0675	0.28	< 0.0675	< 0.0675	< 0.0675	< 0.0675	< 0.0675
<b>Cd (ppb)</b>	< 0.078	< 0.078	< 0.078	< 0.078	< 0.078	< 0.078	< 0.078
<b>Sb (ppb)</b>	1.38	1.28	0.16	1.35	< 0.0885	1.35	< 0.0885
<b>Te (ppb)</b>	< 2.80	< 2.80	< 2.80	< 2.80	< 2.80	< 2.80	< 2.80
<b>Au (ppb)</b>	6.84	5.23	6.21	11.99	6.48	9.70	7.18
<b>Hg (ppb)</b>	4.26	3.29	3.01	6.08	3.74	4.90	3.89
<b>Pb (ppb)</b>	< 0.065	< 0.065	0.25	< 0.065	< 0.065	1.80	< 0.065
<b>Bi (ppb)</b>	< 0.073	< 0.073	< 0.073	0.10	< 0.073	< 0.073	< 0.073
<b>U (ppb)</b>	15.84	14.66	0.07	1.66	0.01	3.01	< 0.0062

**Table 21** Removal efficiency after the treatment with ettringite and DAF.

	Mine A	Mine B (starting point B0 + H <sub>2</sub> SO <sub>4</sub> )
<b>SO<sub>4</sub><sup>2-</sup></b>	98%	98%
<b>S from SO<sub>4</sub><sup>2-</sup></b>	98%	98%
<b>ICP</b>		
<b>S</b>	94%	94%
<b>Na</b>	-74%	-17%
<b>Mg</b>	100%	99%
<b>Al</b>	-57657%	-27087%
<b>K</b>	9%	-17%
<b>Ca</b>	80%	56%
<b>V</b>	55%	55%
<b>Cr</b>	-6526%	-1651%
<b>Mn</b>	86%	95%
<b>Fe</b>	0%	97%
<b>Co</b>	0%	0%
<b>Ni</b>	0%	0%
<b>Cu</b>	0%	73%
<b>Zn</b>	0%	92%
<b>As</b>	90%	69%
<b>Se</b>	33%	0%
<b>Mo</b>	45%	-46%
<b>Ag</b>	0%	0%
<b>Cd</b>	0%	0%
<b>Sb</b>	88%	93%
<b>Te</b>	0%	0%
<b>Au</b>	9%	26%
<b>Hg</b>	29%	20%
<b>Pb</b>	-278%	96%
<b>Bi</b>	0%	0%
<b>U</b>	100%	100%

## **Chapter 8. Conclusions and Future Lines of Research**

In the present work, several experiments were carried out to determine suspended and dissolved solids reduction, particularly sulfates, of mine water samples from two different sources. To accomplish said goal, ettringite precipitation followed by DAF has been implemented at laboratory scale. In addition, the influence of water composition in the performance of DAF was tested.

Two different reagents of calcium aluminate were investigated for the reaction of formation of ettringite. The results proved the importance of initial water and reagent composition in the reaction kinetics. In that regard, reagent Makadam showed worse sulfate removal efficiencies for both Mine A and B as a result of its higher concentration of magnesium. Moreover, the lower removal of sulfate for Mine B than in Mine A suggests that the amount of calcium in the initial water and its addition as lime milk also plays an important role in the kinetics of formation of ettringite.

Furthermore, the composition of the solids formed after ettringite precipitation was studied by SEM. The microscope images proved that the main component of the solids was ettringite with its typical needle-shape crystals. However, SEM-EDS spectroscopy analysis points to the possible degradation of ettringite into to calcium carbonate, gypsum and aluminum hydroxide in some extent.

Regarding flocculant/coagulant screening and DAF tests, undiluted ettringite slurry presented very poor settleability that, coupled with the high concentration of solids, made inefficient the treatment by DAF. The flotation of ettringite slurries at 90 % dilution and initial mine water samples achieved turbidities below 10 NTU for the clarified effluent of all cases. These results confirm that turbidities and amounts of suspended solids above certain levels in the water negatively affect the DAF process. On the contrary, quantity and composition of dissolved solids have influence in the dosage and type of coagulants and flocculants but not in the final clarity of the liquid. The values of final turbidity after DAF treatment and the optimum dosage of coagulants and flocculants are summarized in **Table 22.**

**Table 22** Summary of DAF results and chemical dosage

Effluent turbidity (NTU)	Coagulant		Flocculant	
	Name	Dosage (ppm)	Name	Dosage (ppm)
<b>Mine A</b>	5.88	-	-	Magnafloc M10 0.5
<b>Mine A + ettringite precipitation</b>	1.83	PIX-105 25	Superfloc C494 1.0	
<b>Mine B</b>	7.18	PIX-105 50	Superfloc N100 2.0	
<b>Mine B + ettringite precipitation</b>	3.30	PIX-105 100	Magnafloc M10 1.0	

The analysis of the composition of the final DAF effluent demonstrates that ettringite precipitation followed by DAF can effectively decrease the content of  $\text{SO}_4^{2-}$  in the water. Not only sulfates were removed but also metals being Mg, Ca, V, Mn, As, Sb, and U. Therefore, precipitation of ettringite prior to DAF could be an interesting alternative as water treatment of mine process waters to achieve closed water loops and reduce acid mine drainage with lower negative impact in froth flotation.

On account of the previous results, further lines of research should focus on more detailed characterization of the precipitate formed during ettringite reaction. With a better understanding of the product of the reaction, more efficient and sustainable treatment of the solid residue could be assessed. In addition, determining how the composition of the water affects the kinetics of the reaction may result in more accurate selection of reagents and their dosage.

Additionally, pilot plant DAF tests are needed for more accurate results. Laboratory scale DAF uses bubbles generated by electric current and does not allow to customize the parameters of a typical DAF process. It is possible that more concentrated ettringite slurry can be treated with the appropriate configuration of A/S ratio and hydraulic loading. Finally, experiments emulating a closed water loop could help to estimate the impact on froth flotation of the treated water characteristics, such as reduced redox potential or the presence of high concentrations of Al.

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