Do Clay Minerals affect the thickener operation in Chuquicamata mine, Calama, Chile?

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Abstract
Chuquicamata mine mineralogy has been studied performing both X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) to determine whether there is any influence in the thickener operations. The targeted minerals were the clay group because of their detrimental effect on mining operations as modify the rheology of the suspensions. The operation stages most affected by the presence of the clay minerals are gravity separation, milling, conveyor belts, flotation and specially thickener operations. In order to cope with Chuquicamata production, the plant is constantly fed from a neighboring ore called Radomiro Tomic (RT) ore, a secondary sulfide enrichment. At Chuquicamata, the thickener operator feedback has been pointed out that every time the concentrator plant is fed in high ratio with this so-called RT ore the mineral processing is hindered. For this reason, RT ore samples from a critical operation day were sent to Sweden for mineralogical analysis. In addition, flotation tailings from the three Chuquicamata concentrator plants were also sent aimed to perform thickener pilot tests. In this manner, it was seen if it could be possible to achieve new operational strategies in Chuquicamata thickener operations given the current Chuquicamata mineralogy and physical conditions in the flotation tailings.

From the XRD analysis, the following clay minerals were identified in order of abundance:

Illite>>Kaolinite>Smectite

Thus, illite reached up to 23.3vol% being the highest clay amount, followed by lower case kaolinite up to 2.5% and up to 1% of smectite values correspond for the RT sample. However, the clay content in the flotation tailings samples were less than expected. Also, clay Crystallinity was also assessed for its ability to interfere negatively with the pulp rheology, and the results showed that there is a strong link among poor crystallized smectite clay with the semi-autogenous mill compare to those samples where the milling was performed in the traditional steel media. Along with the three clay minerals found, quartz, potassic feldspar, and plagioclase were also identified, accounting for up to 76% of the representative sample. The silicate minerals are thought to be problematic in Chuquicamata thickener operations given its high amount, especially in <2 µm size.

For the thickener tests, three types of polyacrylamide were used plus the current Chuquicamata flocculant. Prior to the sedimentation batch test, the rheology of the flocculants was measured in a range of 0.02%w/w to 1%. It was found that flocculant concentrations between 0.02 to 0.05%w/w the most suitable in terms of avoiding suspension rheology increase. After establishing suitable flocculant concentrations solutions, these were used in the thickener pilot tests at conditions similar to those performed in Chuquicamata thickener operations. Two criteria were used to analyze the best sedimentation conditions: Initial settling rate (ISR); and Turbidimeter. At pH in a range of 11-12 and 15% solid, bridging flocculation probed to be the most suitable conditions for Chuquicamata thickener operations. Moreover, a polyacrylamide blend was tested aiming to achieve high sedimentation performances. The flocculant blend reached both the highest initial sedimentations rate up to 48m/h and turbidity values below 20NTU at addition rate 5g/t and 7g/t. On the other hand, Chuquicamata current flocculant only reached the highest values of 36m/h and turbidity of 40NTU at an addition rate of 5g/t. In this way, the current work established that conditions at Chuquicamata thickener operation can be improved by understanding the absorption process among particle-polymer and mineralogy of the mine.
Hence, the implication of this work to Chuquicamata mine is a better knowledge of its mineralogy especially concerned with clay minerals. It is believed that clay minerals are not the only mineralogical factors that could be hindering thickener operations in Chuquicamata. Other factors that also could be problematic are: high content of silicates; clay crystallinity, particle size and mixed clay. In addition, the improvement in the thickener sedimentation operations will bring better use of the water by increasing the recirculation towards the concentrator area in a friendly way with the environment and communities that also demand water in the arid region of the Atacama Desert.
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Abbreviations and Nomenclature

Si$^{+4}$: Silicon Ion

Cu$^{2+}$: Copper Ion

Ca$^{+2}$: Calcium Ion

Fe$^{2+}$: Ferrous Ion

Fe$^{3+}$: Ferric Ion

Al$^{+3}$: Aluminum Ion

ISR: Initial settlement rate

NTU: Nephelometric Turbidity Units

mm: Milliliters

RREs: Rare Earth Elements

RT: Radomiro Tomic

PSD: Particle size distribution

SAG: Semi Autogenous

SEM: Scanning Electron Microscope

µm: Microns

XMS: X-Ray Mineral Service

XRD: X-Ray Diffraction

XRF: X-Ray Fluorescence
1.0 General Introduction

Mining activity in Chile is one of the main economic contributions, approximately 13.1% of the Gross Domestic Product, 14.3% of the collected taxes and counting for 57% of exports between 2007 and 2018 (COCHILCO, 2018). In the same address, mining activity accounts for 3% of direct and 10% of indirect jobs. Copper extraction is the main mining activity, whereas one-third of the world’s copper production is produced in Chile. During this activity, water is one of the most essential resources as it is used in several stages of the process, especially in the concentration area. In mining activities, water accounts for 4% of the national water consumption, which is quite low compared to other productive sectors. As it is well known a big part of the industry is located in the north of Chile, a region characterized by being located in a place of water scarcity since this area lays upon the driest desert in the world. With only 87mm of rain every year, water in this area is an essential resource for the inhabitants, the agriculture/crops sustainability, and the ecosystem.

In this scenario, the correct management of water resources is necessary for the development and the environmental care of the region. This is the reason why the mine tailings are processed with the aim to recover as much water as possible since it will be re-used in the concentration plant again. Tailings are materials leftovers produced after the process of separating the valuable minerals from the uneconomic fraction of an ore. The main valuable resources at this stage of the process is water. The use of thickeners through the principle of particle sedimentation is often used as the final dewatering stage of the tailings, this being the main process for recovering the processed water.

However, the exploitation of copper ore in the north of Chile is getting more and more challenging. The Chuquicamata porphyry copper mine located in the Atacama Desert is an example. It is currently facing problems such as water scarcity, decreasing copper grades with increasingly complex mineralogy, and increasing mine depth with high contents of clays. Clay minerals are widely present in various ore deposits as gangue minerals. The processing of high-clay content ores is becoming a significant challenge for the mining industry owing to the negative effect on the different steps in the processing plant, especially in both flotation and solid/liquid separation (Chen et al, 2018; Ramsaywok et al 2009).

The Chuquicamata processing plant is currently fed by two ores; the open pit itself from Chuquicamata and a minor proportion from RT ore. The RT ore is located two kilometers south from Chuquicamata and is characterized by oxidation of a secondary sulfide enrichment blanket. The mineralization is differentiated by mineral assemblage into an upper oxide unit with 40% volume of atacamite, 31% of copper clays and minor chrysocolla.

Anecdotal reports from Chuquicamata plant operators state that every time the plant is fed a high proportion a RT ore, a chain of poor performance in flotation and thickener area occurs. It is believed that a high amount of clay within the RT ore is responsible for this poor processing performance. For instance, in flotation the recovery of copper and molybdenum goes down, affecting also the concentration grade. In the thickeners area, the water in the overflow is cloudy, suggesting a high presence of non-flocculated fine particles. The fine particles in the overflow are not flocculated; hence, the flocculation process is affected by the RT ore mineralogy. Furthermore, the energy consumption for the rake and pump system in the thickener increases due to the increase of the yield stress in the solid discharge, leading in many cases to unscheduled stoppages, which have also been reported.
1.1 Geological Setting and Mineralization of Chuquicamata

Chuquicamata is located in the Atacama Desert at about 2800 meters elevation in northern Chile, approximately 8 kilometers north from Calama city. It belongs to the Chuquicamata district comprising RT, Mina Sur, MM and Chuquicamata mine itself (Focke et al, 2010), also called East porphyry, West porphyry, Banco porphyry, and Fine Texture making up in total 5km large 3km wide and 1km deep. The Chuquicamata Porphyry Complex is shown in Figure 1.

Moreover, the Porphyry complex is related to Eocene-early Oligocene porphyritic intrusions that occur within the middle to late Cenozoic Domeyko fault system. The oldest rocks occur in the north part of the deposit being mainly Paleozoic metasedimentary and metaplutonic rocks. These rocks encompass, metadiorite, gneissic granite, quartz diorite. In the pit, fine-grained sedimentary rocks are intruded, and contact metamorphosed by East porphyry of the Chuqui porphyry complex.

The zone’s porphyries are largely affected by potassic alteration. Composed partially of alkali feldspar polymorphs and albite replacement of plagioclase, the alteration is dominated by a more widespread biotite replacement of hornblende with highly preserved igneous texture. Granular quartz apart from quartz-K feldspar veinlets also exist along with the alteration.

The fault system presented in Chuquicamata complex (Figure 1), had a critical control on the formation of mineralized structures and post-mineral displacement of the ore bodies. For instance, a large part of the copper occurrence at Chuquicamata is in veins and veinlets filling faults and fault related to shear zones. Also, in the main orebody, all these fractures have been opened and mineralized more than once (Osandon et al, 2001). In addition, in veins related to shear of the west fault system, there is pyrite, bornite, enargite, digenite, covellite, and minor coarse sphalerite along with sericite. Also, veins of quartz-molybdenite of 5 meters wide cut all the porphyry’s complex.

Main-stage veins running next to the west fault are concentrated along a structural zone that represents a younger, breakable and shallower environment. The main-stage veins, comprising quartz, pyrite, chalcopyrite, and bornite, opened up during the dextral shear of the west fault system. When the sense of shear on the west fault system changed to sinistral, north-west enargite veins also formed.
Figure 1: The Chuquicamata district, geological units and location are showed (Image modified from Zentilli et al, 2018).
1.2 Thesis Objectives

1.1.1 General Thesis Objectives

Given the scenario in Chuquicamata, the objective of the current thesis project is to investigate the mineralogy of RT ore and assess its effect on thickener pilot tests. For that matter, quantifying the mineralogy of RT ore, especially for clay minerals content, is quite difficult because of their grain size (< 2 µm) and the different orientations in its structures. Thus, performing an XRD protocol method is the best way to achieve it. XRF is performed for the chemical composition. Once this information is available, batch thickener tests can be carried out to find the best flocculation conditions for this type of mineralogy.

By finding the best flocculation conditions in the Chuquicamata thickener area, the plant would not only benefit from new operational strategies, but also would be saving costs in terms of energy, unexpected stops, and most importantly, would be recovering high-quality water, optimum for being used once again in the processing plant.

1.1.2 Specific Objectives

This study investigates the following specific objectives:

- Determine both mineralogical and chemical composition of Chuquicamata tailings and RT ore by performing XRD and XRF analysis.
- Develop a protocol on a pilot thickener in order to:
  - Determine the optimum flocculant dosage and flocculant type for Chuquicamata tailing samples. The flocculant optimal dosage has to be such that any further increase in flocculant dosage rate has no further beneficial effect on both water turbidity in the overflow and particle initial settling rate.
  - Evaluate three types of polyacrylamide flocculants; cationic, non-ionic and anionic, and compare their performance with the one used in Chuquicamata thickener operations.
  - Test mix of flocculants with the aim to have more than one way of flocculant-particle-absorption at alkaline conditions.
  - Link Chuquicamata tailings mineralogy to the thickener test performances.
2.0 Literature Review

2.1 Thickening Process

Gravity thickener sedimentation is one of the most widely used techniques for solid-liquid separation in mineral processing. The solid-liquid separation is accomplished in a sedimentation thickener tank (Figure 2) where the solids separate from the liquid phase by settling. The physical mechanism of particles settling in the thickener tank is that the particles have higher specific gravity than the water. The particles can sediment as free particles or as aggregate particles-particles called flocks. In this manner, the primary purpose of thickening is the clarification of the overflow allowing the water to be reused in aims mineral processing operation. Moreover, the thickener aims to thicken the underflow to a required concentration.

What makes thickening a unique technique is its cost-effectiveness, high capacity process, and besides, involves very low shear forces, thus providing good conditions for flocculation of fine particles. The thickening process consists of two overlapping phenomena; sedimentation and consolidation of the suspended particles:

The sedimentation is the settlement of both free particles and particle-particle agglomeration due to the force of gravity. As the particles settle in suspension, they interact between each other hindering its free particle sedimentation velocity.

The consolidation on the other hand, starts when the sedimentation of the particles reaches the bottom of the thickener column and they start to lay down one upon another. If the particles are incompressible, the thickener process ends there. However, if the particles are compressible, like flocculated tail copper minerals, the upper flock weight compresses the lower flock layer, and, the water is squeezed from the flocculated particles. This phenomenon of water elimination by compression is called consolidation (Concha et al, 2001). Figure 3 shows the before mentioned process of sedimentation and consolidation.

*Figure 2: Illustration of a conventional thickener tank from Chuquicamata division, Codelco Norte, Chile (image captured by Reingenieria Minera company).*
2.2 Thickening Equipment

The thickening equipment has not changed much in terms of appearance since its first invention in 1905 (Concha et al, 2001). However, throughout the years the thickener tank size has become bigger and is made of better materials. Nevertheless, the principal components have kept the same. Within the principal thickener components are (Figure 4):

1. **Thickener tank**: is the main structure of the thickener, usually of a cylindrical shape. However, the shape of the base is conical; this allows a better discharge of the solid thickener. The material of the tank can be wood or steel for structures up to 30 meters in diameter, whereas for structures above 30 meters it is used concrete.

2. **Feedwell**: introduces the feeds with a minimum of turbulence and proper distribution into the thickener, prompting fast settling of the particle. In addition, plays a role in providing the best conditions to flocculate the solids, as is the point where the flocculant is added. A pipe or launder supported by the bridge transports the feed to the feedwell.

3. **Rake mechanism**: the rakes can have a variety of forms and types and are aimed to move the settled solids to the point of discharge.

4. **Drive assembly**: provides a torque control of the rake mechanism. If the torque gets too excessive, it automatically launches a safeguard against structural damage by raising the rakes and stopping the drive.

5. **Overflow Launder**: the peripheral launder located outside the tank is aimed to receive the overflow clear water. The hydraulic capacity of a launder must be enough to prevent flooding, which can cause short-circuiting of the feed and deterioration of overflow density.
Given the basic thickener components, three thickener types can be distinguished that differ from each other mainly in the position of the feedwell and the height (Figure 5):

1. **Conventional**: this type of thickener is characterized by its feedwell assembled at the top part of the thickener. As the feed enters the thickener, this one is mixed with part of the recovered water. The dilution formed settle at a constant velocity forming a distribution layer within the tank (see Figure 6 (a); clear water at the top, a middle suspension in the middle of the tank and the thickened sludge at the bottom of it.

2. **High capacity**: This type of thickener is distinguished for a feedwell that is introduced in a deep position that reaches the sludge bed position. Thus, the flocculated feed is mixed directly with the thickened sludge. An advantage of having the feedwell at lower position is that ultrafine un-flocculated particles will remain trapped in the sludge bed. In this manner, the high capacity thickener generates a clear overflow and a dense underflow. For this reason, it is hypothesized that in a high capacity thickener the free settling zone is eliminated, this is typical in a conventional thickener, therefore two zones can be differentiated, the clear water at the top and the thickened sludge at the bottom, as it can be seen in figure 6 (b).

3. **High density**: this thickener can be either a conventional or a high capacity one, but it is characterized by a higher height compared to the conventional and the high capacity thickener. This feature enables to obtain a higher concentration of the thickened sludge.
2.3 Coagulation and Flocculation Process

In order to achieve high base metal recoveries and thus high economical revenues in the mineral processing industry, it is essential to liberate the valuable mineral through a chain of consecutive operations. Among the operations are size reduction, mineral concentration, solid-liquid separation, etc. The key part of these operations is the reduction of particle size as it is the most expensive one, and without it, it is impossible to recover the valuable minerals. It is essential to achieve a size where the valuable mineral can be separated from the gangue, in this manner the process of concentration can work. However, as the high-grade ores are being depleted, it is necessary to get mineral benefaction from low-grade ores. These low-grade ores have a feature of being finely disseminated in the rock matrix, therefore, it requires a higher time of milling to achieve the optimum liberation size. On the other hand, it is well known that flotation is one of the most performed concentration processes, and its efficiency is determined by the range of the particle size (Figure 7). For instance, big liberated particles cannot be suspended by the flotation cell agitation. Moreover, too fine particles or slime cannot be floated as the probability of bubble-particle collision decreases (Gomez et al, 2013). In the same way, it is well known that the particle size is an important variable when it comes to solid-liquid separation, as the slimes particle sedimentation is very slow, thus, low water recovery efficiency is achieved. Given the current
scenario, on the one hand, it is necessary to grind finer to achieve the liberation size, and often by doing so it becomes problematic for the thereafter operations like flotation and dewatering stage for the fine particles created.

The solution to this problem is to grind as fine as necessary to achieve the liberation size and then agglomerate the particles. By agglomerating the particles, bigger particle size is achieved and can be processed downstream in a proper way, without affecting the process. Nevertheless, the agglomeration is performed occasionally in the flotation area, but its main use is in the solid-liquid separation. Since the agglomeration has a bigger size, it not only improves the sedimentation rate in the thickeners stage but also improves the filtration process by improving the cake permeability formed. It can be distinguished three agglomeration processes within the mining industry; (1) coagulation, (2) Flocculation, and (3) hydrophobic aggregation. These processes can be differentiated by their aggregation mechanism, which will be discussed down below.

![Figure 7: Collection of particles in function of the particle size (Gomez et al, 2013).](image.png)
2.3.1 Coagulation

Coagulation is the process of particle aggregation in a suspension based on the repulsion inter-particle reduction, whether by charge neutralization or electric double charge compression that surrounds the particle (Figure 8) in the suspension. The Electric double-layer surrounding the particle can have a thickness up to several hundred nanometers depending on the composition of the liquid environment. The electrical voltage potential decreases considerably with distance from the particle surface, and its magnitude is interpreted with the measurements of the zeta potential, which is the potential at the plane of slip between a particle and the surrounding liquid (Soo-Jin Park, 2006).

![Figure 8: Schematic illustration of the electrical double layer surrounding a particle suspended in a polar liquid (Soo-Jin Park, 2011).](image)

The interaction between particles in a disperse suspension is due to two types of forces; an attractive force limited to ~10nm from the particle surface called Van der Waals, and a repulsive force related to the superficial charges of the particles. These forces explain the stability of the colloid in sedimentation. For instance, particles agglomerating means that the electrostatic forces are small enough, thus the particles can approach enough for the Van der Waals forces to take place.

The particle’s interaction forces have been quantified by the theory of Derjagin-Landau-Verwey-Overbeek (DLVO). The DLVO theory explains the tendency of colloids to agglomerate or separates by combining two curves of electrostatic repulsion and Van der Waals attraction (Figure 9), like this, the net interaction energy curve is formed.
The primary minimum indicates that the repulsive forces are absent, like this, the particles coagulate in a fast and irreversible way. The primary maximum acts as an activation barrier that must be exceeded for the coagulation to occur. In other words, as the particles get close together, they must collide with sufficient energy to overcome the primary maximum. The secondary minimum could be seen as a coagulated weak state, the particles still need to get closer together with enough energy to cross the potential barrier and coagulate at the minimum energy state. The net curve can be manipulated by pH, and the addition of counter-ions, in this manner the double layer of the particles can be decreased, and particles can colloid.

### 2.3.2 Flocculation

Particle agglomeration through the adsorption of long-chain polymers is called flocculation. The long polymers are referred to as flocculants that are added to accelerate the rate of flocculation or the strength the flocks formed in flocculation. The practical applications generally depend on the adsorption of the flocculants onto the surface of suspended particles (Tarleton et al, 2007). The arrangement of the adsorbed molecules will determine the final performance of the process. Moreover, variations in performances can generally be attributed to differences, such in the arrangement. For instance, uneven distribution between the particles due to poor mixing of the polymer solution and particle suspension can lead to a poor solid-liquid separation performance.

Polymer-induced flocculation typically proceeds by two mechanisms:

1) **Electrostatic flocculation**: is the type of absorption due to superficial charges neutralization between low molecular weight polymers and oppositely charged particle surfaces. These create a “patch” on the surface that is electrostatically attracted to regions of the bare surface on other particles. An example would be a cationic flocculant acting on negative charge suspension particles shown in Figure10. If too much flocculant is added, then the surface coverage increases until a reversal of particle charge takes place. At this point, the suspension is likely to return to a dispersed state with particles charged positively rather than negatively.
2) **Bridge flocculation:** is the type of flocculation where the polymer molecules are simultaneously absorbed onto more than one particle as a result of hydrogen bonding between active groups in the polymer chain and hydroxylated sites on the particle surfaces (Figure 11a). The polymer molecules may be uncharged (non-ionic) or partially hydrolyzed as an anionic polymer. For the case of anionic polyelectrolytes added to negatively charged suspension particles, bridging mechanism can still take place, nevertheless, free metal ions need to be presented in the suspending liquid. Ions such as Ca2+ or Cu2+ act as electrolytes bridges between the anionic flocculant and the negatively charged particles (Figure 12). If the concentrations of flocculant are exceeded, the flocculant will be absorbed completely in the particle, leaving no free particle surface that attaches to another conglomerated particle-polymer (Figure 11b). For this reason, exists an optimum flocculant dosage, which needs to be searched according to the different suspensions. In terms of agglomeration efficiency, electrostatic flocculation is usually effective and consistent but results only in relatively small flocs. The most important type of flocculation is the bridge flocculation as it produces the strongest flocs between the particles in the suspension and the polymer flocculant.

![Figure 10: Schematic illustration of the electrostatic flocculation, negatively charged particles and cationic polymer (Tarleton et al, 2006).](image)

![Figure 11: Schematic representation of (A) Flocculation by hydrogen bridge, (B) re-stabilization due to excess of flocculant dosage (Tarleton et al, 2006).](image)
2.3.3 Coagulants and Flocculants

The most important types of coagulants in the mining industry are the salts of multivalent metal ions as in the case of Ca2+, Fe 2+, Fe 3+, and Al3+. All these ions are absorbed by the particle surface to induce coagulation, whether by charge neutralization or electric double charge compression that surrounds the particle in the suspension as was explained beforehand.

It is important to mention that lime is often used in conjunction with the multivalent metal ions, as it can be used as a pH and precipitation control. For instance, when lime is added along with the irons, it ensures that the iron is precipitated as the hydroxide.

On the other hand, flocculants are water-soluble polymers with a molecular weight that ranges from 1000 to 30E6. They are usually provided as white powders that have a limited storage life. While there is always a trend to hide information from supplier to supplier, it is known that most polymer flocculants are based on acrylamide chemistry. Furthermore, for those that carry charge sites are polyelectrolytes and are classified as anionic (negatively charged) and cationic (positively charged) or amphoteric (negatively charge and positively charge sites). Those that are not carrying charge sites are classified as non-ionic. Figure 13 provides a selection of synthetic anionic, cationic and no-ionic polymers.

Natural derived flocculants, on the other hand, have been utilized for many years but their use has been decreased for the high manufacture cost compared with the synthetic polymers. Natural flocculants are made from animal products and plants, such as polysaccharides (guar gums).
2.4 Batch Sedimentation

The batch sedimentation tests are aimed at measuring thickening parameters by simulating the settlement of particles at laboratory scale. The way to carry one test is first to prepare a solution with a known solid percentage and place it into a test tube (Figure 14 a). Right after, as the time runs, and the solid pulp descends, the height of the clear water with the interface pulp is measured. By having the data of the interface solid-clear water height versus time, the so-called sedimentation curve (Figure 14 b) is then possible to plot, from which it is possible to calculate the initial sedimentation rate. The initial rate of sedimentation (IRS) is the slope of the initial linear portion of the sedimentation curve.

By having the initial rate sedimentation plus the water turbidity, it is possible to assess the effectiveness of the flocculant being tested, and the proper flocculant dosage can be found. Turbidity is a measurement of the "cloudiness" of water. It essentially is the manner to assess the amount of fine solids in the overflow water.
2.5 Clay Minerals

Clay minerals are commonly referred to as a group of hydrous aluminum phyllosilicates that are built in a tetrahedral (T) sheets and/or octahedral (O) sheets. Each tetrahedron consists of a cation coordinated to four oxygen atoms, common cations are Si+4 Al+3and Fe+3. The tetrahedral sheets are attached by sharing three corners with basal oxygen atoms. In this way, it forms an infinite two-dimensional hexagonal mesh pattern (Figure 15a). In the case of the octahedral sheets, they comprise six oxygen or hydroxyl ions, which share octahedral edges. The edge-shared octahedral forms sheets of hexagonal symmetry (Figure 15b). Common Octahedral cations are Al+3, Fe+3, Mg+2, and Fe+2.

Moreover, clays minerals are classified as 1:1 and: 1:2. The 1:1 clay mineral consists of the repetition of a single tetrahedral (T) sheet linked with an octahedral (O) sheet. The number of layers in a clay particle depends on the nature of the clay mineral. For instance, illite particle typically consists of 5 to 20 layers whereas kaolinite layer number ranges from 10 to more than 200. In the same address, the numbers of layers for the smectite clay will be determined with the amount of water in its interlayer, moreover, the amount of layer will increase as the water amount is decreased and the other way around.

On the other hand, clays minerals defined as 2:1 consist of a single octahedral sheet sandwiched by one tetrahedral at each side. Hence, the sandwich arrangement forms one layer that can be linked to a similar layer through interlayer cations that can be replaced by other cations. This cationic replacement is quite important as clays of this type can be chemically altered that could lead to the separation of the layers.

The linkage between layers occurs through the sharing of the apical oxygen among the octahedral and tetrahedral sheet. The two sheets consequently link together through weak intermolecular forces. The space in the clay minerals layers is either empty or occupied by cations that compensate unbalanced layer charge. An important feature of these types of bonding is that the water cannot enter between these layers and therefore these clays are called non-swelling clays (Brigatti et al 2006). An example of empty space in between layers is kaolinite and Serpentine clay (Figure 16a), where the interlayers bonding predominates the van der Waals forces with each other. When the interlayer is unbalanced, cationic replacement compensates the layer unbalanced charge, the non-swelling clay illite (2:1 type) is an
example where the charge compensations consist predominantly of K+ or NH4+(figure 16c). On the other hand, swelling clay minerals are those that attract water into the space between clay mineral layers, an example of this clay kind is smectite. The water amount in the interlayer space is in the function of temperature, applied stress, and origin of the layer charge. The water amount in the interlayer space can produce significant yield stress when this type of clay is in suspension even at low concentrations of 3% volume (Ramsaywok et al 2008).

In the natural environment is not common to find clay minerals as homogenous mixtures of single groups. Instead, they comprise assemblages of mixed-layer clay minerals with contrasting structures, basal distance, different layer displacement or rotation between layers. Common examples of clay mixed-layer mineral are illite-smectite, mica-vermiculite, mica-smectite, chlorite-vermiculite and kaolinite-smectite, among others (Barton et al, 2000). The surface properties of the mixed-mineral particles, is not necessary a simple combination of the properties of their constitutive layers. As a consequence, to fully characterize clay minerals within certain ores may be considerably difficult.

Figure 15: (a) tetrahedral sheet where Ob and Oa refers to basal and apical oxygen atoms; (b) Octahedral sheet. a and b refer to unit cell parameters (Brigatti et al. 2006).
2.5.1 Clay mineral surface characteristic

Clay mineral surfaces are anisotropic and platy morphology, this means that clay particles have an edge and face with different characteristics (Figure 17a). The face of the clay is the larger surfaces and narrow thickness. Also, clay mineral face is characterized by a pH-independent negative surface charge resulting in an isomorphous substitution of cations in the clay layer with lower valency cations. The tetrahedron typically Si$^{4+}$ is substituted with Al$^{3+}$. In the same way, the clay octahedron sheet Al$^{3+}$ is substituted with Mg$^{2+}$ or Fe$^{2+}$. On the other hand, the edge of clay mineral particles can carry either a positive or negative charge depending on acid or alkaline conditions. However, the resulting clay overall charge in most common flotation conditions is negative (Basnayaka et al, 2018).

As a result of the clay anisotropic behavior, in suspension they can be as a single disperse particles or as agglomeration as it can be seen in Figure 17b. When clay aggregates, three modes of linkage can occur, face to face (F-F), edge to face (E-F) and edge to edge (E-E). These associations will be determined by attractive forces of Van der walls and electrostatic forces that exist in suspended particles. Hence, the interactions among clays are both pH and counter ions dependent. Moreover, the EF and the EE structures create three-dimensional “house of cards”, when the matrix of their structure fills the total available volume, the rheology of the suspension increase. The viscosity of the suspension is proportional to the number of these EF and EE linkages, and to the strength of individual linkages.
2.5.2 Clay Mineral Identification and Quantification

XRD has been the most suitable method to identify and quantify clay minerals (Kahle et al, 2002). The analysis is based on measuring the basal spacing between equivalent crystal plane at a specific angle and x-ray of known wavelength according to Bragg’s law:

\[ d = n \frac{A}{2\sin\alpha} \]  

(1)

where \( d \) = basal spacing; \( n \) = order of diffraction; \( A \) = X-ray wavelength; and \( \alpha \) = diffraction angle. Thus, the diffraction spectra at different angles corresponding to a specific clay mineral basal spacing, as the resulting diffraction spectra peaks are matched against those patterns of all known crystalline substances in the powder diffraction database. Advanced computer software is available for such applications. In the same way, the diffraction peak intensities are used for quantitative estimations. When the basal space is overlapped like the case in smectite and chlorite, for instance, the measurements are based on specific diffraction peaks shifts followed by solvation with specific ions and heating treatment (Artiole et al, 2017). Scanning Electron Microscopy (SEM) and thermal analysis (TA) are also methods performed for identifying clay minerals but mainly used as complimentary mineral characterization of the XRD analysis.

2.6 Effect of Clay in Minerals Processing

Clay minerals are widely present in several ores (iron, base metals, precious metals, coal deposits) primarily as gangue (Ramsaywok et al, 2009). It is commonly agreed that the increase of clay minerals in the deposit is due to the inevitable depletion of high-grade ores, resulting in the processing of more and more low-grade and complex ores with high clay content. The processing of high clay content ore has become a challenge for the mining industry owing to the poor performance in several of the processing steps, including, pumping systems, milling, flotation, solid-liquid separation, gravity separation etc. (Mohan et al., 1993, Shabalala et al. 2011, Ramsaywok et al 2009, Chen et al, 2018).
Broadly speaking, the most common clay minerals present in ore deposits can be classified into three groups (Cheng et al, 2018): Broadly speaking, the most common clay minerals present in ore deposits can be classified into three groups (Cheng et al, 2018):

1. Kaolinite group: typically (1:1) cause lots of gangue entrainment and the suspension viscosity increases only at high concentrations (above 10%).
2. Smectite group: this group (2:1) s one of the most problematic clays minerals in mineral processing as it increases the pulp viscosity even at low concentrations (4%).
3. Illite group: this group of clays (2:1) have the least negative effect on mineral processing, as the viscosity is not affected drastically, only at concentrations above 25% is starting to be problematic.

Researches on clays minerals have pointed out that the negative effect showed in mineral processing is related to the network structures formed in suspension, affecting primarily the rheology of the suspension (Ndlovu et al. 2011). In addition, it is claimed that the type of structure that clay form will determine the complexity of the viscosity. For instance, edge to edge (E-E) and (E-F) network structures are distinguished by non-Newtonian flow with the development of high yield stress and high viscosity in suspension, whereas the formation of face to face yield lowers yield stress and lowers viscosity. Lastly, non-coagulated or dispersed clay also increases the viscosity of the pulp due to its high surface area. Figure 17 shows the dependency of clay structures with pH and shear stress. Although the clay structure is dependent on pH it is also dependent on the type of ore deposit and hence Figure 18 can vary.

![Image](image)  

*Figure 18: Interpretation of the effect of pH on the Bingham yield stress on kaolinite particles in a way of the mode of particle interactions (image modified from Ndlovu et al. 2011).*

The main negative effect of clay minerals on some steps in mineral processing are discussed below:
2.6.1 Crusher, Milling and Classification

In the crusher stage, the performances are reduced as the high clay content ore sticks to the crusher liners and plates while blinding the opening of crushers. To avoid this situation, bypass the ore into the milling is the best alternative when it comes to an ore with high clay content (Connelly et al, 2011).

When it comes to the grinding stage, clay mineral structures affect the rheology of the suspension, and the yield stress, which refers to the stress at which the slurry starts to flow. Higher yield stress in the mill suspension has several direct implications such as, increasing both the mill and pump system power consumption, hinders the breakage rate, and difficult the suspension flowing out of the mill.

Furthermore, as the clay minerals presence increases the rheology within the mill, operations need to be held under low densities leading to run the mill stage at lower throughput, reducing thus the plant capacity. Moreover, the higher viscosity effect in the mill stage in the presence of clay mineral is more noticeable during ultrafine grinding (Connelly et al, 2011)). The transportation problems are related to the mineral getting stick in the surface of the conveyor belt and pump liners, as clay minerals are quite sticky in the presence of water. To address this problem more water is required for a readily transportation through both conveyor belts and pump systems. Also, the rheology problem in the mill stage can be addressed by adding rheology additives aid, such as water-soluble low molecular weight polymers. In this way, mill operations are kept at both low viscosity and density for easier pulp transportation for the next mineral processing stage.

Lastly, gravity and centrifugal device use the movement and gravity differences of the particles to achieve the separation of valuable mineral from the gangue. However, the separation can be negatively affected in the presence of clay, as they alter the rheology of the slurry hindering thus the movement of the particles and difficulties in maintaining the specific gravity differences to achieve particle separation (Wills and Napier-Munn, 2006). Nonetheless, recent studies claim that by using centrifugal gravity concentrators techniques such as Knelson concentrator, clay minerals can be effectively removed from the processing stream (Yu et al, 2017a). Clay minerals are not dense material, hence, they can be separated from denser materials at high both agitation and shear rates. Unfortunately, knelson concentrators are not used in the industry of porphyry copper as it mainly used in the gold industry for its good ability to recover high liberated gold at both low environmental impact and cost.

Nowadays, the Chilean copper industry has been planning to address the clay problems by adding selective flotation of clay minerals on key points in the mine (Ortega, 2018):

1) Clay mineral selective flotation in the hydrocyclone overflow located in the steel media circuit, in this way, increases steel mill capacity and improve flotation.
2) Clay mineral selective flotation before thickener operations. By adding a selective flotation at this point, the particle sedimentation, water quality recovered and filtering, and amount of water sent to the tailings dump can be improved. Additional, economical base metals not recovered in the previous flotation can be recovered.

The setting up of any new selective flotation requires large planning that encompasses investigations to develop operational strategies for fine particles flotation, cost analysis and the start-up of a new plant stage. Nowadays, there are not Chilean mines that have implemented any of the above-mentioned clay solutions as clay mineral hindering mineral processing is still a mystery in the Chilean mines.
2.6.2 Heap Leaching

Heap leaching is well known as one of the most cost-saving hydrometallurgical techniques for concentrating different metals such as copper, gold, nickel, uranium, among others (Meschac-Bill Kime et al, 1993). Plugging of the pore space is the most relevant contributor to decrease the recovery of the economic minerals as ore permeability is reduced. High clay content is one of the mechanisms that drive the plugging in the leaching operations and high reagents consumption. As mentioned above, clay minerals are usually less than 2 µm with a high surface area and can be classified as swelling and non-swelling clay (Brigatti et al. 2013). In this manner, three mechanisms (Figure 19) have been described for clay minerals plugging the heap leaching:

1) **Migration of clay particles**: this case is for non-swelling clay such as kaolinite (1:1), they tend to detach from the rock surface and migrate, like this, they can get trapped in the pore throat, causing a decrease in the particles pore permeability (Figure 19a).

2) **Swelling of clays particles**: clays like the case of smectites (2:1) can swell water with changing ionic conditions, the increase in the volume of the swelling clay reduces the effective area of flowing causing the reduction in the ore permeability (Figure 19b).

3) **Swelling-induced migration of clay minerals**: When the clay particles swell molecules of water can dislodge fine particles in the process, like this, high chances for the pore to clog (Figure 19c).

*Figure 19: Three different mechanism of decrease on permeability caused by the presence of clay minerals. (a) Migration, (b) swelling and (c) swelling-induced migration (Image modified from Meschac-Bill Kime et al, 1993).*
2.6.3 Flotation

The flotation stage is not the exception of clay minerals hindering the process. It has been well documented the clay minerals issues in flotation (Shabalala et al, 2011, Chen et al, 2018, Jeldrez et al, 2019, Zhang et al, 2015c, Wang et al, 2015b) The main flotation issues can be divided into four categories:

1) **Rheology modification**: it has been highlighted that the dispersion or/and aggregation of clay minerals have a direct influence on the modification of viscosity in suspended particles (see Figure 18). The modification of the rheology in flotation has several direct consequences in the hydrodynamics of the cell. For instance, the increase in the viscosity reduces the gas-hold up, decreases the mobility of particles and bubbles in this way reduce the probability of bubble-particle collision reducing the flotation performance. The hydrodynamic modification will depend on both the type and the concentration of clay minerals. For example, swelling smectite clay at concentrations 5% can alter significantly the rheology of the suspension (Zang and Peng, 2015a; Zang and Peng, 2015b) meanwhile, non-swelling kaolinite at solid concentration 10% affects the rheology suspension. Dispersant additives have been effectively used in reducing the slurry viscosity by preventing clay mineral to agglomerate. In general, the dispersants effective for clay mineral suspensions can be classified into inorganic dispersants and polymer dispersants (Lauten et al, 2014).

2) **Slime coating**: particles tend to coat when there is an electrostatic attraction due to differences of charges in the particle’s surface. Under flotation conditions, clay minerals have a negatively charge under most pH values used. Hence, when the valuable mineral surfaces are positively charged there are high chances that clay coat the desire mineral surface thus restricting the collector adsorption and hindering the bubble-particle attachment. For the case of chalcopyrite and multiple sulfide ores, at alkaline conditions, the particles' surfaces yield a negatively charged same as the clay minerals, and therefore, the clay coating is not possible (Peng et al, 2011). Nevertheless, sulfide minerals tend to become positively charged when they are oxidized and like this, the clay coating can take place due to the differences of charge. For instance, Peng et al (2011) observed that chalcocite flotation was difficulted due to bentonite coating as chalcocite particle surfaces become slightly positively charged in the grinding stage due to oxidation.

3) **Mechanical entrainment**: particle entrainment is the mechanism in which slime particles are reported in the flotation concentrate as they are trapped in the water between bubbles motion, and it does not involve selectivity. Entrainment depends on parameters such as water recovery, gas flow rate, rheology, and particle size. Moreover, the entrainment is more likely to occur in particle size below 30µm, thus clay minerals are the perfect candidate for entrainment in flotation concentrate given its size below 10 µm. The main implication of clay entrainment is that it reduces the grade of the economical mineral.

4) **Froth stability**: froth stability is very important in flotation performance, and it needs to be stable for optimum flotation performances. For instance, if the froth is unstable means that it cannot hold the material recovered, and it will collapse before the collection of froth, resulting in a dropping of the collected material into the pulp again. On the other hand, and overly stable froth layer will lead to problems relating to handling and transportation, increase of gangue entrainment, and thus reducing the economical mineral grade in the concentrate. In this scenario, clay minerals have been reported in a contradictory way regarding froth stability, as clay minerals have been observed that can increase or decrease froth stability. For example, Wang et al. (2015b) observed that froth stability improved in the presence of kaolin. Nevertheless, froth stability
decreased with the addition of bentonite clay. The study from Wang et al (2017) pointed out that froth stability decreases when the pulp contains bentonite is due to the apparent viscosity increased as bentonite is a swelling clay, therefore, results in a poor bubble dispersion given the possibility that bentonite absorbs frother in its surface. On the other hand, the froth stability improvement in the presence of kaolinite minerals can be due to that the entrainment of kaolinite improved froth stability conditions. Since there are contradictory observations on the effect of clay on froth stability, further studies are needed.

2.6.4 Thickening, Filtration and Tailing dam
Thickening as was mentioned in Chapter 2.1 is applied to the dewatering method to separate solids from the water. In this manner, water is recovered and can be reused in the processing plant once again. Also, it was said that flocculants are used to boost the settling of the particles as faster settling behavior of solid is favorable for better thickener performance. Nevertheless, the presence of clay minerals in the thickener has the potential to reduce the efficiency of the process attributing lower solid settlement rates (Harris et al, 2018; Liu et al, 2018). The lower settlement rate of clay minerals is the result of the fine particles <2um, anisotropic particle shape, and low density that in consequence affect the settling rate. This situation can generate a dirty overflow that can cause problems with the downstream process. When the dirty water overflow is recovered the first hassle is reflected in the pump house, which is the place where the recovered water is pumped back again towards the concentration plant. Figure 20 shows Chuquicamata pump house had an unscheduled stop given poor flocculation in the thickener operation. The main consequence of this solid sludge in the pump house are:

1) Pump liners get damage as the fine solids increase the abrasion of the vertical pump liner. Also, the liner material is only considered for water operations only and not pulp form. Therefore, the liner wear-life lasts less, causing the plant to stop replacing the liner and therefore, spent more time and money.
2) The solids present in the pump house get dirty the new water arriving, in this manner the fine solids are returned to the process, generating problems in the concentrator area.
3) Time consuming of the thickener operator, as is the one in charge to remove manually the solid sludge out of the pump house.

Furthermore, clay minerals have been reported to increase the sediment yield stress in the thickener discharge, leading to an increase in the energy consumption of the stirring system and the pump circuit systems. This is attributed to swelling clays increase the yield stress of the sediments in the discharge by absorbing water in its interlayer. Which in turn increases the torque of the thickener stirring system, causing eventually unscheduled stops (Ramsaywok et al 2009).

In some mines companies, the thickener discharge prior to being sent to the tailing dam is filtered to get the maximum clean water recovered, an example is the iron industry. The filtering operates through pressure differences that is applied to the slurry while passing into the filter medium. When it comes to filtering high clay content thickener discharge, the filter medium reduces its porosity and permeability, resulting in a low filterability. A lower filterability is related to a lower throughput rate of large-scale mines such as porphyry copper and iron industry. Another impact of lower filterability is the increase of the moisture in the filtered cake, which increases the cost of transportation and storage (Hung et al, 2017). The lower filterability due to clay problems can be mitigated by adding flocculants in the thickener discharge, in this manner, the clay mineral agglomerates and do not clog the filter media. For instance, in the dewatering studies of Hung et al (2017), improved the dewatering of kaolin by adding a cationic polymer, nevertheless a new polymer addition means extra operational cost.
Right after the tailing slurry is thickened and filtered it is sent to the tailing dam through a pipeline. The thickened and filtered material sent to the dam is composed of 50-70% particles in size range of 10-120 um and the rest is water. The propose of establishing the tailing pond is to safely store tailings to protect the natural environment and people’s life from damage, therefore keeping the tailings pond safe and stable is one of the most important challenge tasks in the entire mining process. When the sludge material that will be discharged in the tailing dam contains high clay amount, two main consequences can arise that can lead to tailing dam failures:

1) **Larger tailing dam is needed**: as it was mentioned above, a large amount of water is lost in the thickener discharge and filtering as clay minerals hinder both processes, in this manner, more water goes to the tailings dam and therefore its height increases. Besides, if the dam permeability is low, the water is discharged at a slow rate, that could result in the overtopping phenomenon, that can drastically affect the stability of the dam. This situation can even lead to more chances of a tailings dam collapsed due to overtopping (Zongjie Lyu et al, 2019). Tailing dam failures is a serious issue worldwide and clay mineral can affect it, however, there is a lack of studies in this matter.

2) **Geotechnical instability**: this point is related to the soil foundations where the tailing dam lays upon. When the foundations of the tailing dam contain a high amount of clay mineral the permeability decrease as the clay absorb water, thus the clay pore pressure increase and the effective stress decrease. The effective stress is the force that keeps a collection of particles rigid, if the effective stress decrease, it can generate the surface to slide downstream generating a tailings dam failure.

An example of this type of failure occurred in the mine Los Frailes, Spain in 1998. The tailing dam failed due to the rockfill foundations slid forward (Zongjie Lyu et al, 2019). Moreover, the tailings dam was built on a surface of high carbonate plasticity clay, known as Guadalquivir blue clays. The design of the dam did not consider the thickness and the lack of permeability of the clay, thus the rate of water flowing out of the tailing dam was slow, generating instability in the soil, and eventually, the soil slid downstream. The catastrophe released 1.3 million m3 of fine pyrite tailings and 5.5 million·m3 of tailings water (Figure 20b), and the consequences still can be seen in the surrounding areas, like in rivers and soil.
Figure 20: Pump house in Chuquicamata mine affected by a poor flocculation process (image captured by Reingenieria Minera company) and b) Illustration of Los Frailes tailings dam failure, Spain, 1998 (Sassoon et al, 1998)
3 Experimental Work

3.1 Introduction
To meet the objectives of the thesis project, it was necessary to design experimental protocols in which it would be possible to assess not only the clay minerals content in Chuquicamata’s tailings and feed but also test the particle settling and flocculation behavior, under different conditions and flocculants types. This chapter is hence to provide a full characterization of the sample, as well as a description of the mineralogy measurements performed. Also, in this chapter a detail description of the thickener pilot test methodology, and a summary of the experimental program is developed.

The mineral samples used in this investigation were taken and sent from Chuquicamata mine site and are described and characterized in section 3.2. The methods and the equipment used to research the mineralogy is explained in section 3.3. The thickener tests to investigate the settling and flocculation behavior of the Chuquicamata’s tailing are described in section 3.4. Finally, the summary of the experimental program is presented in section 3.5.

3.2.1 Mineral Samples
In this research project, seven different sample batch were collected and sent from Chuquicamata mine, Calama, Chile to Lulea University of Technology, Sweden. Six of the seven samples are flotation tailings that feed the thickener operation, whereas the other sample is a pre-milling sample collected in the crushe stage. This pre-milling sample is labeled as “RT” standing for Radomiro Tomic sample, as it is from RT ore, a Chuquicamata neighbor ore deposit. This sample was collected by the thickener operator on November 11th, 2018; during this day both flotation and thickener operation performances were down, and the thickener operator managed to collect samples from the ore that day.

The Flotation tailings from the other side were collected from three different concentrator plants, A0, A1 and A2 on two consecutive days, December 4th and 5th of 2018. Figure 21 illustrates Chuquicmata’s flowsheet linked to the sample point collection of the three different plants. It is worthwhile to mention that the main differences between the concentrator plants are both the comminution and the flotation cells type. For instance, the comminution type of plant A0 and A1 are conventional steel media mill (rod and balls combine), whereas the comminution type in plant A2 is a SAG mill. The flotation cells used in plant A1 and A2 are conventional whereas in the plant A0 the main flotation equipment used is pneumatic cells. Nevertheless, the common characteristics of the plant A0, A1 and A2 are that the concentrate in the flotation overflow goes to a cleaning process followed by reverse flotation to separate copper minerals from molybdenum minerals. On the other hand, the tailings of the flotation process, are sent directly to the thickener area aimed to both recover the water and to reuse it back into the concentrator process and thickening the solid to pump it toward the tailings dam. In this scenario, tailing samples from the flotation stage are collected and labeled as KPA0, KPA1, and KPA2. The “KP” term stands for the Spanish word “Kolas primarias” which means primary tailings.

It is important to mention that KP samples are a mix samples from the Chuquicamata ore itself and in minor proportion with RT ore. However, the ratio of Chuquicamata to RT ore for KP is unknown.
Figure 21: Chuquicamata Flowsheet illustrating at which stage the samples studied were taken (Figure provided by Codelco, Chile).
3.2.2 Polymers and Additives

The polymer reagents used in the flocculation test were three types of polyacrylamides; high molecular weight anionic; low molecular weight cationic; and non-ionic (Figure 22). These polyacrylamides were supplied by the Chinese company Y&X Beijing Technology. In addition, a polyacrylamide flocculant sample used in the Chuquicamata thickener operation was sent to Lulea University of Technology to compare flocculation performances. For reasons of confidentiality, more details about these reagents will not be provided. To match alkaline conditions performed in real thickener operations in Chuquicamata mine, sodium hydroxide (NaOH) 5%wt was used to adjust the pH. The pH was kept in a range between 11-12 and a pH meter brand BERGMAN &BEVING (manufactured in Copenhagen, Denmark) was used to control the pH range before mentioned. Figure 22 shows the three polyacrylamide flocculants plus the Rheomax sample used in current thickener operations and Figure 23 shows the pH Metter set up.

*Figure 22: Image illustration of the Rheomax flocculant sample (left) and the three polyacrylamide (right) used in this study.*
3.3 Mineral Characterization

3.3.1 Particle Size Distribution

The flotation tailing samples were already ground and milled in Chuquicamata comminution operation plants. For this reason, it was just necessary to conduct a particle size distribution and to get a representative sample of each batch for further mineralogical characterization analysis. The particle size distribution of the different samples was determined using a Taylor Mastersizer, manufactured by Taylor, USA (Figure 24a). For getting representative samples a set of different riffles (Figure 24b) were used to get 20 grams of a representative sample of each batch to be further characterized. The results of the particle size distribution, as well as the d80, are presented in chapter 4.
3.3.2 Powder X-Ray Diffraction

Powder X-ray diffraction (XRD) was performed to identify clay minerals presented in the tailing and feed samples. The structural diversity of the clay mineral makes their identification difficult, due to the formation of extraneous organic, carbonates or iron compounds, which often occur and obscure peaks and result in increased peak intensity, which is undesirable for XRD analysis. For this reason, representative samples were sent to a company in the United Kingdom who specializes in clay minerals quantification called X-ray Minerals Services Ltd (XMS).

The procedure that XMS follow is shown in Figure 25. The representative sample is crushed to a suitably small grain size before sample weight reduction. Right after the sample is quartered until achieving a representative sample of 20 gr. Moreover, the sample then is disaggregated gently using a pestle and mortar until reach a ~2gr representative sample. This material is then ‘micronized’ using a McCrone Micronising Mill to obtain an XRD ‘powder’ with a mean particle diameter of between 5-10 µm. This powder is front-packed into an aluminum cavity mount, producing a randomly orientated sample for presentation to the x-ray beam. This procedure is the method for the analysis of the so-called “whole-rock”.

At the same time, a sample of < 2 µm is obtained from the quarter previously done for the whole rock analysis. The size < 2-µm fraction is achieved by ultrasound and centrifugation ready to be mounted in the XRD machine. This analysis is done simultaneously to feedback the whole rock analysis as some clay minerals spectra are not found in a size above 2µm.

Finally, the XRD spectra were obtained using an Analytical X’Pert3 Diffractometer with PIXcel 1-D detector. The samples were run with a copper anode at 40KV, 40Ma. The identification is achieved by using “Traces” and “Search –match” software to compare XRD pattern from the unknown sample with the International Center Diffraction Data (PDF-4 MINERAL DATABASE) containing reference patterns for more than 157.000 phases. Since this method takes only crystalline phases into account, amorphous content is not considered.
Finally, the result is normalized to 100% based on the assumption that the complete mineral content of the sample is accounted for in the diffractogram.

![Diagram](image)

**Figure 25: Illustration of the XRD procedure performed by X-ray mineral services company.**

### 3.3.3 X-Ray Fluorescence Analysis

The elemental composition of each mineral was determined using two different methods: the Bead method for major element analysis and the Pellet method for trace element analysis. The analysis of these methods was done once again by XMS. The calibration of both methods rely on the geologically relevant references that ensures accurate and repeatable analysis. The equipment used in the bead method was Vulcan Automatic Fusion machine and a Rigaku Supermini200 WD-XRF Spectrometer. On the other hand, the pellet method equipment is Pulverisette 6 ball mill, Specac 25-ton press and Rigaku Supermini200 WD-XRF Spectrometer.

The main difference between these two methods is the sample preparation. For instance, the fused bead is the method where the sample is mixed with suitable flux, which is then fused into a glass with a specific diameter. In the pressed pellet method, the sample powder with or without a binding agent, is compressed to get a solid tablet of powder.
3.4 Thickener Test

3.4.1 Experimental Design

An experimental approach was designed before starting any pilot thickener test. Designing an experimental approach is a way to sort out all the experiments that were run in a way to achieve the objectives set up in this research. Table 1 shows a summary of the experimental design. From table 1 five variables were chosen, sample id, pH, solid percentage dosage and Flocculant type. The operation values were selected according to parameters fixed on the High Capacity thickener from Chuquicamata operations. The samples are the flotation tailings from each of the three different plants previously described (chapter 3.2.1). Moreover, four types of flocculants were used in the test at concentrations fixed according to the feedback from the operational mine. The three mixes of polyacrylamide flocculants were studied under the hypothesis to increase the chances of particle-polymer interactions based on the different types of polymer absorption reviewed in the literature review (chapter 2.3.2).

Table 1: Experimental design summary.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample ID</td>
<td>KPA0, KPA1, KPA2</td>
</tr>
<tr>
<td>Flocculant type</td>
<td>Three types of Polycrylamide +Current Chuquicamata flocculant</td>
</tr>
<tr>
<td>Flocculant dosage</td>
<td>4g/t, 5g/t, 7g/t</td>
</tr>
<tr>
<td>pH</td>
<td>11-12</td>
</tr>
<tr>
<td>Solid percentage %w/w</td>
<td>15%</td>
</tr>
</tbody>
</table>

3.4.1 Test Methodology

For the pilot thickener test, the solution was prepared with the six flotation tailings batches at fixed 15%w/w in a total volume of 100ml. This range was chosen for both to match the operation parameters of the high capacity thickener in Chuquicamata and to meet the volume of the test tube used in the pilot test. The solution was stirred for 15 minutes at 300 revolutions per minute (rpm), and the pH was adjusted with sodium hydroxide drops (NaOH 5%w/w) to reach a pH range between 11-12. Right after to reach the desired pH range, the flocculant is added at dosages according to the experimental design (Table 2) and stirred for another two minutes at 300 rpm. Finally, to achieve the sedimentation curve, the flocculated solution is introduced into the 100 ml graduated cylinder. The descent of the supernatant sediment interface was recorded as a function of time, and average readings were taken after inverting the cylinder three times. At the third time of inverting the cylinder and after 30 seconds of the test starting, samples of the water are taken to measure its turbidity. The complete test set up is shown in Figure 26.

The effectiveness of the flocculation process through the different flocculants available in this study was determined by measuring three key parameters:
1) The viscosity of the flocculant solution
2) Initial settling rate (ISR)
3) Turbidity of the clear water

These three parameters, as well as the due equipment, are described in the next subchapter.

![Image of equipment setup](image)

**Figure 26**: Image illustrating the thickener test Set-Up, a) Left the Turbidimeter; in the center the cylinder graduated tube; and in the right the viscometer. In (b) pH meter and the magnetic stirring for sample preparation.

### 3.4.2 Flocculant Rheology Measurements

Identifying the flocculant solution rheology was an important experimental starting point to choose the right dosages of flocculants for the pilot thickener test. As was mentioned before (chapter 2.6.4), high viscosity suspensions values lead to a chain of negative effects within the thickener, for this reason, it is necessary to work at low flocculant solution viscosities. Usually, low viscosities of flocculants are achieved at low flocculant concentrations. Moreover, to get a full characterization of the impact of the flocculant on the viscosity of the pulp, it is highly recommended: to measure the viscosity of the sedimented sludge in the bottom, but in this study was not the case as the viscometer available could not measure it.

For the determination of the flocculant solution rheology, a viscometer BROOKFIELD model DV-II+ was used, and two spindles of different viscosity range were used to achieve the viscosity measurements of the different flocculant concentrations. For the calibration of the viscometer, a Brookfield Viscosity Standard Fluid was used. When verifying the calibration of the DV-II+, the instrument and the viscosity standard fluid error must be combined to calculate the total allowable error. The DV-II+ is accurate (+/-) 1% of any full-scale spindle/speed viscosity range and the Brookfield Viscosity Standards Fluids are accurate to (+/-) 1% of their stated value. The full Rheometer set up is shown in Figure 27.
The viscosity (cp), shear rate (1/sec) and Shear stress (Dynes/cm2) are calculated and displayed in the Viscometer after each packet of data and are obtained from the following equations:

\[ \text{Viscosity}[cP] = \frac{100}{\text{RPM}} \times TK \times SMC \times \text{Torque} \]  
(2)

\[ \text{Shear Rate}[1/sec] = \text{RPM} \times SRC \]  
(3)

\[ \text{Shear Stress} \left[\frac{\text{Dynes}}{\text{cm}^2}\right] = TK \times SMC \times SRC \times \text{Torque} \]  
(4)

where:

**RPM**: Current Viscometer spindle speed in RPM

**TK**: Viscometer torque constant

**SMC**: Current spindle multiplier constant

**SRC**: Current spindle shear rate constant

**Torque**: Current Viscometer torque (%) expressed as a number between 0 and 100.

*Figure 27: Image illustration of the viscometer along with the different spindles and the standard calibration solution.*
3.4.3 Initial Settling Rate

The initial settling (ISR) rates as a function of polymer dosage are based on changing the settling rate by recording the mudline over time, as shown in Figure 28. The slope of the initial portion of the plot is the initial settling rate and its units are in centimeter per second (cm/s). The ISR is directly linked to the flocculation performances under certain conditions. For instance, a good flocculation test yields a high initial settling rate or high initial slope. In the same way, in poor flocculation the settling curve yields a low slope. Consequently, the flocculant type, pH, the dosage and the type of minerals in suspension are key parameters for a high or poor flocculation performance.

Figure 28: Plotting illustration of the settling curve.
3.4.4 Turbidity Measurements

The Turbidity test aimed to evaluate the quality of the water in each sedimentation test according to the test methodology presented. If the water sample contained a high quantity of fine solids, it means poor flocculation performance and high turbidity. On the other hand, the low content of fine solids in the water sample is linked with good water quality related to good flocculation performance.

For the turbidity test, a turbidimeter brand HACH model 2100is, with a maximum range of 1000 Nephelometric Turbidity Unit (NTU) was used. For the calibration of the instrument, standard turbidity samples were measured, and thus a calibration curve is possible to add to the setting of the instrument. The whole turbidity set up is shown in Figure 29.

![Figure 29: Image illustration of the turbidimeter along with the calibration standard samples](image-url)
3.5 Experimental approach

The experimental plan was divided into two phases. The first phase consisted of investigating the morphology of the tailing samples, especially aiming to identify the clay minerals. With a good understanding of the morphology of the samples, the flocculation process could be studied in the second phase. That being said, the second phase encompassed the study of the flocculation process by measuring the initial settling rate and the water quality using a wide gamma of flocculants and also an anionic and non-anionic blend. Additionally, the second phase also encompassed the study of the flocculant rheology for a wide concentration. The experimental program and outcomes of the measurements conducted in this study are summarized in Figure 30.

Figure 30: Experimental programme developed for this study.
4 Results and Discussion

In this chapter, the results are introduced and discussed given the experimental program in chapter 3.5. The first set of the results presented are the particle size distributions of the flotation tailing samples followed analysis by XRF and XRD. Finally, Flocculant dosing rates were determined, and compared well to those currently experienced at the thickener operations at Chuquicamata mine.

4.1 Particle Size Distribution Experiments

The particle size distribution (PSD) showed a good correlation between the six tailing samples as can be seen in Figure 31. However, as expected the PSD of the feed sample (RT) yielded a higher percentage of coarse particles compared to the tailing samples, as the RT sample was taken from the crusher stage. When it comes to comparing the plant’s comminution size type, it is clear that the samples from plant A2 yielded a higher percentage of fines. This can be seen clearly in the particle size distribution (orange line) and from Table 2 where the comminution type is linked with the d80 of the 3 different plants. Hence it can be stated that the ore of Chuquicamata mine achieves a smaller particle size in the SAG mill, as it creates a higher quantity of fine particles when it is compared with the steel media mills from plant A0 and A1.

In this work, the effect of the particle size in the thickener pilot test was not assessed, since the samples were not separated into size fractions, on the contrary, they were treated as homogenous sample. The direct implication by not assessing the particle size fraction effect into the thickener pilot test is that it is not possible to point out if Chuquicamata particle size is the most suitable size for the thickener sedimentation operations. For instance, from the work studies performed by Garmirsi et al (2017) on thickener batch test for a complex copper ore, it realized that as the size fraction is decreased in the range size of 44 to 120μm the amount of flocculant dosage had to be increased to reach the same particle rate of sedimentation of the coarser particles. Besides, the coarser material (above 120 μm) had better compressibility compared to the fine particles. In this way, fine grinding in copper concentrators has several detrimental effects on thickening operations.

So, it can be inferred that besides clay mineral, particle size could be playing a detrimental role in Chuquicamata thickener operations, as by analyzing the particle size distribution of the tailing samples (Figure 31), more than 50% is in a range below 100μm. However, to confirm the before mentioned, experiments according to particle size fraction should be run and compare between each other, thus a critical particle size could be found at which the particle sediment rate and compressibility are not longer efficient at a given flocculant dosage.
Figure 31: Particle size distribution of both the a) feed sample (RT) and b), c) the flotation tailing samples.

Table 2: D80 of the different samples studied

<table>
<thead>
<tr>
<th>Comminution type</th>
<th>Sample</th>
<th>D80[um]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crusher Stage</td>
<td>RT</td>
<td>1800</td>
</tr>
<tr>
<td>Steel media</td>
<td>KPA0-3</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>KPA0-4</td>
<td>250</td>
</tr>
<tr>
<td>Steel media</td>
<td>KPA1-3</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>KPA1-4</td>
<td>280</td>
</tr>
<tr>
<td>SAG</td>
<td>KPA2-3</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>KPA2-4</td>
<td>215</td>
</tr>
</tbody>
</table>
4.2 X-Ray Fluorescence Experiments

In this section, the chemical composition is presented in a way to assess the efficiency of the Chuquicamata mine operation. The main concern in the copper concentration is the growing of deleterious elements as the environmental impact regulations are also increasing. To meet these regulations, separation of deleterious elements from the final saleable copper concentrate may be vital to avoid severe financial penalties from smelters. Therefore, the efficiency of the plant must be assessed constantly throughout the whole process by analyzing the chemical composition of key sampling point of the plant. Furthermore, since the copper grades are constantly decreasing, new potential by-products can be taken into consideration for the future economical revenues by analyzing the chemical composition of the plant. Such new by-products elements could be rare earth minerals, rhenium, and precious metals among others.

Given that the samples utilized in this research are feed and flotation tailings, it is possible to assess the losses of the valuable elements such as copper and molybdenum. Additionally, penalty elements like iron and arsenic are also possible to assess. Figure 32 shows the percentage and parts per million of copper (a), iron (b), molybdenum (c) and (d) arsenic along with their distribution throughout the different Chuquicamata concentrator plant A0, A1, and A2.

For the case of the copper in the RT feed sample it has a grade of 1.15%, and the losses in the tailings are in the order of 0.060 to 0.070%. This means that the recovery of copper in the concentrator plant is in the order of 94%. Iron grade in the feed is 1.52%, and it is only depressed by 54% in plant A0, 57% in plant A1 and 91.7 % in plant A2. The molybdenum was found in trace, as only 170 ppm is in the feed of RT ore, and an amount up to 92ppm was found in the tailings, meaning that more than half is lost in the tailings. Nevertheless, the RT ore is only a minor part of the real feed of the concentrator plant. As it was discussed before, the Concentrator plant is fed by RT ore and the Chuquicamata open pit itself. The Chuquicamata open pit has a grade of 0.9% copper and 510 ppm molybdenum (Pinget et al, 2011), this means that the losses of molybdenum in the flotation tailings are in the range up to 20 %, as the flotation samples are a mix of the feeds before mentioned. Still, twenty percent of losses is an alarming rate, and measures from the concentrator division must be taken into consideration. Moreover, the levels of arsenic were found to be low, as only 12 ppm in the RT feed and not even detected in the concentrator plant A0 and A1. Nonetheless, plant A2 was found 32ppm of arsenic, which means that the Chuquicamata pit ore could contains another amount of arsenic minerals.

Another important penalty element that was targeted in the XRF analysis is the bismuth (Bi), as it creates a brittle final copper product during the refining process of the copper being the main issue on the smelter, reducing thus the value of the final product. Moreover, to get a refined copper of 99.99% purity the brittle copper must be treated to reach the before mentioned purity. Also, Bi requires certain waste limits restrictions for proper element disposal, since it is considered one of the most toxic heavy metals. This being said, the XRF result did not detect any trace of bismuth in the Chuquicamata samples.

Lastly, lanthanum and Cerium two elements from the rare earth family were found in economical grades in the RT feed (Figure 32e). Both elements are in high demand nowadays as they are used in high-tech products and renewable energy technology. These findings could open the door to buffer the high demand on rare earth in the world by investigating Chuquicamata mineralogy deeply in terms of targeting RRE. Thus, a new processing technique would be needed to incorporate in Chuquicamata concentration process to obtain a new by-product. Also, the tailing dam is believed to be a future source for a whole new concept of mining, given the years of the mine operation (since 1915), and the whole resources that
lay down there, that can be seen by analyzing the chemical composition of the tailings that goes into the discharge.

Figure 32: Chemical composition of the samples studied, a) copper, b) iron, c) molybdenum, d) arsenic, and e) rare earth minerals.
4.3 X-Ray Diffraction Experiments

In this chapter, the XRD measurements were made with the aim of identifying the types of clay minerals presented in the Chuquicamata plant and its distribution throughout the three different concentrator plants A0, A1, and A2. Moreover, by identifying and quantifying the clay mineral it is possible to assess their impact on the thickener test performances. As was mentioned before (chapter 3.3.2), the measurements were obtained from the company X-ray Mineral Services Ltd (XMS), a specialized company in identifying clay minerals with offices in the United Kingdom.

The results are presented in two different ways; the first results are XRD measurements of the representative samples of mean particle size <2 µm the clay fraction analysis. The second XRD analysis results are the whole rock analysis from the representative samples between 5-10 µm. The whole rock analysis is the interpretation and quantification of the whole sample, whereas the clay analysis fraction results are used to feedback the whole rock results, as some clay minerals spectra above the size of 2 µm are difficult to be found, such as the smectite that often is not visible in the “whole-rock” preparation.

Hence, the < 2µm clay-fraction analysis is a targeted and refined analysis of all clay species and is particularly good for the identification of swelling clays such as smectite and mixed-layer clays as illite/smectite, kaolinite/smectite, and chlorite/kaolinite among others. This detailed information on the proportion of clay species in the < 2µm fraction is fed back into the whole-rock data which then reflects the absolute abundance of swelling clay in each sample. Finlay, another information that will be provided in the clay fraction analysis is an indication of the clay minerals crystallinity based on the peak width for each component.

4.3.1 Clay Fraction Analysis

Table 3 shows the overall result of the clay fraction analysis in the particle size <2 µm. The table has been organized according to the sample collection point, comminution type of the plant linked to the collection point, date and sample type. Also, it is noted whether the sample was received dried or in the pulp form. The wt.% in the sixth column of Table 3 corresponds to the percentage of the amount of the representative sample in the range size <2µm. Additionally, Table 3 shows the clay mineral crystallinity based on the subjective assessment of the clay spectra steep, and width where: “P” stands for Poorly Crystallised; “M” for Moderately Crystallised; “W” for Well Crystallised; and “VW” for Very well Crystallised.

It is evident from Table 3 that three types of clay were found in the following order: Illite>>Kaolinite > smectite. Illite is found well crystallized, kaolinite well to medium crystallized, while smectite is found poorly to medium crystallized. Clay minerals crystallography has been a matter of studies in its effect on increasing the rheology of suspensions. For example, Zhang et al (2014) noticed that a poorly crystallized kaolinite contributed to more than 30% of the total area, showing that crystallinity can have a significant impact on the rheological behavior of the suspension. Besides, the poorly crystallized kaolinite yielded a slower settling rate and lower settled bed density compared to well-crystallized kaolinite. Exactly the same was noticed to swelling smectite clay when comparing to poorly crystallized smectite to well-crystallized smectite as the poorly crystallized one yielded higher yield stress in the suspension. It has been stressed out that the poorly crystallized clay mineral resists the transformation of loose edge-face structures to dense face-face structures under introduced shear forces, contributing to higher apparent viscosity of the poorly clay crystallization. Therefore, studying the physical morphology of the clays is important as it plays a decisive role in controlling the pulp rheology behavior. In this context, and given all the feedback from the plant, it is highly possible that the poorly crystallized smectite present in RT sample could be the reason for the low efficiency in both flotation and thickener operation when it comes to feeding the plant in high RT proportion.
Also, quartz is found in the almost same ratio as smectite, which opens the debate that quartz particles could be also affecting thickener performance due to fine trace quartz particles were found in the <2µm analysis. As was discussed before (chapter 2.6.4), very small particles such as the case of clay minerals (<2µm) hinder the flocculation process in the thickener operations attributing lower solid settlement rates (Harris et al, 2018; Liu et al, 2018). Consequently, fine quartz particles can be thought as problematic in terms of thickener operations mainly affecting the quality of the water recovered in the overflow.

To understand and analyze better the results from Table 3, the clay minerals content in the <2µm results were normalized by taking out the quartz content. Thereafter, the normalized results were plotted in a ternary chart shown in Figure 33. As was expected, the clay content specially the swelling clay was higher in the RT sample as it is a feed. In the Plants, A0 and A1 the flotation tailing samples were reported to have a higher amount of both kaolinite and smectite as it can be seen in the zoomed ternary chart of Figure 33b. On the contrary, in the plant A2, the amount of smectite is less and poorly crystallized. The plant A2 uses Semi-Autogenous (SAG) mill at the difference of the conventional steel media mill of plant A0 and A1. This arises the possibility to link poorly crystallized smectite clay with the particle reduction size mechanism of the SAG mill. The observation opens the door to future works to corroborate the connection between the swelling clay content and crystallography with the mill type. If there was any link among the SAG particle size reduction mechanism and clay crystallography, it would lead to rheology suspension modification after the pulp exit the SAG mill, which could hinder the process downstream, which also needs to be assessed in future works.

Table 3: XRD summarize result for the clay mineral analysis <2µm (data provided by XMS)

<table>
<thead>
<tr>
<th>Stage</th>
<th>Sample</th>
<th>Conminution type</th>
<th>Sample type</th>
<th>Collection Date</th>
<th>Wt. % &lt;2µm</th>
<th>Illite</th>
<th>Kaolinite</th>
<th>Smectite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>% A</td>
<td>Crys</td>
<td>% A</td>
<td>Crys</td>
</tr>
<tr>
<td>Feed RT        Crusher Dry 10-11</td>
<td>5.1</td>
<td>61.8</td>
<td>W 17.7</td>
<td>M 20.6</td>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flotation Tails A0 KPA0-3</td>
<td>Steel media dry 03-12</td>
<td>4.6</td>
<td>68.1</td>
<td>W 23.3</td>
<td>M 8.7</td>
<td>M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KPA0-4 dry 04-12</td>
<td>4.3</td>
<td>68.8</td>
<td>W 19.8</td>
<td>M 11.4</td>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flotation Tails A1 KPA1-3</td>
<td>Steel media dry 03-12</td>
<td>4.0</td>
<td>71.2</td>
<td>W 20.9</td>
<td>M 8.0</td>
<td>M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KP A1-8 wet 08-12</td>
<td>3.7</td>
<td>73.2</td>
<td>W 16.3</td>
<td>M 10.4</td>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KP A1-9 wet 09-12</td>
<td>4.2</td>
<td>71.1</td>
<td>W 19.1</td>
<td>M 9.8</td>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flotation Tails A2 KPA2-3</td>
<td>SAG dry 03-12</td>
<td>4.4</td>
<td>85.3</td>
<td>W 14.7</td>
<td>M 0.0</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KP A2-8 wet 08-12</td>
<td>4.5</td>
<td>80.7</td>
<td>W 14.8</td>
<td>M 4.5</td>
<td>P</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KP A2-9 wet 09-12</td>
<td>4.5</td>
<td>77.0</td>
<td>W 16.6</td>
<td>M 6.4</td>
<td>P</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Figure 33: (a) Ternary plot of normalized clay fraction in the particle size fraction <2µm analysis and (b) the zoomed ternary plot.
4.3.2 Whole Rock Analysis

The whole rock analysis as it was explained before, is the final XRD outcome of the feed and tailing representative samples that have been calibrated from the XRD clay fraction analysis. The results are shown in Figure 34 for the RT sample and the flotation tailings of the three concentrator plants A0, A1, and A2. The pie charts show the distribution of the different clay minerals throughout the plants. The main minerals found can be divided into three groups:

1) Clay minerals: illite and mica (III+Mic), Kaolinite (Kao) and Smectite (Sme);
2) Silicates minerals: potassic feldspar (Kf), quartz (Qtz) and plagioclase (Plg); and
3) Iron mineral: Pyrite (Py).

The silicates minerals are found in a range of 74.8%-82.6%, pyrite in minor trace between 0.1%-0.5%, whereas clay minerals are found in a range of 17.1%-25.2%. By focusing only on the RT sample (RT), that it has been collected on a critical operation day as it was explained before (chapter 3.2.1), contains 23.3% of clay and 76.1 silicates being the highest amount the quartz reaching up to 45.3%. The critical mineral that is targeted as problematic within the RT sample is the swelling clay minerals which in this case is the smectite accounting only to 1% followed by non-swelling clay kaolinite 2.5% and illite/mica 19.8%. The main issue as it was discussed before with clay minerals is that it affects the rheology of the suspension by increasing it, especially swelling clay. Zhang et al (2014) and Ndlovu et al (2014) studied the critical clay concentration at which rheological problems start to affect suspensions. Furthermore, smectite in suspensions become problematic at a critical concentration as low as 4% solids, kaolinite suspensions only become problematic at concentrations higher than 10% solids, and illite and muscovite suspensions do not show yield stress even at 30% solids concentration. These finding make questioning the RT clay content as it is below the critical problematic concentration. Thus, it might another mineralogical factor within the RT sample that could be affecting thickener operation by the alteration of the rheology of the suspension. To answer the question four possible theories have been developed:

1) Other possible problematic minerals besides swelling clay are the group of the silicate minerals, which were found up to ~75% and up to 10% in the <2μm clay fraction analysis, being quartz up to 45.3% the most abundant among potassic feldspar and plagioclase (Figure 34). In the same address, the studies done by Ndlovu et al (2013) investigated the rheological properties of suspensions of binary mixtures comprising quartz and different clays minerals such as muscovite, vermiculite, and chrysotile. The binary mixtures were compared to that of the pure phyllosilicates as a function of pH. In this manner, the study was aiming to determine whether the clay minerals dominate the rheological behavior of the mixture suspensions. Within the results, the increasing presence of quartz in the binary suspension resulted in an antagonist rheological effect when compared to suspensions with only clay mineral. Hence, quartz-clay mineral interactions can increase notably the rheology in the suspension, even though quartz suspension solely barely increases the rheology as the quartz% is increased. These interactions have not been fully understood and neither investigated in its totality. Therefore, it is important to keep looking at the clay minerals interactions with silicates minerals to better understand the rheological behavior of these minerals in the mineral processing industry.

2) Another theory rely on the high amount of illite and mica found. Illite corresponds to a non-swelling clay mineral and as it was stated only 30% can affect the suspension rheology (Zhang et al, 2014). Nonetheless, this type of clay can be transformed into a swelling clay. The
transformation of illite to a swelling clay has been well documented (Bracke et al 1995, Ndlovu et al 2013). Illite and micas may be transformed by the replacement of the interlayer of K+ by exchangeable hydrated cations. Like this, the loss of the K+ layer and the increase of water and silica would affect thus the swelling properties of Illite and micas. In consequence, the alteration would affect the rheology of the suspension at concentrations as low at 4%.

3) The mineralogical problem of the RT sample could also rely on the clay mineral crystallinity degree. In addition, no matter the clay mineral type, the degree of crystallinity also plays an important role in the rheological behavior of clay mineral suspensions. For example, Zhang et al (2015a) reported that poorly crystalline kaolinite produced higher apparent viscosity and yield stress than the well crystalline kaolinite. Poorly crystalline clay minerals are composed of thinner plates, in this way more edges and corners are available to initiate friction during shearing, resulting in higher yield stress and viscosity. Moreover, Du et al. (2010) showed that complex surface morphology of poorly crystalline clay minerals endured the transformation of loose E–F structures to dense F–F structures under shear that can also lead to an increase in the viscosity. These studies indicate that the clay crystallinity must be considered when investigating the pulp rheology in mineral processing regarding the clay mineral type.

4) Lastly but not least, the thickener operation hindered when in high ration feed with RT ore, could be linked to particle size fraction. It was mentioned before (Chapter 4.1) from the work of Garmisiri et al (2017) as the particle size decrease in the range size of 44 to 120μm the amount of flocculant dosage had to be increased to reach the same particle rate of sedimentation of the coarser particles. Besides, the coarser material (above 120 μm) had better compressibility compared to the fine particles. This conclude that fine grinding in copper concentrators has several detrimental effects on thickening operations, and the tailings samples studied more than the 60% of the where in a range below of 120 μm indicating that settlements problems may be due to this reason as well.

The four above mentioned theories on RT mineralogy affecting Chuquicamta thickener operation maybe that the four of them are occurring simultaneity and linking with each other and affecting the operation performances. However, to address the problem precisely more research must be carried on in terms of particle size effect on thickener operation and assessing the clay mineralogy of Chuquicamta open pit. Like this by analyzing Chuquicamata open pit ore and RT ore combined, a more detail examination can be performed, such as mass balance in the concentrator plant, to check where is the most likely to find the clay minerals flow and to point out critical elements in the open pit.
Figure 34: XRD Average of the whole rock analysis for the feed (a) and flotation tailing samples (b, c, d).
4.4 Thickener Experiments

In this chapter, both flocculant rheology characterization, and batch thickener tests are presented. The Thickener experiment results are divided into two subchapters; the first subchapter is the rheology characterization of the flocculant solution at different concentrations. The aim of the flocculant rheology characterization is to assess the respond of the four flocculants, anionic, no-anionic, cationic and the current Chuquicamata flocculant at different concentration, thus select a proper addition rate for the thickener pilot test afterward.

The second subchapter is the sedimentation batch results by using the previous different flocculants mentioned to perform particle flocculation given the mineralogy of Chuquicamata flotation tailings. The aim of this subchapter is to reach such a dosage and addition rate of flocculant that can improve the current flocculation at Chuquicamata thickener operation. Therefore, the results will be presented in a way to compare the flocculant performances with the Chuquicamata flocculation performance.

4.4.1 Flocculant Solution Rheology Characterization

The flocculant solutions were prepared in a range of 0.02 %w/w to 1%w/w aiming to carry out rheological measurements. These measurements were done as a starting point to select suitable flocculant concentrations, to later perform the thickener batch test. As pointed out before, a suitable flocculant solution should be the one that does not interfere with the rheological properties of the pulp solution and improve the agglomeration of fine particles like clay minerals. However, as the particles flocculate in the sedimentation thickener test, the rheology of the sludge changes accordingly to the flocculant being used (ADDAI–MENSAH et al, 2007), unfortunately, these measurements were not possible to assess given the viscometer features. By knowing the solid discharge rheology is possible to reach a critical flocculant addition that will be conditioned by the thickener rheology limits. If the torque gets too excessive due to the flocculation process, the drive lift automatically lunches a safeguard against structural damage by raising the rakes and stopping the thickener unit. Moreover, high rheology in the thickener discharge also leads to difficulties in transportation of the sludge towards the tailing dam as the pump system starts to collapse. Consequently, the flocculant concentration must be selected carefully and accordingly to the thickener features, as in contrary case a chain of problems would arise.

Table 4 shows the rheological characterization for 3 polyacrylamide flocculants plus the one used in Chuquicamata thickener operations. As expected, the cationic and non-anionic flocculants yield a lower viscosity as the concentration increase compared to the anionic polyacrylamide. The reason for these flocculant viscosity differences rely on the molecular weight in its structures, being the highest molecular weight the anionic followed by the Cationic and No-anionic (Flocculants Material safety data sheet, Y&X Group, China). On the other hand, the Chuquicamata flocculant yielded similar concentrations as the non-ionic polyacrylamide, nevertheless, more information about this flocculant has not been obtained.

Based on the rheology results of Table 4, the concentrations of the flocculants were selected for the thickener pilot test. The maximum permitted solution criteria selected was up to 150cp, based on the results of Chuquicamata flocculant. Therefore, the concentrations of the solutions of the different flocculants were selected as follow:
1. Cationic: 0.02 and 0.05 %w/w;
2. Non-Ionic: 0.02 and 0.05%w/w;
3. Anionic: 0.02%w/w; and
4. Chuquicamata: 0.02%w/w.

<table>
<thead>
<tr>
<th>Concentration[%w/w]</th>
<th>Cationic</th>
<th>Non-Anionic</th>
<th>Anionic</th>
<th>Chuquicamata</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80000</td>
<td>75000</td>
<td>202400</td>
<td>58760</td>
</tr>
<tr>
<td>0.8</td>
<td>49000</td>
<td>46800</td>
<td>143600</td>
<td>34100</td>
</tr>
<tr>
<td>0.5</td>
<td>8900</td>
<td>9800</td>
<td>65200</td>
<td>12000</td>
</tr>
<tr>
<td>0.25</td>
<td>1350</td>
<td>1280</td>
<td>36250</td>
<td>3220</td>
</tr>
<tr>
<td>0.1</td>
<td>120</td>
<td>100</td>
<td>3740</td>
<td>340</td>
</tr>
<tr>
<td>0.05</td>
<td>40</td>
<td>20</td>
<td>650</td>
<td>180</td>
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<tr>
<td>0.02</td>
<td>&lt;15</td>
<td>&lt;15</td>
<td>160</td>
<td>100</td>
</tr>
</tbody>
</table>

### 4.4.2 Thickener Batch Test

The thickener batch test results are presented based on two criteria of flocculation performances: Initial settling rate (ISR) and Turbidity. The pulp solution was prepared at 15% solids at a pH in the range 11-12 to match conditions operations at the Chuquicamata high capacity thickener.

Figure 35 shows the results for the 3 different polyacrylamides, anionic, cationic, and no-ionic plus the current flocculant used at Chuquicamata thickener operation. Furthermore, a mix of two polyacrylamide flocculant labeled RM-1 was tested and presented also in Figure 34. The flocculant addition rates were selected at 5g/t (figure 35a) and 7g/t (figure 35b). The results were plotted based on two criteria of flocculation performance; IRS and turbidity of the thickener overflow water. Hence good flocculation performances are those results that have fast ISR and low turbidity i.e. water with lack of fine in the overflow. The good consistency of the flocculation results can be seen by comparing the flocculant addition rates at 5g/t with the ones at 7g/t, where the performances of the different flocculants followed the same behavior, being the best flocculation conditions for the flocculant blend RM-1 and the worst flocculation result was using the cationic flocculant. The anionic and the non-anionic polymer results were such that could match the flocculation result performed by Chuquicamata flocculant.

The Cationic flocculant results had the worst performance results yielding low initial settling rate and high turbidity. At pH alkaline where a negligible positive charge exists at the clay particle edge and silicates (Nabzar et al, 1988; Yawen et al 2018), it is thought that neutralization of charges would be the primary mechanism of absorption among particle and polymer. Nevertheless, by comparing the cationic results at additions rate 5g/t and 7g/t is possible to observe a slight improvement at 7g/t, reaching Initial settling rate up to ~23m/h and turbidity up 180 NTU. This suggests that the cationic flocculant must be added at a concentration above 0.05%w/w and higher addition rate to achieve charge neutralization among particle surface and the polymer at alkaline conditions. However, higher addition of cationic flocculant
could lead to an increase in the pulp viscosity thus generating problems of discharge, pump circuits and in the thickener rakes system.

On the other hand, non-ionic (green dots) and anionic flocculant (blue dots) performances were such that matches the one at Chuquicamata conditions (red dots). Given the good results of non-anionic and anionic flocculation, the bridge absorption mechanism (reviewed in chapter 2.3.2) among particle surface-flocculant is the one predominates at alkaline conditions. Based on the good results of the two types of bridge absorption mechanism for anionic and non-anionic respectively, they were mixed and test them on the settlement test. The main criteria to test the flocculant blend was to look in a synergism effect that could lead to improve the flocculation process of current mine operations. In this manner, by mixing the two flocculants, the particles have more chances to attach to the polymer and hence start agglomeration to speed up the settlement rate. The flocculant blend is shown in the label "RM-1" (purple dots) and it yielded the best flocculation performances by reaching a record ISRT and turbidity of 47m/h and >20 NTU respectively. The outstanding flocculant blend performance was possible to observe not only at addition rates of 5g/t but also 7g/t. These findings suggest that Chuquicamata thickener operation can be improved by understanding the mechanism of particle-polymer absorption and finding the right flocculant dosages and addition rate without affecting the rheology of the suspension. While the sludge rheology was not measured, in the future to accept the polymer blend performance the agglomeration rheology must be taking into account. Like this, is possible to examine if the thickener unit is able to work under the sludge rheology created by the polymer blend. Also, an industrial scale trial is highly necessary to assess the flocculant response when is worked in continuity flow, and the mineralogy is not constant all the time.

Even though the flocculation process could be improved, is thought that it can be improved even more by decreasing the electrical double layer of the particle by adding coagulants. By decreasing the double layer of the particle, repulsive forces related to particle superficial charges are depressed, thus the particles are closer together and can collide easily. For instance, from the work of Addai–Mensah et al (2007), it was possible to improve copper tailings sedimentation by a controlled metals ions addition acting as coagulants such as Mn+2 and Ca+2. These ions would facilitate polymer bridging absorption due to electrical double-layer compression (reduced zeta-potential), a. Nonetheless, increasing solution metal ion concentration beyond an optimum value, the flocculation performance may fall because of over complexation between carboxylate groups of the polymer and unabsorbed metal ions.

Lastly, it was not possible to assess a direct link among the mineralogy of the different flotation tailings and the settling test, as the mineralogy of the samples was quite constant in terms of clay minerals and silicates content as it was shown in chapter 4.3. For example, samples that had good settlement performance are mineralogically similar to those having poor settlement performances at the same conditions; therefore, it was difficult to assess any direct link among mineralogy and settling test, as more parameters are affecting from sample to sample, such silicates content, pH, the presence of ions acting as coagulants, zeta potential of the solution, among others.
Figure 35: Thickener Batch results on (a) 5g/t of flocculant addition and (b) 7g/t of flocculant addition.
5 Conclusions

In this study, Chuquicamata mineralogy characterization of feed and flotation tailing samples was successfully achieved by performing XRD and XRF techniques. The characterization aimed to find clay minerals and other possible potential minerals that could be hindering thickener operations. Within the analysis. Three groups of clay minerals were identified in the same ratio for both the whole rock and <2µm fraction analysis:

Illite > Kaolinite > Smectite

The RT sample had the highest amount of swelling clay as expected for being a feed sample, followed by flotation samples from plant A0, A1. However, swelling clay content from the plant A2 showed slightly less.

The swelling clays minerals have a detrimental effect on mineral processing especially in thickener operations, where it increases the viscosity by absorbing water due to a cationic replacement in its interlayers leading to several problems of thickener discharge, high energy consumption, and low quality water recovered. Nevertheless, based on the results is not possible to assess that the content of clays minerals affects the sedimentation in Chuquicamata thickener operations. Thus, other minerals such as silicates in the form of quartz, potassic feldspar, and plagioclase may also be affecting particles settling behavior since it is present in <2µm and in high percentage in the whole rock analysis, reaching up to 76% of silicates. Also, factors that have been found in previous studies regarding clay mineral crystallinity degree and transformation of illite/mica into swelling clay can be also hindering the settlements of particles, by modifying the rheology of the suspension. Moreover, given the high amount of illite/mica up to 23% content, it is also possible that within its structure network swelling clay can be hidden, and thus the XRD spectra peak of the swelling content is not detected in the analysis.

A particular observation was that all the swelling clay found in the plant A2 was poorly crystallized. It is thought that the SAG reduction size mechanism could be affecting somehow the swelling clay crystallinity, and thus affecting positively the downstream process. This observation raises the possibility to start research on this matter and thus reaffirms the link among SAG particle reduction size mechanism and swelling clay crystallinity that was found.

From the pilot thickener campaign, information was generated to confirm that the current thickener operations at Chuquicamata mine can be improved by both understanding the microstructure of adsorbed polymer layer at the solid-liquid interface and by selecting suitable flocculant dosages given Chuquicamata mineralogy. In this scenario, the flocculant blend that was tested proved to be more efficient than the current flocculant at the mine. These findings not only provide enhanced insight into the phenomena that govern flocculation but also give additional strategies to thickener operators at Chuquicamata, cost savings, high-quality water ready to be used again in the concentrator process and also opens the possibility to increase processing rate in the thickener. Moreover, polyacrylamide blends could open the door to bring new optimization in dewatering not only in the mining industry but also in the oil, paper, and Municipal water treatment sectors.

Lastly, it was not possible to link Chuquicamata mineralogy with the sedimentation test as the mineralogy of the flotation tailing samples was quite constant in terms of clay minerals and silicates content. Hence, point out that small differences in the clay and silicates content led to high differences in sedimentation behavior results would be misleading information.
5.1 Future works

This work opens the possibilities to develop a proper method that could link ore mineralogy characterization with mineral processing. For instance, by taking samples with a logistic methodology in a Mining Company can lead to solving problems from the ore stage to mineral concentration. An early ore mapping could solve problems related to clay minerals in mineral processing. In this manner, some critical zone with high clay content in the ore could be avoided exploited, without the need to process it in the concentrator area. Although this project was not possible to certainty affirm that the content of clay minerals in Chuquicamata flotation is affecting the thickener operations as it seems that the total clay amount found it’s not enough to affect the rheology of the thickener. Furthermore, given the high amount of silicates founded in the XRD analysis in the form of quartz, potassic feldspar and plagioclase could be also hindering the thickener operations. For this reason, it is important in the future to assess silicate-clay interactions impact in both suspension rheology and particle sedimentation behavior.

The pilot thickener test proved to be an excellent tool to select both suitable flocculant types and dosages. Nevertheless, this project did not consider the flocculant rheology impact into the suspension as it only took into consideration the flocculant solution rheology. Therefore, in future work, the flocculant rheology impact into the suspension needs to be assessed to ensure viscosity limits within the thickener, as the flocculation process must not affect the solid discharge, rake and pump system. Also, it was found that the blend of polyacrylamide improved with respect to Chuquicamata operations, however, it is important that in future work new blends must be tested on a wider range of pH, addition rates and blend ratio. In addition, it is important to test the impact of metallic ions that act as coagulants that could enhance flocculant polymer bridging into the particle surfaces by electrical double-layer compression and thus a close approach interaction among polymer-solid particles. Consequently, it is important to assess both the rheological impact and zeta potential of the suspension before and after the addition of the coagulants. In this manner, by finding the right dosages and type of coagulants and flocculant not only increase the tailing thickening capacity but also lead to better water management. Increasing high-quality water reuse amount in the thickener operations saves operation cost dramatically and affect positively the environment and communities as the mines water demand would be reduced. Moreover, it is difficult to quantify how much cost Mines Companies would save by achieving the right flocculation as the industrial test must be performed. Thus, an economical inspection could be achieved by comparing old thickener operation performances with the new strategies proposed.

Finally, a link among swelling clay crystallinity with the SAG reduction size mechanism was observed. This could open the research in the matter by confirming the relation. Also, SEM to obtain clay mineral images would help to reaffirm clay crystallinity-SAG dependence.
6 EIT Chapter

6.1 Circular economy—Mine water management and rare earth opportunities in Chuquicamata tailing dam.

In this work, the main objective was to assess Chuquicamata mineralogy and its impact on the water management that’s carry on in the thickener operations. As was mentioned, the northern Chilean porphyry copper deposits are characterized for being located in the Atacama Desert, well known for being the most arid place in the world. In this area, not only mining companies demand the water resources for its operations but also is essential for the inhabitants, agriculture, crop sustainability and the ecosystem in general. As the mines needs and insane amount of water for the concentrator process, many times this situation leads to drought in the area, being the most affected the people. Therefore, the correct management of the water resources used in the mine companies is necessary for the development and the environmental care of the region. Mine tailings, which are the materials left over after separating the valuable minerals from the uneconomic mineral are processed to obtain the water in the tailings slurry for being reused in the mine concentrator area. The thickener operations through the principle of particle sedimentation and additives than enhance settlement are used as the final dewatering stage of the tailings. Therefore, in a place like Chuquicamata, water resource is treated a product as well, something that is processed, enriched and delivered. So, water resources follow the same strict rules applied to any other product in a circular economy. When water is treated as durable, it must be kept in a closed-loop, meaning zero liquid discharge and reuse as much as possible. However, zero liquid discharge in mining operations is extremely difficult as there are many factors that can hinder the solid-liquid separation. The main factor nowadays in Chuquicamata is the mineralogy, such as clay minerals that have the ability to hinder the thickener operations as well as many stages of the mineral processing (Mohan et al., 1993; Shabalala et al. 2011; Ramsaywok et al 2009; Chen et al, 2018; Ndlouv et al. 2011). Moreover, clay minerals can contribute in generate failures in the tailing dam that could cause big environment, economic, and social impact (Sassoon et al, 1998).

In this scenario, the contribution of this project is a better understanding of how the ore mineralogy can affect the operation in the water management stage. Nevertheless, was not possible to state that the amount of clay found is the only factor affecting the thickener operations as more combinations of mineralogical factors could be hindering the thickener operations in Chuquicamata mine. These factors can be, silicates minerals, particle size, clay mineral crystallinity among others (chapter 4.4.2), that need to be further analyzed with future works. Furthermore, the improvement in the pilot thickener test (chapter 4.4.3) by finding suitable additive dosages given Chuquicamata mineralogy, will bring better use of the water by increasing the recirculation towards the concentrator area in a friendly way with the environment and communities that also demand water in the arid region of the Atacama Desert. Nonetheless, an industrial scale trial is highly necessary to assess the flocculation respond when it is run in continuity flow, and the mineralogy is not constant all the time.

At the same time, by studying the tailings samples mineralogy is possible to assess the kind of minerals that are being dumped towards the tailing dam. Therefore, this gives the possibility to examine potential economical minerals that could be processed as by-products. Rare earth minerals were found in interesting concentrations of La (110ppm) and Ce (102ppm), both elements are in high demand in the high-tech products and renewable energy technology.
Nowadays, the dominance of China in regard to the current rare earth elements (RREs) ore reserves (80%) and beneficiation plants poses a major concern to Europe and the rest of the world by securing the supply of RREs. Recycling and exploring new RREs deposits seem to be the solution. Consequently, the finding in Chuquicamata tailing dam regarding RREs could open the door to buffer the high demand on rare earth in the world by investigating Chuquicamata and the tailing dam mineralogy deeply in terms of targeting RREs.

6.2 Potential to develop an innovative business activity
Since this research project was sponsored by a mining company, a potential business can be developed. For instance, it was studied the mineralogy of Chuquicamata by targeting clays minerals for its ability to hinder all the stage of mineral processing. Therefore, it is possible to develop a proper mineralogical control by combining XRD and XRF to mitigate clay minerals impact in the mineral processing operations. Moreover, taking the mineralogical sample and analyzing them with a logistic methodology in a mining company can lead to solving problems from the ore stage to mineral concentration. An early ore mapping could solve problems related to clay minerals in mineral processing. In this manner, some critical ore zone with high clay content could be avoided, without the need to process it towards the concentrator area. In addition, in this project, a proper flocculant dosage was found that improve the current one used in Chuquicamata operations. This could also lead to potential business activity by assessing thickener operations at batch scale. Mine companies always require an external assessment to get the best out of it, by hiring expertise in any stage of the process, or even sponsoring students that study industrial scale problems like the one developed in this project.

The weaknesses of start a new consultancy business in this regard is to get to the right people, it is not easy to access the mine companies and convince them with your ideas. Once you have the regular access to the mine, a second stage is faced, the monopoly of the big external companies that also provide services for many years. That’s is why for any consultancy assessment to a mining company it must stand out over other services in terms of innovation, efficiency, and reliability of the service.
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