The characterization of industrial process water properties, a methodology case study from the mining industry

Thi Minh Khanh Le
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Abstract

The dynamicity and variability in terms of quality of recycled mining process water (PW) brings challenges in the recovery and the quality of the final products. By turning water quality into operating parameters, its properties could be controlled and modified to hopefully provide added value to the process outputs.

This thesis aims to explore the challenges for transforming water quality into a set of operating parameters in mineral processing. This study focuses on three aspects for effective management of water towards optimizing process performance: (1) a database for linking water quality to flotation performance output and serving as a base to explore the PW characteristics, (2) tools for monitoring and controlling PW quality and (3) a laboratory protocol for creating and predicting the plant PW for testing and plant design. The traditional methods for those mentioned aspects developed for effluents (environmental purposes) have neglected the three major characteristics of recycled process water: dynamic, complex and mine specific, a shortcoming this thesis addresses.

Using two case studies, this thesis show that traditional, standardized methods that have been developed for sampling, preserving, and analyzing mining effluent for environmental purposes failed to apply for process water. Employing generalized standard methods without optimization to the prevailing conditions may cause high uncertainty of analysis results. This thesis also highlights that a weekly or daily sampling for monitoring effluents for environmental purposes is not suitable for operation purposes due to the high variation of process water quality. The sampling procedure should be customized. Moreover, controlling and monitoring complex water matrixes call for multivariate data analysis methods. Advance statistical parameters results of multivariate statistical models could allow monitoring both operating range of the inputs and the correlation between variables, i.e. the thermodynamic state of the water. Finally, the dissolution loop (D-loop) laboratory protocol described in this study is an important tool that permits the prediction of the water quality variation over time due to the dissolution of the ore when the plant is operated in closed water circulation. With the D-loop, recycled water that contains nearly the same impurities as the process water at the particular plant could be produced to replace distilled water or synthetic water for laboratory testing. Such an approach is realistic and appropriate to solve the challenge of undefined and unspecific water matrix in laboratory testing.

The knowledge obtained through this dissertation increases the chance of closing the water loops with less impact on operating performance. Additionally, it challenges our theoretical understanding of mining water management by introducing a focus on the lack of tools and mindset for dealing with process water in the context of the operation.

Keywords
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Espoo, March 31, 2021

Thi Minh Khanh Le
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AMD</td>
<td>Acid Mining Drainage</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>D-Loop</td>
<td>Dissolution Loop</td>
</tr>
<tr>
<td>DLW</td>
<td>Dissolution Loop Water</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>Eh</td>
<td>Redox potential</td>
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<tr>
<td>HF</td>
<td>High Frequency</td>
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<tr>
<td>MSPC</td>
<td>Multivariate Statistical for Process Control</td>
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<tr>
<td>OP</td>
<td>Operating parameter</td>
</tr>
<tr>
<td>OVAT</td>
<td>One Variable At a Time</td>
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<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional-Integral-Derivative</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle Size Distribution</td>
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<tr>
<td>PW</td>
<td>Process Water</td>
</tr>
<tr>
<td>FW</td>
<td>Fresh Water used on mine site</td>
</tr>
<tr>
<td>SDSE</td>
<td>Standard Deviation of Sampling Error</td>
</tr>
<tr>
<td>SPC</td>
<td>Specific conductance (i.e Conductivity at 25 °C)</td>
</tr>
<tr>
<td>SS</td>
<td>Suspended solids</td>
</tr>
<tr>
<td>SW</td>
<td>Synthetic Water</td>
</tr>
<tr>
<td>TSF</td>
<td>Tailings Storage Facility</td>
</tr>
<tr>
<td>1D lot</td>
<td>One dimensional lot</td>
</tr>
<tr>
<td>$j$</td>
<td>Lag parameter</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of increments extracted</td>
</tr>
<tr>
<td>$V$</td>
<td>Variogram function</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Nugget effect</td>
</tr>
<tr>
<td>$a_i$</td>
<td>Analytical result of increment $i$</td>
</tr>
<tr>
<td>$M_{s_i}$</td>
<td>Sample size or flow rate at the time of sampling</td>
</tr>
<tr>
<td>$\bar{M}_s$</td>
<td>Mean sample size or the mean flow rate</td>
</tr>
<tr>
<td>$h_i$</td>
<td>Heterogeneity contribution</td>
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This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by the word Publication followed by its number both in bold.


Author’s Contribution

**Publication 1:** TMKL defined the research plan with input from MM, was responsible for the analysis and wrote the manuscript under the supervision of NS and OD. MM contributed to the validation of the methodology. NS and MM critically reviewed the discussions and conclusions.

**Publication 2:** TMKL was responsible for the experimental design with the input from NS, performed the experimental work, analyzed the corresponding results, and wrote the manuscript under the supervision of NS and OD. NS critically reviewed the results and conclusions.

**Publication 3:** TMKL defined the methodology with input from NS, MB, and HM. TMKL was responsible for the execution of the experimental work, investigation of the results, and writing the manuscript under the supervision of OD. MB and HM contributed to the interpretation of the results. NS critically reviewed the results and discussions.

**Publication 4:** TMKL defined the methodology, was responsible for the data analysis and the interpretation with input from QD and BM. TMKL was responsible for writing the manuscript with input from QD and under the supervision of NS and OD. QD contributed to the computing program and critically reviewed the results and discussions.
1. Introduction

Access to water is one of the most critical aspects of mining activities (Levy et al., 2006; Nguyen et al., 2014). Today, global withdrawals for mining are estimated to be 6 to 8 billion m$^3$ per year (Gunson, 2013). On the global scale, water used for mining operations is not significant compared to agriculture or domestic use. In the USA in 2015, the mining industry only consumed 1% of total fresh water withdrawals (Dieter et al., 2015). Nevertheless, the water used in the mining industry is expected to increase further due to (1) the increase in the processing tonnages, (2) the decrease in ore grades, and (3) the increase in metal demands (Mudd, 2010). For the industrial processing conditions theoretically, about 2.5 m$^3$ of water is needed for a ton of ore. Generally, water use is often over 4 m$^3$/ton (Gunson, 2013).

In moderate to high-risk water areas, water consumption for mining activities could be dominating (Northey et al., 2016), exacerbating local water stress and the environment (Northey and Haque, 2013; Punkkinen et al., 2016). The extraction of fresh surface water and deep groundwater will become more restricted by tighter permitting in many jurisdictions. Therefore, reducing fresh water consumption is becoming a critical factor in sustainability (Gunson et al., 2012).

Due to the tightening of environmental regulations (Kinnunen et al., 2021), and the negative environmental reputation of mining activity (Bebbington and Williams, 2008; Northey et al., 2016), mining companies will be forced to reduce the volume of discharge effluents towards nil. Today, the major concern of the local communities and the downstream population is the contamination of the water supply due to mining activities (Bebbington and Williams, 2008). Typically, discharged waters from mine sites are regulated and the limits are set on both discharged effluent quantity and pollutant concentration (Northey et al., 2016). In some countries obtaining a water use license is even easier than getting a discharge license (Kinnunen et al., 2021).

Attempts to implement the re-use of water have started already in the 1970s (Forssberg and Hallin, 1989; Pickett and Joe, 1974; Rao and Finch, 1989). The efforts were particularly focused on recycling water from the tailings ponds, where only simple cleaning technologies were applied (e.g., lime addition to raising the pH to a higher value for metal hydroxide precipitation). However, already then the changes in water quality due to closing the water loop were shown to have an impact on operations treating sulfide ores (Forssberg and Hallin, 1989; Johnson, 2003; Schumann et al., 2009).
1.1 Water management in mining industry

The water in mining industry is typically managed for fulfilling environmental regulations by mostly using end-of-pipe solutions (Zotter, 2004). Those technologies aim at cleaning the effluent, and the obtained waste is considered to be valueless. By definition, end-of-pipe solutions do not affect the operation performance since they target the final effluent of the process and can be operated independently from the production operation (Zotter, 2004). The advantages of those solutions are the mature technologies used and the higher legal security since they are recognized by the official authorities (Kinnunen et al., 2021). Increasing the water recycling rate and reducing the volume of effluents further with end-of-pipe solutions will either require much more efficient and costly cleaning technologies (e.g., reverse osmosis with solutions for handling of the reject fraction) or accepting the effects of higher contamination concentrations on recovery of the valuable constituents.

Managing water in a context related to operating performance, instead of end-of-pipe solutions can offer a more effective possibility to achieve the goals required by permitting and social license to operate (Zotter, 2004). Integration of water recycling with flotation chemistry has a vital role in saving fresh water resources and reducing effluent volumes. It may offer the possibility to design a zero-emission minerals processing plant (Punkkinen et al., 2016, Northey et al., 2019). However, the process-integrated solutions will generally increase the complexity of the system, therefore create new challenges for both researchers and engineers (Zotter, 2004, Kinnunen et al., 2021).

This thesis explores such challenges.

1.2 Water intensive technologies in mining

1.2.1 Grinding

Sulfide ores contain typically valuable minerals locked with other sulfides and with gangue minerals such as silicates and carbonates. To liberate the valuable minerals the ore is ground together with water to a slurry. Usually, mild steel grinding media is used. A part of the water is added with the crushed ore to the mills and part to classification to dilute the slurry from the mills to a suitable lower pulp density for efficient classification (Wills and Finch, 2015).

The water property matrix starts to change rapidly in grinding as mineral free surface area increases in a reductive environment.

1.2.2 Froth flotation

Froth flotation is the most common method for recovery of valuable minerals (Wills and Finch, 2015) and the most water-intensive unit operation in a mine (Gunson et al., 2012). It facilitates the mining of low-grade ores and complex ore bodies otherwise considered as uneconomic (Wills and Finch, 2015). The separation process is based on natural or induced differences in the surface properties of the minerals. Precisely, the mineral surface can be either wetted by water (i.e., hydrophilic) or water repellent (i.e., hydrophobic). During the flotation, reagents are used to activate, depress, disperse, clean the surface of minerals, and control pH (Wills and Finch, 2015). Under the right conditions, a mineral surface can become hydrophobic, and attach to air bubbles, be floated, and recovered into the froth phase. Per se, the flotation system is already a very complex
system with interactions of three phases (solids, liquid, and air) and the interaction of chemical and physical parameters. All additional changes in ore, operating condition, temperature, water quality could severely affect the interactions of the phases and therefore, the flotation performance (Levay et al., 2001; Slatter et al., 2009).

In flotation, the composition of the ore and its texture characteristics are the most important factors that dictate the flotation regime for the recovery of the valuable minerals (e.g., flotation reagents and the sequence of flotation) (Bulatovic, 2007). Quite often, the ore contains several minerals of interest that have similar flotation characteristics. Notably, some minerals of interest have very similar properties to valueless gangue minerals (Lynch et al., 1974; Manouchehri, 2017). Therefore, there is a very narrow window where the operator can treat the ore to induce the difference in surface properties of the minerals, make a successful recovery and maintain the performance (Schumann et al., 2009). The variation of water quality can render the task even more challenging (Bulatovic, 2007; Wills and Finch, 2015; Slatter et al., 2009). A short literature review about the effect of closing water circuits on the water quality and the effect of water quality on flotation performance can be found in Chapter 1.3.1.

1.3 Closing the water loops in mineral processing

Two types of water recycling systems are recognized in the literature: long and short recycle (Figure 1) (Johnson, 2003; Levay et al., 2001). They differ fundamentally in the process of separating the liquid and solid (i.e., the dewatering method). There are many dewatering processes, including screening, conventional or paste thickening, filtration, and sedimentation in the tailings dam.

In the long recycle, the tailings are often deposited in a dam as a 20-35 w/w % slurry directly after flotation without any thickening (Figure 1B). Solids sediment to the bottom of the main storage dam of the tailings storage facility (TSF). The decanted water is recirculated from the storage dam through clarification pond(s) back to use or discharged as effluent. The residence time of water in the long cycle range from a few weeks to several months (Kinnunen et al., 2021; Muzenda, 2010).

The short recycle water circuit comprises dewatering and filtration units (Levay and Schumann, 2006). The thickening process of a short recycle often involves the use of gravity-assisted thickening methods or additional use of selected chemicals for flocculation and coagulation, which results in thickened tailings or paste tailings (Dunne, 2012). Compared to conventional tailings deposition, the percentage solids of deposited tailings and paste tailings are high, around 60-70% solids, and >70% solids, respectively (Moolman and Vietti, 2012). The thickened tailings and paste tailings are stored as moist or semi-dry stacks in the TSF (Dunne, 2012), reducing the potential risk of dam failure and water contamination due to acid drainage (Jones and Boger, 2012). The recovered water from the thickening processes is recirculated back to the flotation process within a few hours. Compared to the conventional tailings disposal (tailings dam), the thickened tailings and paste tailings (Figure 1C) significantly increase the water recycling rate and water efficiency (Adiansyah et al., 2015; Ihle and Kracht, 2018).
1.3.1 Effect of closing the water loop on flotation performance

Even without water recirculation, pulp chemistry can cause several challenges on flotation performance (Bulatovic, 2007; Wills and Finch, 2015). Interactions between dissolved elements from the ore, reagents, microorganisms, and suspended solids in the flotation system can interfere with any of the three phases involved in flotation: mineral surfaces, air bubbles, and the aqueous phase (Levay et al., 2001).

Recycling water can create a higher variation in water quality and create even more challenges in pulp chemistry (Slatter et al., 2009). Generally, the most common variations observed in the recycled water quality are the changes in the chemical and physical properties, the accumulation of recycled reagent, and the increase in microbiological activities (Johnson, 2003; Schumann et al., 2009). Major factors are responsible for those variations (Figure 2): difference in terms of quality of water sources available on the mine site, water blending strategy, seasonal variations, dissolution of contaminants from the gangue or mineral species, reactions in the TSF, biological activities, operating conditions (Forssberg and Hallin, 1989; Johnson, 2003; Levay et al., 2003; Schumann et al., 2009; Liu et al., 2013a).

Figure 2 outlines the complexity of the causes and effects of water quality in mineral processing by flotation. The most dangerous variation is the change of pH and Eh (Wills and Finch, 2015, Levay et al., 2001). The right pH and Eh values are critical for the mineral surface properties, hence the adsorption of collectors (Wills and Finch, 2015, Grano, 2010). However, in practice, process engineers can only rely on the balance between reagent concentration and pH to maintain the selectivity of the process since it is difficult to monitor and modify Eh in a slurry (Wills and Finch, 2015). Additionally, the speciation of the collector can change with pH (Figure 2). For example, in the flotation process that uses amine as a collector, a rise of pH to 12 results in a severe decline in flotation as the molecular form of amine becomes dominant (Wills and Finch, 2015). Another example is the decomposition of xanthate to dixanthogen at low pH affecting the selectivity of the flotation (Shen et al., 2016). It is also documented that the sudden changes in pH and Eh can precipitate colloidal particles as crystallites and gels which turns the particle surface hydrophilic (Levay et al., 2001). Moreover, dissolved species precipitating as metal hydroxide or unsoluble salts (such as gypsum) due to the pH adjustment process can coat
the minerals and then reduce the recovery of the valuable minerals (Fornasiero et al., 2006; Senior et al., 1991; Grano et al., 1995).

The dissolved species in recycled water may have positive effects on the performance of a flotation process. For example, the presence of salt in water is needed to stabilize the froth (Farrokhpay and Zanin, 2011). The positive effect of high salt concentration on the flotation of nickel sulfide minerals was documented by Wellham et al. in 1992 as it induces particle coagulation and reduces the electrical double layer between particles and air bubbles (Kurniawan et al., 2011). Nevertheless, very high concentrations of species combined with a change in thermodynamic conditions to favor precipitation can represent a threat to the process.

Water closure could also increase suspended solids in the process water, particularly in the short recycle water system (Slatter et al., 2009). The formation of slime coatings on the surface minerals can, for example, dramatically reduce pentlandite flotation due to the modification of surface charge (Edwards et al., 1980).

The accumulation of reagents and their derived decomposition compounds is common but not always observed (Schumann et al., 2009). The recycling of reagents can be beneficial for reducing the reagents consumption both in the milling and flotation circuits (Pickett and Joe, 1974) as long as the reagents are still in their original form and no decomposition products that might have detrimental effects are present. Recycling process water can reduce 50% of the previously used amounts of reagents (Forssberg et al., 1989). However, the recycled collectors could represent a threat in the case of sequential flotation circuits (Muzinda et al., 2018).

Furthermore, the accumulation of heat and nutrients can favor the development of microorganisms. The effect of bacteria on the flotation and the mechanism are largely unknown. However, it could act as surface activators, dispersants, or flocculants and interfere with the flotation process (Forssberg and Hallin, 1989; Levay et al., 2001; Levay and Schumann, 2006; Liu et al., 2013a; Rao and Finch, 1989; Liu et al., 2013b)
Figure 2: The causes of water quality variation and its effects on the flotation performance
1.3.2 Challenges to manage PW towards improving plant performance

There are very few studies on the increase in complexity of the production system (Zotter, 2004) or the new balance obtained when water recirculations are implemented in a process (Kinnunen et al., 2021). The transformation of water quality into an operating parameter so that it could be modified to suit the requirements of particular process steps is the requirement for process integrated solutions. A parameter can be considered as an operating parameter only when its effects on the process performance are known (i.e. the optimal operating range could be defined) (Wills and Finch, 2015). Additionally, its value should be monitored easily and adjusted quickly (Laurila et al., 1998). Ideally, its variation due to the change of ore type, availability, and quality of different water sources (Kunz and Moran, 2016), and climatic changes (Gao et al., 2017) should be predicted so the adjustment could be anticipated beforehand.

All mine waters have different characteristics (Wahlström et al., 2016). However, they are all very mine-specific, dynamic, and complex (Figure 3).

![Figure 3: Key characteristics of mining recycled process water](image)

The recycled process water characteristics are mainly defined by ore mineralogy, enrichment process, mine water circuit, plant location, and local seasonal water regime (Gunson et al., 2012; Wahlström et al., 2016). All those parameters are unique for any mine site. Therefore, the water matrix composition and its variation patterns vary highly from one mine to another (Wahlström et al., 2016). Consequently, solutions for evaluating, controlling, and purifying process water need to be customized for every mine site. This characteristic of the recycled process water induces a challenge in predicting the
effect of water quality on the flotation performance in greenfield cases, as no information about the future water matrix is available.

Additionally, the recycled mining process water characteristics are dynamic. The decrease of the water residence time in the TSF from months to hours results in a disequilibrium of the thermodynamic condition (Muzinda, 2010). Therefore, the dynamicity is characterized by the fluctuation of the process-related variables, the way water is managed on-site (Johnson, 2003), the instability of constituents due to microbiological action, and continuing, kinetically-controlled reactions of dissolved species (Levay et al., 2001). The local hydrological and climatic setting of the mine can also contribute to the dynamicity of the recycled water by altering its composition via precipitation and evaporation (Kinnunen et al., 2021; Muzinda and Schreithofer, 2018; Westerstrand and Öhlander, 2011).

The process water matrix defines its quality (Levy et al., 2006). The composition of process water in mineral processing is not characterized by one parameter but many parameters that can be classified into four major groups: physical, chemical, physicochemical, and biological properties (Figure 3) (Levay et al., 2001; Levay and Schumann, 2006). The relations between those parameters are complex and interdependent (Schumann et al., 2009). Therefore, any changes in one parameter may result in changes in other parameters as well. Such complexity in terms of matrix and correlation makes the evaluation and control of process water quality challenging. However, when investigating the effect of water quality on flotation performance, very few researchers and mineral engineers consider such complexity. Most of their tests have been performed with synthetic water and were focused only on a few specific compounds (Manono et al., 2013, 2012; Yenial and Bulut, 2014). Such an approach could not reflect the complex nature of the process water, therefore, contributing to the gap between laboratory results and true plant performance (Pietrobon et al., 2004).

The afore discussed complexity, dynamicity, and mine-specificity of mining process water in a closed water loop system challenge the attempts to evaluate, monitor, adjust and predict its quality and variation (Levay et al., 2001; Rao and Finch, 1989; Schumann et al., 2009).

1.4 Rationale and importance of the study

The most important aspect of this work is its attempt to show the complexity, dynamicity, and mine-specificity of the mining process water in the case of closed water recirculation and the importance of adapting, modifying current tools for evaluating, monitoring, controlling, and predicting its quality and variation. This work’s rationale arises from a question concerning how the methodologies for handling industrial water for operation purposes differ from environmental needs. It is essential to understand how methodologies developed for discharge effluent for fulfilling environmental regulations need to be modified when applying on process water. Up to date, there is no effort devoted to answering these questions.

This study aims to challenge the applicability of standard generic methods, traditional thinking, and practices developed for environmental monitoring purposes for studying mining process water. Such studies are significant since they are crucial for (1) designing a proper database that allows linking the water quality to the plant performance, (2) for establishing an effective automatic approach for water management in the mining industry towards operation performance improvement, and (3) for adjusting process design...
and process selection in the early phase. Those are fundamental elements that allow for turning water into an industrial business case.

Indeed, to be able to adjust the water quality for improving process performance, one needs to be able to understand the effect of the water quality of a concentrator (Kinnunen et al., 2021; Wills and Finch, 2015). Many studies and decisions related to processing plants rely on the analysis results provided by certified, accredited analysis laboratories. To date, there is no study questioning the accuracy of applying generic standardized methods developed mostly for environmental monitoring purposes for evaluating mining process waters, which are very mine specific and very dynamic.

Moreover, to investigate the influence of water quality on flotation performance, laboratory experiments are still the primary choice (Biçak et al., 2012; Ikumapayi and Rao, 2015; Manono et al., 2013, 2012). Nevertheless, (big) data-driven approaches such as statistical analysis, machine learning, or even neural network analyses are becoming better candidates due to their power to overcome the complexity of the flotation systems (Brzychczy et al., 2020; Qi, 2020, Jahedsaravani et al., 2014). The second approach is currently limited by the amount and quality of data available. To predict plant performance, mineralogy, water quality, and operating condition data are needed to train the predictor system. While ore mineralogy data is relatively abundant for most orebodies and online monitoring is also available in many cases ((Becker et al., 2014; Bushell, 2012; Peltoniemi et al., 2020), this is not the case for water quality data. Generally, the sampling frequency is sparse and determined by environmental regulations (Westerstrand and Öhlander, 2011). Such an approach might not be relevant for capturing the variation of process water quality and therefore is not suitable to provide any meaningful relation to processing plant performance. This study aims to discuss the way that water quality data should be collected to obtain relevant information for process control purposes.

Additionally, to maintain or modify water quality, it is important to have a monitoring system that sets off an alarm when the water matrix drifts away from the acceptable regime (Punkkinen et al., 2016) or when the water matrix needs to be modified into a “right composition” due to changes in ore characteristics. This study aims to understand how methods developed for monitoring discharge effluent for fulfilling environmental regulations need to be modified when applying on process water.

Moreover, very little work has been conducted on the dynamicity and complexity of mining process water when performing laboratory testing, plant design, and process selection. Ignoring those properties might lead to the wrong conclusion on a laboratory scale and an inappropriate plant design that might require further expensive modifications in plant-scale (Pietrobon et al., 2004). Additionally, the modeling of water effects will be a key for the final closure of water circuits. Much of the models have been single variable models. This work explores to create a further understanding of how to move towards multi-variable models.

1.5 Objectives of the thesis

This work focuses on how the methodologies used for evaluating, monitoring, controlling, and predicting the quality of mining process water need to be modified so process water quality can be turned into an operating parameter. The case study objects are two European mine sites.

The ambitious objectives try to point out the need for new ways of thinking when dealing with mining process water.
The objectives also emphasize the importance of revising the traditional practices and implementing new tools for process water handling towards improving the process performance.

The objectives of the work are:

- To understand the properties of mining process water that make it so challenging to evaluate, monitor, control, and predict.
- To evaluate the current practices concerning water handling in mining and how they needed to be modified to take into consideration those above properties.
- To explore the different sources that contribute to the variations of mining process water.
- To identify the required tools needed for creating a reliable water quality database to improve operating performance-related context.

The following hypothesis was set up based on the initial observations made at the study objects and literature review:

- Water can only be considered as a possible operating parameter when and only when: (1) the effects of its properties on the operating performance are known (Wills and Finch, 2015), (2) its variations can be spotted rapidly, (3) its composition can be modified quickly (Laurila et al., 1998).
- The relevant water property matrix is always multidimensional and dynamic. No effect on the process can be attributed solely to a single variable or parameter.
- The relevant complex features can be captured by advanced mathematical and statistical methods supported by specially designed industrial data-sets and laboratory test work.
- Due to the dynamicity, complexity, and mine-specificity of mining recycled process water matrix, the water characterization for environmental needs is not sufficient and does not capture the relevant features affecting operational efficiency.

The hypotheses were approached through the following research questions:

- What levels of complexity, dynamicity, and mine-specificity should be expected when dealing with recycled process water in mining industry? (Publications 1, 3, and 4)
- What are the main drivers behind those characteristics? (Publications 1, 3, and 4)
- What are the limitations of the current methods that are used to evaluate water quality? (Publications 3 and 4)
- What is the definition of a good database for identifying the effect of water quality on process performance (Publications 1, 3, 4)?
- What is the most suitable statistical method for monitoring a complex water matrix (Publication 1)?
How can the variability of water quality be predicted and integrated into the water management plan? (Publication 2)

1.6 Structure of the thesis

The core of this study examines current practices applied in the mining industry for managing process water to optimize the operating performance. It is essential to understand how those practices should be modified and integrated into plant design and water management systems if the water is becoming a fully recycled enabler of the flotation process and not an environmentally risky effluent.

This study focuses on three aspects for effective management of water towards optimizing process performance (see Chapter 2.1): (1) a database for linking water quality to flotation performance output and serving as a base to explore the process water behaviors and characteristics, (2) tools for monitoring and controlling process water quality and (3) a laboratory protocol for creating and predicting the plant process water for testing and plant design. To achieve those objectives different tools are needed (Table 1).

In order to create an appropriate database, water characterization procedures applicable for mining process water are needed. Such a procedure should be taken into consideration the high variation, unstable and mine-specific characteristics of mining process water.

To control and monitor process water quality, databases and methods for monitoring are required. However, they are currently set up for monitoring water effluent in order to answer environmental regulations. Therefore, they might not be suitable to apply on process water for process performance optimization purposes (see Chapter 2.1.1 and 2.1.2).

Finally, to be able to anticipate beforehand the changes of process water properties on process performance, tools for predicting the future changes in terms of water quality due to the closed water recirculation are needed. Additionally, there is a need for a protocol that allows to create a “laboratory process water” that mimics the real process water for laboratory testing. Currently, such a protocol are still missing.

Hypothesis on the restraints of the current practices related to mining water is summarized in Table 1 along with the objectives that this thesis attempts to achieve.
<table>
<thead>
<tr>
<th><strong>Target/challenge</strong></th>
<th><strong>Tool requirements</strong></th>
<th><strong>Current practices</strong></th>
<th><strong>Hypothesis on the restraint of current practices</strong></th>
<th><strong>PW properties supporting the hypothesis</strong></th>
<th><strong>Thesis objective</strong></th>
<th><strong>Support</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Creating database to link water quality to flotation performance and to understand the plant water matrix and its behavior</td>
<td>Water characterization procedure</td>
<td>Spot sampling</td>
<td>Spot sampling gives a very high sampling error</td>
<td>Highly fluctuating</td>
<td>Investigating the magnitude of water quality dynamicity and its driving forces</td>
<td>Publication 1, 3-4</td>
</tr>
<tr>
<td>Monitoring and controlling water quality</td>
<td>Database</td>
<td>Water is monitored for environmental purpose</td>
<td>Monitoring frequency is too scarce to capture the full variation of water quality</td>
<td>Highly fluctuating</td>
<td>Design a potential &quot;good&quot; database for monitoring</td>
<td>Publication 1, 3-4</td>
</tr>
<tr>
<td>Predicting water quality variation to improve the design in the early phase</td>
<td>Monitoring methods</td>
<td>Focus on few specific parameters obligated by environmental regulations</td>
<td>The database is not suitable for monitoring the water quality for process performance optimization purpose</td>
<td>Complex</td>
<td>Applying multivariate approach for monitoring water quality</td>
<td>Publication 1</td>
</tr>
<tr>
<td>Creating a &quot;laboratory&quot; water similar to process water for testing</td>
<td>Alaboratory protocol for predicting the potential water matrix created by closed water recirculation of the plant</td>
<td>Literature mostly focused on predicting wastewater quality (e.g. AMD). Predicting model is based on either thermodynamic laws or leaching kinetics</td>
<td>Not suitable for predicting PW since the ore is not in the same pathway</td>
<td>Novel laboratory protocol for predicting and producing &quot;laboratory&quot; PW</td>
<td>Publication 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Use of synthetic plant water to study the effect of water quality on flotation performance</td>
<td>The use of synthetic water is not suitable to study the effect of PW quality on flotation performance since synthetic water does not have the key properties of PW</td>
<td>Mine-specific, complex and dynamic</td>
<td>Potential use of the &quot;laboratory&quot; PW for studying the effect of water quality on the flotation performance</td>
<td>Publication 2</td>
</tr>
</tbody>
</table>
2. Theory framework and research materials

2.1 Tools for making water a business case

This chapter aims to define the three major cornerstones which are indispensable for making water a business case. It also discusses why those tools are so important and the challenges related to their development and application.

2.1.1 Database

One of the ultimate goals in studying water quality effects on flotation performance is to predict the flotation outcomes (e.g., grade, recovery) of the valuable minerals, which depends on ore composition, mineralogy, liberation, mineral surface characteristics, reagents dosages, the water quality, and operating conditions used (Bournival et al., 2019; Levay et al., 2001). However, the prediction is not an easy task due to the lack of appropriate databases (Westerstrand et al., 2011). Most of the datasets are either too sparse of observations (Westerstrand et al., 2011) or way too oversimplified in terms of parameters (Brzychczy et al., 2020). For example, in a study published in 2020, when studying the effect of water quality of the flotation of coal, Brzychczy et al. used only SPC and pH as the water matrix indicators. Such a simplification of the water matrix could ease the experimental design and computation but does not provide any meaningful information concerning the water composition.

Additionally, according to Laurila et al. (1998), more than 100 parameters can affect the flotation outcome, and water-related parameters are just a part of it. Any change in one of the system components will likely affect several other system parameters (Levay et al., 2001). Therefore, to match the plant performance outcome with the water quality, the dataset should contain, not only water-related parameters but other relevant parameters such as operating conditions (f.ex. PSD, air rate, and reagents dosage.), mineral surface conditions, and mineralogy (Bournival et al., 2019, Levay et al., 2001). Lack of any of those parameters will likely lead to a failure of the model.

Moreover, most of the water datasets available on-site are designed to meet the environmental monitoring needs (Westerstrand et al., 2011). This means that the sampling frequency is sparse and only focuses on the parameters regulated by the law (Bebbington and Williams, 2008). Such a dataset is not suitable for presenting the complexity and dynamicity of the mining process water. Therefore, using an environmental water dataset for the operation control and optimization purpose is not an appropriate approach.

All in all, useful datasets designed for operation control purposes, and suitable for applying advanced mathematical analysis and modeling are crucial to deal with the challenge of linking water quality and flotation performance. Currently, such datasets are still not readily available.
2.1.2 Monitoring system

The success of a flotation process depends on the interactions of the three phases present in the system: mineral surfaces and their composition (solid), the composition of the flotation media (liquid), and the state of the air bubble (gas) (Bulatovic, 2007; Wills and Finch, 2015). In mineral processing, quality control is one of the most critical issues and is mostly applied to the output products (grade and impurities) and feed quality. It is evident for mineral processing engineers that the ore’s varying and uncontrollable quality leads inevitably to a variation in the outputs and the consequent trade-off (Napier-Munn, 2014).

The mineral processing plants use largely PI(D) controllers for operational stabilization (Daniel and Villar, 2010). Water quality variation is considered together with ore variation as unmeasured and uncontrolled process disturbances. As a second control layer, different model predictive control schemes have become common in recent years (Quintanilla et al., 2020) improving the limited control efficiency obtained with PID controllers for interacting variables. However, very little attention has been given to control water quality towards improving process performance.

Control methods applied for the process could also be validated for controlling process water quality. However, unlike process performance which is usually characterized by few parameters (e.g. grade, recovery, impurities), process water is more complex. It is characterized by several interacting variables that are all relevant to the process/product quality. Therefore, they need to be monitored and controlled simultaneously (Alt and Smith, 1988). For a large number of variables, the OVAT approach is not practicable since the human brain is not made to examine a high number of univariate graphs simultaneously (Rogalewicz, 2012). Additionally the OVAT approach is well-known for its inefficiency in monitoring the variables when there are correlations between them. Thus, the measurement of one variable cannot reflect the whole system’s change (MacGregor and Kourti, 1995). Therefore, to monitor and control the process water matrix towards improving process performance, multivariate statistical approaches are needed instead of the OVAT method.

2.1.3 Protocol for predicting and creating PW matrix

The mining industry’s first attempt to evaluate the effect of recycling water on flotation performance started already in the 1970s (Pickett and Joe, 1974). Testing with fresh process water plant water remains as the best choice since using aged water is ineffective and inaccurate due to change in the water matrix caused by the continuing oxidation of thiosalts and biological activities (Levay et al., 2001; Grano, 2010). However, fresh process water is not always available, which is often the case. Therefore literature indicates that synthetic plant water is still mainly used to approach the issue (Bıçak et al., 2012; Ikumapayi and Rao, 2015; Manono et al., 2013, 2012). Even though synthetic water provides a flexible condition and allows to investigate the effect of water composition under specific conditions, it is mostly stable, oversimplified, and the ore might never get into contact with such a water matrix in the real plant. Researchers using the synthetic water approach have ignored some fundamental characteristics of the process water in a closed water recirculation: the process water in a closed water circuit is complex, dynamic, unstable, and mine-specific.

Furthermore, typical plant design and optimization are still based on several metallurgical batch flotation and pilot-scale tests using fresh tap water in the location where the
testing is done. Such an approach deliberately ignores the impact of the future recycled water on the flotation performance (Pietrobon et al., 2004). Consequently, there is a gap of validation between laboratory testing and plant performance (Pietrobon et al., 2004). More importantly, the fact that changes in water quality are not considered in the early phase of the plant design could lead to severe financial risks due to declining plant performance or unexpected plant maintenance needs (e.g., due to scaling/gypsum formation).

There is an important need of predicting the variation of process water quality due to the closed water circuit. However, very few references were found on the prediction of mining water quality (Abbassi et al., 2009; Declercq et al., 2017; Muniruzzaman et al., 2018). They are mostly based on thermodynamic calculation and focus on wastewater only. The thermodynamic calculations might help to predict the final chemical stage of the water constituents, but do not consider reaction kinetics (Declercq et al., 2017). In a recycling water system, especially in a short water cycle, the kinetics might govern since the water quality variation can be fast (Muzenda, 2010). Therefore, a test protocol to (1) empirically predict the water variation due to water closure in mineral processing plants and (2) produce recycled water that contains nearly the same impurities as real process water for laboratory testing needs to be built.

2.2 Research materials

Data and materials from two mine sites were available for this study, named Mine 1 and Mine 2 for confidentiality reasons. The characteristics of these two mines are detailed in Table 2.

Table 2: Characteristics of Mine 1 and Mine 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mine 1</th>
<th>Mine 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>South of Europe</td>
<td>Nordic countries</td>
</tr>
<tr>
<td>Climate</td>
<td>Mediterranean</td>
<td>Subarctic</td>
</tr>
<tr>
<td>Ore type</td>
<td>VMS, high-grade Cu-Pb-Zn ore</td>
<td>Low sulfide grade deposit, Cu-Ni-PMG ore</td>
</tr>
<tr>
<td></td>
<td>High pyrite content</td>
<td>Silicate minerals as the major phase</td>
</tr>
<tr>
<td></td>
<td>Strong variation of mineralogy as a function of the ore bodies</td>
<td></td>
</tr>
<tr>
<td>Processing method</td>
<td>Two separate flotation plants</td>
<td>Sequential circuit</td>
</tr>
<tr>
<td>Tailings deposit method</td>
<td>Paste deposition</td>
<td>Conventional wet tailings pond</td>
</tr>
<tr>
<td>Water circuit</td>
<td>Short water cycle</td>
<td>Long water cycle</td>
</tr>
<tr>
<td></td>
<td>Short residence time in the tailings storage facilities (TSF)</td>
<td>Long residence time in the TSF</td>
</tr>
<tr>
<td>Water matrix characterisation</td>
<td>High TDS (&gt;10 000 mg/L)</td>
<td>Cyclic variations due to the formation of an ice cap in the tailings pond during winter-time</td>
</tr>
<tr>
<td></td>
<td>High amounts of thiosalts</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Saturation in term of gypsum</td>
<td></td>
</tr>
</tbody>
</table>

The nature of the processed ore types, climate, processing method, tailings deposit method, and type of water circuit has a significant effect on each mine site’s water matrix properties. Both mines process sulfide ore. The main valuable minerals of interest are chalcopyrite, galena, sphalerite for Mine 1, and chalcopyrite, cubanite, pentlandite for Mine 2. A considerable variation in terms of mineralogy is observed throughout the ore bodies of Mine 1. Different ore bodies differ significantly in metal content as well as mineral composition. The content of pyrite can vary from 40% to 90% throughout the ore
bodies. Compared to Mine 1, Mine 2’s ore does not have such significant variations characteristics. The sulfide content of the ore is homogeneously low, less than 10%. However, mineralogy can locally vary significantly. Some of the mined blocks could have a higher concentration of some gangue minerals than others.

The water circuit of Mine 1 is complicated and subjected to many changes over the last decade. Before 2012, Mine 1 had a long water cycle. The tailings slurry was stored in a conventional wet tailings pond. The overflow water from the pond was directed back to the plant via the industrial water tank. The residence time for water recirculation from the tailings ponds to the plant was a few weeks.

Between 2010-2015 a transition took place from long water recycle circuit to short water recycle circuit. The paste plant was commissioned in November 2010. The new reservoir for industrial water (CDM reservoir) was completed in April 2015. During that interim period, the paste thickened tailings were stored in the tailings pond’s internal areas, limited by waste rock berms, leaving the external areas for industrial water. Since the completion of the CDM reservoir, and the paste plant’s full commissioning Mine 1 adopted a short water circuit (Figure 4). Currently, the tailings are deposited as a paste. The water from the paste plant’s dewatering process is redirected to the processing plants via the water reservoirs. The residence time for the recirculation of water from the paste plant to the plant is only a few hours. The current overall water circuit of Mine 1 is complicated with at least 11-12 different streams.

Figure 4 presents the current simplified water circuit of Mine 1. Two main water consumers are observed: the processing plants and the mine. The tailings from the processing plants are mixed and directed to the tailings pump station where the coarse tailings are separated from the fine tailings. The coarse fraction is then directed to the mine for underground paste filling. The fine fraction is transferred to the paste plant together with the clarifier underflow from the mine. The paste plant which is a series of paste thickeners thickens the tailings and discharges most of the water to the industrial water tanks. Excess water from water tanks is reported to the mine or the CDM reservoir. The same reservoir receives mine’s surface water.

There are two water treatment plants in Mine 1: ETAM and Fenton-HSD. ETAM treats the mines’ clarifier overflow to provide gland seal water used in the processing plant. The Fenton-HSD treats thiosalts in the CDM reservoir by oxidation into sulfate and removed the latter as precipitation of gypsum.

Figure 4: Simplified water circuit of Mine 1 (Figure from Publication1)
Mine 2 has a long water circuit since the beginning of its operation in 2012. The tailing slurry from the processing plant is stored in two tailings ponds: high sulfur tailing pond effluent (TSF B), low sulfur tailing pond effluent (TSF A) (Figure 5). The TSF B output is conducted to the TSF A. Water from the TSF A is directed either to the water reservoir or the processing plant water tank. The reservoir also collects surface runoff from the site and the waste rock dump area. Water from the reservoir is mostly pumped to the process water tank in the plant. If there is excessive water in the system, the excess will be released after treatment. Most of the fresh water supply to the plant is withdrawn from the nearby local river. Fresh water is mostly used for chemical preparation and as gland seal water.

The percentage of water being recycled in both plants varies depending on the season. Mine 1 cannot discharge water during the dry season when there is no water in the river. Therefore, the only way water leaves the plant during the dry season is via evaporation. During that period, the percentage of water being recycled is closed to 100%. However, not all water recycled is used again in the processing plant. Depending on the water quality and the plant performance, recycled water could be stored, treated or diluted with fresh intake water. During the wet season, water is discharged only when the water balance is positive. For mine 2, the recycled water counts for almost more than 90% of the water used in the mine. Most of the discharge happens during spring when the snow melts or in summer when the water balance is positive.
3. Methodologies

3.1 Data analysis methods and their application

3.1.1 PCA

Principle Component Analysis (PCA) is a data-driven modeling technique used for data compression and information extraction (Bro and Smilde, 2014; Wise and Gallagher, 1996). The method aims to translate a set of correlated variables into a smaller set of new variables called principal components (PCs). The most important characteristics of the PC are that they are uncorrelated and retain most of the information of the original dataset.

PCA method uses Equation 1 to decompose the initial matrix data:

$$X = T \times P^T + E = \sum_{i=1}^{n} t_i p_i^T + E$$

Where

- $T$ is the score vector that contains the information on how different observations relate to each other.
- $P$ is the loadings vector that contains the information about the correlation between variables
- $n$ is the number of the components retained in the model that must be less than or equal to the smaller dimension of the initial matrix $X$.
- $E$ is the residual matrix.
- $T$ is the transpose operator

The reliability of the model depends on the number of retained PCs. There are different criteria to choose the number of PCs. However, the most practical way is to look at the cumulative fraction (%) of the original variance captured by the few first PCs and choose the number of PCs that capture the most or desirable variability of the data (Bro and Smilde, 2014).

3.1.2 Variogram and multivariogram

The semi-variogram (referred to as variogram for the remainder of this thesis) is useful in summarizing the heterogeneity of 1D lots or continuous moving stream (Petersen et al., 2005; Saunders et al., 1989). It describes the variation observed between units as a function of the distance (in time or space) between them (Petersen et al., 2005). Mathematically, the variographic data modeling characterizes half of the average analyte concentration differences between increments, calculated as a mean squared difference, as shown in Equation 2 below:

$$V(j) = \frac{1}{2(N-j)\sigma^2} \sum_{m} (a_{m+j} - a_m)^2$$

Where
- $N$: Number of increments extracted
- $j$: Lag parameter, describes the distance between two extracted units
- $a_i$: Analytical results of increment $i$
- $a_l$: Lot Average value of the analytical results

The information about the complexity of the variation along the profile is presented via three main features: the range, the sill, and the nugget effects (Figure 6). The range indicates the limit of the inter-lag distance after which autocorrelation is no longer observable. The sill informs on the total variability of the lot for the properties considered. Furthermore finally, the nugget effect ($V_0$) is considered as the discontinuous random part of the variogram (Minkkinen and Esbensen, 2014). $V_0$ was estimated by backward extrapolation of the variogram towards the origin or added experiment with a very high sampling frequency. The meaning of three key parameters within the realm of TOS will be found in Chapter 3.3.1.

The shape of the variogram reflects the characteristics of the process. The variogram of processes displaying a drift is mostly an increasing variogram, which may or may not level off after the range (Minkkinen and Esbensen, 2014).

![Figure 6: Typical variogram, illustrating the key parameters](image)

The experimental nugget effect $V_0$ is the value of the variogram at the origin and accounts for all variance of fundamental sampling error, grouping and segregation error, incorrect sampling error and total analysis error. The range is the lag distance beyond which no further autocorrelation occurs, and the sill which reflects the overall process variance is the flat part of the variogram.

In the case of multi-related variables, each variable exhibits these common characteristics, but to a varying degree. In this sense, the correlations between the variables are as important as the variables themselves. Bourgault and Marcotte (1991) were the first to formalize the principle of a multivariate variogram (denoted as multivariogram in this work) which is defined in a way similar to that of the traditional variogram but in a p-multidimensional space.

The multivariogram is defined by Equation 3 (Dehaine et al., 2016):

$$V(j) = \frac{1}{2(N_u - j)} \sum_{m} \{H_{m+j} - H_{m}\} M \{H_{m+j} - H_{m}\}^T$$  \hspace{1cm} (3)

Where:
**Methodologies**

- $H_i$ is a vector of $p$ elements that characterizes the individual heterogeneity contributions of variables considered for the study in the position $i$, defined as $H_i = [h_1, h_2, h_3, ..., h_p]$ with $i = 1, ..., N$ and $p$ the number of parameters,

- $T$ is the transpose operator,

- $M$ is a $p \times p$ positive definite symmetric matrix that defines the metric in calculating the “distance” between the units. This metric defines the relation between the variables. When $M =$ the identity matrix, the experimental multivariogram is simply the sum of all the elementary experimental variograms. In the case of a strong correlation between variables, the inverse of the covariance matrix is used as the metric matrix. This kind of matrix described the Mahalanobis distance between the variables (De Maesschalck et al., 2000).

This approach allows to summarise the variability of all variables in a single variogram. The heterogeneity contribution can be defined as the deviation of the analytical result, $a$, of the increment $i$ from the lot mean $a_L$. There are two way to define the heterogeneity contribution, either as relative (dimensionless) or absolute as shown in Equation 4 and 5, respectively.

Relative heterogeneity contribution:

$$h_i = \frac{(a_i - a_L) M_{S_i}}{M_S}$$

Absolute heterogeneity contribution:

$$h_i = (a_i - a_L) \frac{M_{S_i}}{M_S}$$

Where $a_i$ is the analytical result of the increment, $M_{S_i}$ is the sample size of the flow rate at the sampling time, $\bar{M}_S$ is the mean sample size or the mean flow rate

### 3.1.3 Application

Analysis methods such as PCA, variogram, and multivariogram were computed on datasets received from the mines to investigate the correlation between variables and the tendency of variations over time.

Two datasets were obtained from Mine 1. Dataset 1 contained information about the process water stream that fed to the plant. The quality of that stream was monitored over 16 years, from 2002-2018. From the beginning of 2002 to the end of 2014 only six parameters (pH, SPC, DO, calcium, COD, and sulfate) were monitored monthly. In total, this portion of the dataset contains 144 observations. From 2015 to 2018, five parameters (total alkalinity, carbonate, bicarbonate, hydroxide, and thiosalts) were added to the monitoring plan. In total, from 2015, 11 parameters were monitored daily. This portion of the dataset contained 638 observations. The univariate overview of the parameters is found in Table 3. PCA analysis was applied on the portion of the dataset that contains pH, SPC, DO, calcium, COD, and sulfate for investigating the correlation between variables and evaluating the historical variation of water quality. The portion of the dataset that contained all 11 parameters, collected from September 2015 to May 2018 was used for MSPC (see Chapter 3.4). Dataset 2 contained 14 variables: pH, magnesium, metals
(sum of copper, iron, zinc, aluminum), sulfate, total sulfur, chloride, sodium, potassium, calcium, nitrate, thiosalts, COD, and sulfide that have been monthly monitored in 14 major streams of Mine 1 during the year of 2014-2015. PCA was applied in this dataset to investigate the complexity of water quality in the Mine 1 water circuit.

Table 3: The univariate (range, mean and standard deviation) overview of Mine 1, Dataset 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Monitoring period</th>
<th>Range</th>
<th>Mean</th>
<th>Std</th>
<th>Count</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1/2002-5/2018</td>
<td>3-12</td>
<td>9</td>
<td>1</td>
<td>797</td>
</tr>
<tr>
<td>SPC (µS/cm)</td>
<td>1/2002-5/2018</td>
<td>3700-10200</td>
<td>7467</td>
<td>1652</td>
<td>797</td>
</tr>
<tr>
<td>DO (%)</td>
<td>1/2002-5/2018</td>
<td>0-100</td>
<td>33</td>
<td>23</td>
<td>797</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>1/2002-5/2018</td>
<td>3-2116</td>
<td>872</td>
<td>145</td>
<td>797</td>
</tr>
<tr>
<td>COD (mg O₂/L)</td>
<td>1/2002-5/2018</td>
<td>0.31-1400</td>
<td>514</td>
<td>255</td>
<td>797</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>1/2002-5/2018</td>
<td>1600-5500</td>
<td>3319</td>
<td>758</td>
<td>797</td>
</tr>
<tr>
<td>Tot. Alkal. (mg/L)</td>
<td>9/2015-5/2018</td>
<td>0-850</td>
<td>60</td>
<td>51</td>
<td>638</td>
</tr>
<tr>
<td>CO₃²⁻ (mg/L)</td>
<td>9/2015-5/2018</td>
<td>0-170</td>
<td>40</td>
<td>31</td>
<td>638</td>
</tr>
<tr>
<td>HCO₃⁻ (mg/L)</td>
<td>9/2015-5/2018</td>
<td>0-69</td>
<td>9</td>
<td>11</td>
<td>638</td>
</tr>
<tr>
<td>OH⁻ (mg/L)</td>
<td>9/2015-5/2018</td>
<td>0-755</td>
<td>10</td>
<td>36</td>
<td>638</td>
</tr>
<tr>
<td>Thiosalts (mg/L)</td>
<td>9/2015-5/2018</td>
<td>128-3669</td>
<td>1818</td>
<td>453</td>
<td>638</td>
</tr>
</tbody>
</table>

Two datasets have been provided by Mine 2: a high-frequency (HF) dataset and a weekly monitoring dataset. The HF was obtained by implementing the YSI ProDSS multi-probe in the water process for one week with a reading frequency of 1 per 10 minutes. The probe allowed to monitored 5 properties of the process water: SPC, pH, Eh, turbidity, and DO. To ensure the quality of the reading, the probe was daily checked with the YSI confidence solution. In total, the dataset contains 980 observations. The weekly dataset (dataset 2) contained 60 observations, taken over 14 months, from May 2017 to July 2018. The sample was taken from the tailings ponds discharge where water is recycled and fed back to the plant. The sampling method was spot sampling. This dataset contained 12 variables as shown in Table 4. PCA and variogram were applied to those datasets to (1) investigate the tendency of correlation between variables, (2) evaluate the range and frequency variations, and (3) design the sampling method (see Chapter 3.3.1).

Table 4 summarizes the characteristics of the dataset, methods that have been applied to them, objectives of the analysis, and chapter than the results can be found.
### Table 4: Characteristics of the dataset, analysis method, the objective of the analysis and support chapter that the results can be found

<table>
<thead>
<tr>
<th>Dataset number</th>
<th>Description</th>
<th>Method</th>
<th>Objectives of the analysis</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mine 1 Dataset 1</td>
<td>The process water stream that fed the concentrator was monitored over 16 years, from 2002-2018. The dataset from 2002 to the end of 2014 contained six parameters: pH, SPC, DO, calcium, COD, and sulfate. The water was monitored monthly during that period, with 144 observations in total. From 2015 to 2018, total alkalinity, carbonate, hydrocarbonate, hydroxide, and thiosalts were added into the monitoring dataset. They were monitored daily. This portion of the dataset contained 638 observations.</td>
<td>PCA</td>
<td>Investigate the correlation between variables</td>
<td>4.1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Evaluate the variation of water quality</td>
<td>4.2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MSPC</td>
<td></td>
<td>4.4</td>
</tr>
<tr>
<td>Mine 2 Dataset 1</td>
<td>This dataset contains 14 properties: pH, SPC, magnesium, metals (sum of copper, iron, zinc, aluminum), sulfate, total sulfur, chloride, sodium, potassium, calcium, nitrate, thiosalts, COD, sulfide that have been monitored in 14 major streams during the year of 2014-2015</td>
<td>PCA</td>
<td>Investigate the diversity in term of quality of available water sources in the mine</td>
<td>4.2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mine 2 Dataset 1 (HF dataset)</td>
<td>This dataset was obtained by monitoring with the YSI ProDSS multiprobe in the process water for one week. In total five properties were monitored: SPC, pH, Eh, turbidity, DO. The frequency of recording was 1 per 10 minutes. In total this dataset contains 980 observations</td>
<td>PCA</td>
<td>Correlation between variables and kinetics of variation in PW quality</td>
<td>4.1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vario-gram</td>
<td>Evaluating the current practice sampling</td>
<td>4.3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Multi-vario-gram</td>
<td>Design sampling scheme for process performance purpose</td>
<td>4.3.1</td>
</tr>
<tr>
<td>Mine 2 Dataset 2 (Weekly dataset)</td>
<td>The weekly monitoring dataset contained 60 observations, taken over 14 months, from May 2017 to August 2018. The water was taken from the discharge of the tailing ponds. This dataset contains 12 variables: pH, SPC, calcium, sulfate, magnesium, nitrogen, phosphorus, thiosulfate, iron, nickel, manganese, silica</td>
<td>PCA</td>
<td>Correlation between variables</td>
<td>4.1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vario-gram</td>
<td>Tendency variation overtime of individual parameters</td>
<td>4.1.3</td>
</tr>
</tbody>
</table>

### 3.2 Quantifying the variation of process water quality

#### 3.2.1 Kinetic of variation of process water

Easy to measure physicochemical parameters such as SPC, Eh, pH, DO, and turbidity have been used for a long time as proxies describing water quality (Mohamad Basir et al., 2019). Any major changes in those parameters indicate a change in the water matrix. Indeed, SPC measures the ability of the material to conduct electricity. In the case of water, a change in SPC indicates changes in the electrolyte’s nature and concentration, the size of the ions produced, and the viscosity (John De Zuane, 1997). Eh represents the redox potential of water (Grano, 2010). Eh variation can represent changes of oxidizing agents (such as oxygen) and reducing agents (such as sulfur oxyanions or bacteria) (John De Zuane, 1997, Kinnunen et al., 2020). Due to the oxidizing nature of oxygen, DO and Eh usually strongly correlate (Grano, 2010; Greet, 2010). DO represents the degree of oxygen dissolved into the water. The variation of DO depends on temperature and the water matrix. pH is a measurement of the acidity or alkalinity of the solution. The variation of pH indicates the change of the compounds’ solubility, biological activities, concentrations of metals, etc. Turbidity is the measure of relative clarity of a liquid. Change in process water turbidity is a proxy of the change of suspended solids in the water.
3.2.2 Evaluating the change in proxy parameters (pH, Eh)

The combined measurement Eh and pH define the thermodynamic stability of the species present in the system (Grano, 2010). Thermodynamically, the change in Eh and pH should be correlated as described by the Nernst equation (Greet, 2010). The nature of Eh and pH changes could be identified by comparing with the water-oxygen line. The water oxygen line describes the fundamental relation between pH and Eh when no redox reactions happen. Above the line, water decomposes and oxygen is generated. Below the line, water is stable. Mathematically, for an oxygenated aqueous solution with no well-defined redox couple, such relation is expressed by Equation 6 (Greet, 2010).

\[ E_{O_2} = 0.9 - 0.059 \, pH \]  

(6)

The water-oxygen line describes the relation between Eh and pH in the condition that equilibrium is maintained in more general terms. The change in Eh and pH must result in a line parallel to the water-oxygen line if there are no redox reactions in the media. If the Eh and pH changes are perpendicular to the water-oxygen line, oxidative reactions are occurring (Greet, 2010).

3.3 Procedure for sampling, preserving, and analyzing process water

The quality of the results for water quality assessment depends on three major procedures (Figure 7): a proper sampling procedure to obtain a representative sample, a suitable preservation method to conserve the water matrix until the analysis, and an appropriate analysis method to overcome the water matrix effects.

![Figure 7: Three procedures that influence the PW quality assessment results: sampling, stabilizing, and analyzing.](image)

This chapter aims to design a suitable sampling protocol for monitoring water quality in an operation-related context and investigating the disadvantages and limitations of the current practices in mining industry for preserving and analyzing process water. The results of this chapter can be found in Publication 3, Publication 4, and Chapter 4.3.

3.3.1 Frequency of sampling and representativeness

The Theory of Sampling (TOS) developed by Pierre Gy (Gy, 1998, 1992; Pitard, 1993) provides a simple set of rules and guidelines that allow reducing the sampling errors (variance). Process water stream and flowing slurry in a pipe are seen in TOS as 1D lots since their projection in the flow direction is more significant than its two-dimensional cross-section (Gy, 2004a). TOS introduces the variogram as the most suitable tool to design an optimal sampling protocol in 1D lots. The most recommended method for sampling 1D lots is composite sampling (Minkkinen and Esbensen, 2009) which involves taking individual increments of the entire stream over a specific period of time and then aggregating the individual increments together to make the final sample (Gy, 2004b). Three sampling models can be used (Esbensen et al., 2007):
- Systematic sampling (denoted ‘sy’): increments are extracted equidistant over the runtime of the process.
- Stratified random sampling (denoted ‘st’): an increment is extracted at random within equally sized intervals.
- Random sampling (denoted ‘ra’): the increments are extracted randomly over the sampling period.

The choice of the sampling mode is crucial since it changes the calculation of the lot’s mean. Generally, if the same number of samples is taken from the lot, the order of variances is variance (‘ra’) > variance (‘st’) > variance (‘sy’) (Petersen and Esbensen, 2005). However, although systematic sampling will lead to the lowest variance, stratified sampling is preferred when periodic phenomena occur (Esbensen et al., 2007).

For variographic data modeling, the systematic modes are employed universally, and each increment is considered and treated as a single sample (Petersen and Esbensen, 2005). A sufficient number of units extracted systematically over the process interval of interest is required to design the sampling scheme with a variographic approach. The variogram is then computed following equation 2. Important information about sampling variances could be obtained from the sill, nugget effect, and range of the variogram. Precisely, the sill informs the total variability (i.e. the maximum variance possible) of the properties considered (Esbensen et al., 2007). The nugget effect reflects the total variance in the 1D measurement series that is not due to process variability, but only to sampling, sample preparation, and analysis variance (Esbensen et al., 2007). The range is the inter-increment distance beyond which autocorrelation is no longer observable (Gy, 1992). The range indicates, in the case there is no periodic variation, the minimum sampling frequency. If the variable of interest possesses a cyclic variation with a given frequency, the Nyquist frequency is the minimum frequency of sampling required. In theory, this frequency is defined as twice as the frequency of the cycle of interest (Napier-Munn, 2014). In practice, it is preferable to have a sampling frequency of 5-10 times the frequency of the cycle of interest (Napier-munn, 2014). After extracting valuable information from the variogram, the auxiliary functions and the error generating functions can be calculated for each sampling scheme to express the sampling variance. The error generating functions provide the sampling error as a function of the number of increments that make up the final sample and the sampling model chosen.

Nevertheless, the traditional variographic approach used in mining and mineral processing has always been limited to one variable only (Esbensen, 2017). Since water quality is characterized by a range of properties, the sampling plan designed solely based on the property with the highest heterogeneity will underestimate the global sampling variance by not considering the multivariate aspect of heterogeneity and the correlations between individual properties (Dehaine et al., 2016). For such cases, the use of the multivariogram for sampling design is adequate. The multivariogram could be used as a complement to the univariate variogram to summarize global time variation for multiples properties of interest (Dehaine and Filippov, 2015). However, the resulting multivariate global variance may be relatively high and lead to a high number of increments to be sampled to form the lot’s final representative sample. To reduce the number of increments, Dehaine et al. (2016) suggested combining PCA with the multivariogram by applying the latter to the PCA scores instead of the raw data, as the PCA helps to reduce the dimensionality of the data and filter the noise. The application of the multivariogram on the first few principal components of a PCA allows reducing the global variance while
summarizing the essential information about variability (Minkkinen and Esbensen, 2014).

In this study, all (multi-) variograms and auxiliary functions were calculated using the same algorithm as in Dehaine et al. (2016) based on the tutorial by Petersen and Esbensen (2005) for univariate variograms. Both algorithms took raw data as input then transformed them into heterogeneity contributions which were used for (multi)-variogram calculations.

### 3.3.2 Preservation and analysis procedure

The methodology for investigating the accuracy of the procedures for preserving and analyzing mineral processing plants’ water matrices provided by a European certified laboratory was detailly described in Publication 3. However, for the sake of the reader, it will be summarized in this chapter.

The procedure for sampling and analyzing mining water is well-documented in the literature and followed by worldwide laboratories (Fowlie et al., 2001; Myers, 2006; The European Commission, 2018). However, the procedure is mostly described for sampling and analysis of mining effluents and for answering the need for monitoring water quality to fulfill environmental monitoring requirements. Therefore, the accuracy of chemical analysis in certified laboratories was investigated. For that, samples were collected from different locations in the concentrators and water circuits of both mines. The samples and control samples were sent for analysis to two European certified laboratories. The preparation procedure followed the laboratory recommendations, as presented in Table 5. Furthermore, tests for investigating the kinetics of water degradation during the sample preparation procedure and the effect of the water matrix on the analysis results were set up.

Table 5: Preparation procedure for water before sending to analysis (N/A: Not Applicable) (Publication 3)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Laboratory of Mine 1</th>
<th>Laboratory of Mine 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH, 25 ºC</td>
<td>No filtration, cool preservation</td>
<td>In-situ measurements</td>
</tr>
<tr>
<td>SPC</td>
<td>Filtering 1.6 µm + Cold (4 ºC)</td>
<td>Filtering 1.6 µm + Cold (4 ºC)</td>
</tr>
<tr>
<td>TDS</td>
<td>N/A</td>
<td>Filtering 1.6 µm</td>
</tr>
<tr>
<td>Polythionates</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S-O3²⁻</td>
<td>Filtering 1.6 µm + 1 mL of EDTA at 1%+ Cold (4 ºC)</td>
<td>N/A</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Filtering 1.6 µm + 2 mL of Zinc Acetate 8.5&lt;pH&lt;9.0 with NaOH</td>
<td>N/A</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Filtration 0.45 µm + 1&lt;pH&lt;2 with HNO₃</td>
<td>Filtration 0.45 µm to a bottle rinsed with HNO₃</td>
</tr>
<tr>
<td>Cations</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Degradation of process water before the preparation**

As observed in the two case study objects, during the sampling campaigns most of the samples were taken altogether in the morning and then transferred to the on-site laboratory for preparation. Due to the high number of samples and the limited number of personnel, a lot of samples needed to wait some time before the preservation and stabilization processes. Because of this delay, it was reasonable to assume that degradation had taken place. Therefore, a degradation test was set up to answer the question: “How long the samples could be kept before being prepared?”. For this study, 10 L slurry of Mine 1’s plant 1 flotation feed was collected directly into a bucket. The concentration of
DO was monitored using YSI ProDSS multiparameter probe immediately after collection. The measurements were performed by directly inserting the probe in the bucket whilst the pulp was gently stirred. DO was measured every two hours. The bucket was closed with a lid between measurements.

Additionally the degradation of water samples during transportation was investigated via proxy parameters such as pH. In this case, pH was measured on the fresh sample and just before analysis in the laboratory. Any change in pH indicates a change in the water matrices.

**Investigation of the accuracy of the analysis results: Control samples**

Control samples were prepared to investigate the accuracy of the results provided by the certified laboratory. The composition of the control samples was decided beforehand based on historical data recorded on-site. Dry compounds were weighed on an analytical balance in the Aalto university laboratory and dissolved in distilled water on-site. Plant water samples and control samples were preserved in the same way. The theoretical values of the control samples are reported in Table 6.

In total, one control sample was prepared for Mine 1 and three control samples for Mine 2. Among the three control samples for Mine 2, the first sample (S1) was sent together with plant water samples during the sampling campaign. The second (S2) and third (S3) control samples were prepared and sent for analysis a month later. The first and second control samples had a similar composition. In contrast, the third control sample contained a higher amount of reduced sulfur compounds such as tetrathionate (S\(_4\)O\(_6^{2-}\)) and sulfite (SO\(_3^{2-}\)) as presented in Table 6.

<table>
<thead>
<tr>
<th>Parameter (mg/L)</th>
<th>Mine 1 Sample</th>
<th>Mine 2 Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S1</td>
<td>S1</td>
</tr>
<tr>
<td>TDS</td>
<td>6319</td>
<td>711</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>661</td>
<td>59</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>535</td>
<td>248</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>2570</td>
<td>217</td>
</tr>
<tr>
<td>K(^+)</td>
<td>31</td>
<td>37</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1106</td>
<td>104</td>
</tr>
<tr>
<td>S(_2)O(_3^{2-})</td>
<td>351</td>
<td>7</td>
</tr>
<tr>
<td>SO(_3^{2-})</td>
<td>275</td>
<td>0</td>
</tr>
<tr>
<td>S(_4)O(_6^{2-})</td>
<td>616</td>
<td>0</td>
</tr>
<tr>
<td>Total S</td>
<td>1553</td>
<td>76</td>
</tr>
</tbody>
</table>

**Investigation on the effect of water matrix on the analysis results**

A 1.5-litre sample of process water was collected from Mine 2 and synthetic water was prepared on-site (denoted as PW and SW, respectively). The initial composition of the process water and synthetic control sample (i.e. the baseline samples) can be found in Publication 3.

The bulk sample was divided into three portions of 500 mL each, and the 500 ml samples were labeled as Fraction 1, Fraction 2, and Fraction 3, respectively. Fraction 1 represented the baseline sample. Fraction 2 was spiked with thiosalts. Fraction 3 was spiked with the same amount of thiosalts as Fraction 2 and an additional amount of metals (Cu, Ni, Fe). Details about the concentration of thiosalts and metals can be found in Publication 3. All the samples were preserved by vacuum filtration using 0.45 µm pore-
size, glass microfiber filters, and fast freezing the sample bottle in a mixture of acetone and dry ice before sending to the laboratory for analysis.

3.4 Multivariate Statistical Process Control (MSPC)

MSPC is an advanced process control technique that aims to reduce the information provided by all parameters into statistical parameters through the application of statistical modeling (Bersimis et al., 2005). In this thesis, the application of PCA for MSPC applied in controlling water quality was investigated. The details of the procedure can be found in Publication 1.

For such a method, a historical dataset was needed. It was named as the training dataset. PCA model can be built on the training dataset and the projection of the new data on the model will help to detect abnormalities (Sánchez-Fernández et al., 2018). In the case of PCA model, Q residue and Hotelling’s $T^2$ are used as diagnostic tools for identifying faults. Mathematically, Q residue presents the variation that is not captured by the PCs retained in the model. On another hand, Hotelling’s $T^2$ indicates the location of the observation within the PCA model subspace. Geometrically, in the case that two PCs could describe the dataset, Q residue describes the Euclidean distance between the observation and the plane created by the 2PCs model, whilst Hotelling’s $T^2$ is the distance between the plan center and the projection of the observation onto the plan (Figure 8).

Figure 8: Geometric explanation of Q residue and Hotelling’s $T^2$, illustrated by a case

Compare to the OVAT method, using Q residue and Hotelling’s $T^2$ for process monitoring are much more advantageous. Indeed, they allow controlling the range of the variation (Hotelling’s $T^2$) and the correlation matrix (Q residue) at the same time. Theoretically, there are many ways to define “out-of-control” situations. However, in practice, the process is considered as out-of-control when at least two consecutive observations are out of the control limits (i.e., Q residue and Hotelling’s $T^2$ values fall outside the limits for a specific confidence interval) (Sánchez-Fernández et al., 2018). Finally, in order to identify the main parameters that contribute to the fault, Hotelling’s $T^2$ and Q residue contribution should be computed and investigated. The results of this study can be found in Publication 1 and Chapter 4.4.

3.5 Dissolution loop protocol (D-loop) and application

3.5.1 Motivation and hypothesis behind the D-loop

The D-loops’ primary motivation is to predict the tendency of elements to accumulate due to water loop closure and create a “laboratory process water” that has the same level
of impurities as the plant process water for laboratory testing. The D-loop test protocol is set up based on five assumptions.

1. Firstly, process water is mine-specific, dynamic, unstable, and complex. Since synthetic water cannot have those properties, investigating the effect of water quality on plant performance using a pure synthetic water approach is not an ideal option.

2. Secondly, if clean water (besides the own mine recycled water) is used as the main source to feed the plant, the most important factor that influences the process water quality is the ore. Therefore, the prediction of the water quality variation is feasible if we mimic the ore pathway in the plant. The easiest way to mimic this is by using the laboratory flotation procedure used by the same plant.

3. Thirdly, the effect of water quality on the flotation and plant maintenance could be forecasted if the future recycled water quality could be predicted.

4. Fourth, if the existence of one or several potential components that might affect the process performance or maintenance (e.g. scaling of gypsum) is known, plant design can be modified in the early phase of the planning so the negative effects of process water quality could be minimized.

5. And finally, the water created by the D-loop protocol will be a better candidate than the traditional pure synthetic water approach for studying the effect of recycling water on flotation performance. Indeed, the D-loop water could be used as a “laboratory process water” since theoretically, it will be designed to conserve the most important characteristics seen in the real plant water (i.e. specific, dynamic, unstable, and complex). Additionally, the effect of specific compounds can be detected by spiking the D-loop water with different compounds that are expected to accumulate.

3.5.2 D-loop set-up

A detailed description of the D-loop protocol could be found in Publication 2. Generally, one round of the dissolution loop consisted of two main steps: grinding and dissolution (Figure 9). The ore sample was subjected to grinding in a laboratory mill to obtain a close PSD defined in the plant’s flotation procedure. After milling, the pulp density was adjusted, and the slurry was transferred to a flotation cell for the dissolution test. The dissolution procedure followed the mine laboratory flotation procedure in terms of percentage of solids, duration, rotor rotation speed, airflow rate, pH condition but without the addition of reagents (except pH modifier). Therefore, there was no froth removal during the test. pH modifier can be added under monitoring with a pH-meter. After dissolution, the slurry was filtered with a vacuum pump. The solids were discarded while the filtered water was recovered. Starting water was added to the remaining filtered water to compensate for the loss and was used in the next dissolution round.
The conditions for the dissolution loop of the Mine 2 ore are given in Table 7. After milling crushed ore for 39 minutes with a laboratory rod mill, the slurry was subjected to 55 minutes of dissolution. In total, one dissolution loop contains eight rounds. A 10 g/L lime solution was used for modifying the pH. Tests were performed at constant temperatures. The mill was maintained at low temperatures with dry ice and high temperatures with heating bags. The temperature of the slurry during the dissolution was maintained by ice, dry ice, and heating elements wrapped around the flotation cell. The slurry temperature was frequently monitored during the dissolution by a thermometer.

<table>
<thead>
<tr>
<th>Grinding time (minutes)</th>
<th>T (°C)</th>
<th>Dissolution time (min)</th>
<th>pH modifier</th>
<th>Number of rounds</th>
<th>Sampling point (round)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>5, 20, 35</td>
<td>55</td>
<td>Lime</td>
<td>8</td>
<td>0, 1, 3, 6, 8</td>
</tr>
</tbody>
</table>

Water samples were collected at the end of the 1st, 3rd, 6th, and 8th rounds. The details of the dissolution loop can be found in Publication 2.

### 3.5.3 Application: Performance sensitivity over water quality

The study consisted of using the dissolution loop to create the “potential future process water” referred to in the following text as DLW. Then, the flotation tests were carried with both fresh water used on-site (in this case is the nearby river water) and DLW. The objective was to demonstrate that recycling water would result in a different water matrix than the initial fresh water matrix and that the effects of the matrices on flotation would also differ. For methodology validation, the flotation of the actual process water of the plant was carried out and compared with the flotation results with DLW.

Flotation tests were conducted according to Mine 2’s laboratory standard flotation procedure. Four concentrates were recovered from each flotation test: two copper concentrates (Cu_C1 and Cu_C2) followed by two nickel concentrates (Ni_C1 and Ni_C2). The details of the flotation test conditions of Mine 2 are given in Publication 2.
4. Main results

4.1 A meta-stable, unchanged process water – a fairy-tale

4.1.1 Kinetics of the variations

The installation of the YSI probe in the process water of Mine 2 showed that the change of process water’s physicochemical variables could be fast, happening in a matter of hours (Figure 10). This result suggested that the process water on site is far from being stable.

The YSI reading over 7 days indicated that all parameters possessed daily variation. Furthermore, a sudden variation was observed in all parameters around day 3.5. pH and SPC displayed a very similar tendency of variation. Both parameters showed a significant drop around day 3.5. The PCA analysis confirmed their positive correlation since they were all negatively loaded on PC1. Eh and DO were positively correlated and they were negatively correlated with SPC and pH. Correlation between Eh and DO is expected if oxygen is the strongest oxidant in the media. The DO variation would directly affect the redox condition and hence the Eh. The negative correlation between Eh and pH was in agreement with the Pourbaix diagram of water (Greet, 2010).

Turbidity displayed a very large variation in the first half of the monitoring period. The magnitude of variation was lower during the second half. High variation of turbidity during winter, the season when the data was collected, was a characteristic of the Mine 2’s process water. During winter, the formation of an ice cap reduced significantly the volume of the tailings pond. Furthermore, due to the change in discharge point or shortcut channel created in the pond, sometimes the tailings water which had high pH, suspended solids, and dissolved solids can return faster to the processing plant than in normal condition. This explained the positive correlation between SPC, pH, and turbidity along PC1.
4.1.2 Intercorrelation of the variations

The correlation between the measured physicochemical parameters in the water (Figure 10) suggested that the changes in chemical parameters were not independent. Indeed, the PCA applied on the Mine 1 and Mine 2 datasets (Publication 1 and 4, respectively), proved that there are correlations between chemical parameters of the water matrix. Loadings of parameters that were monitored in Mine 1 were projected in the (1) PC1 vs. PC2 and (2) PC1 vs. PC3 factorial plans, which in total accounts for 76% of the original variability (Figure 11).

PC1, which expressed 44% of the total variability, captured the positive correlation between pH, carbonate, total alkalinity, and hydroxide. Such a correlation was expected and in agreement with thermodynamic theory. A positive correlation between pH and calcium was also captured via PC1. This correlation was foreseen since hydrated lime was used as pH regulator. Together with PC1, PC2 which explained 18% of the total variability, captured the correlation between thiosalts, COD, and calcium. The correlation between COD and thiosalts has been documented in the literature (Kuyucak, 2014). The study suggested that a positive linear correlation existed between COD and thiosalts. This correlation was due to the fact that COD measured all oxygen needed for oxidizing reactions and thiosalts were the major oxygen consuming compound. The reason for the correlation between them and Ca remained unclear. PC3, which explained 16% of the total variability, was highly loaded in sulfate and SPC. Since sulfate was one of the major compounds that contributed to the water matrix, such a correlation was expected. Except for a negative correlation with pH (and all parameters that positively correlated with pH) DO seemed to be independent of all other parameters.
Main results

For Mine 2, the 3D loadings plot (Figure 12) indicates a negative correlation between metals, metalloids, and pH. This correlation was consistent with the thermodynamic relation between metal hydroxide solubility and pH (Boardman et al., 2004; Kuyucak, 2006). The correlations between SPC, calcium, and sulfate were expected since calcium and sulfate were among the major compounds found in the process water. The positive correlation between magnesium, nitrogen, and thiosulfate was observed. However, the reason underlying this correlation remained unclear. The 3-dimensional scores plot shows a tendency of clustering between summer and winter observations (i.e., from June to September versus the rest of the year). In summer, the concentration of metals tended to increase in the process water while the SPC and concentration of other compounds decreased. An opposite trend was observed during winter, characterized by an increase in pH, SPC, and decrease of metals. The high concentration of metals in summer probably was due to the increase of bacterial activities and ore oxidation in the tailings pond and the ore pit.

Figure 12: PCA analysis of the Mine 2 weekly dataset. 3D plot of loadings (left) and scores (right) projected on the PC1 vs PC2 vs PC3 factorial plane.

4.1.3 Range and frequency of the variations

The objective of this chapter is to show that the range and frequency variations of parameters that contribute to water quality are not necessarily similar. Indeed, they can differ significantly. To illustrate, the variograms of the 12 properties that were weekly monitored in Mine 2 (see Table 4) were computed and the results are shown in Figure
In practice, it was not recommended to compute the variogram further than $j = N/2$ (Esbensen et al., 2007). However, since some of the variograms displayed a potential cyclic fluctuation over $j = 35 = N/2$, to capture the full cycle, the author chose to display the variogram until $N-j = 20$ (i.e., 50 lags).

The results showed that all variograms displayed cyclic variations. To ease the reading, the cyclic frequencies of each parameter are summarized in Table 8.

![Figure 13: Variogram of 12 variables of the Mine 2 weekly dataset (Figure from Publication 4)](image)

Table 8: Difference in cycle of variation observed in the univariate variogram of the 12 properties monitored in the weekly data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Long cycle frequency</th>
<th>Short cycle frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lag</td>
<td>Month</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>23</td>
<td>5</td>
</tr>
<tr>
<td>$S_2O_3^{2-}$</td>
<td>40</td>
<td>9</td>
</tr>
<tr>
<td>N</td>
<td>45</td>
<td>11</td>
</tr>
<tr>
<td>P</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>$Ca^{2+}$</td>
<td>25</td>
<td>6</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>45</td>
<td>11</td>
</tr>
<tr>
<td>Mn</td>
<td>45</td>
<td>11</td>
</tr>
<tr>
<td>Ni</td>
<td>45</td>
<td>11</td>
</tr>
<tr>
<td>Si</td>
<td>45</td>
<td>11</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>25</td>
<td>6</td>
</tr>
<tr>
<td>SPC</td>
<td>24</td>
<td>5</td>
</tr>
</tbody>
</table>

As seen in Figure 13, variograms for thiosulfate, nitrogen, magnesium, manganese, nickel, and silica displayed a very similar tendency, characterized by a long-range cyclic variogram shape with a period around $j = 45$ lags = 11 months. Among them, magnesium had an additional shorter-range cyclic variation with a period of $j = 10$ lags = 2.3 months.
Variograms for SPC, pH, sulfate, phosphorus, and calcium suggested a common cyclic phenomenon with a frequency $j = 15-25$ weeks $\approx 4-6$ months. Since calcium and phosphorus in the process water were mostly originated from the reagents used in the flotation plant, this medium-range cyclic fluctuation could be the consequence of adapting operating conditions in the plant with the seasonal variations and the storage time in the tailings pond. Additionally, phosphorus and calcium possessed an extra short-range cyclic variation characterized by a $j = 2.5 = 2.5$ weeks. Those variations might reflect the daily change of the operating conditions.

The variogram for iron showed only short period cyclic variation of $j = 4-5 \approx 1$ month. This tendency could be attributed to oxidation of the Run Of Mine ore pad and storage stockpiles. Indeed, ore mineralogy fed to the Mine 2 processing plant was kept as consistent as possible over periods of one month. Therefore, this cyclic variation may be due to changes in ore mineralogy and oxidation of the stockpile.

4.2 The main driving force behind the variation of PW quality

4.2.1 Tailings storage methods: Effect of the tailing ponds

An analysis of historical data from Mine 1 and Mine 2 revealed the effect of the tailings storage methods on the process water matrix. Figure 14 shows that before the water’s full reticulation, the SPC profile of Mine 1 had a cyclic behavior with a tendency of increasing SPC during the dry season due to evaporation. The range of SPC was around 4000 $\mu$S/cm to 6000 $\mu$S/cm. From 2015, the SPC increased linearly to 10000 $\mu$S/cm. The tendency of cyclic variation was lost, and the fluctuation became linear and noisy. The current variation tendency of the Mine 2 SPC is very similar to the Mine 1 before its reticulation. The highest SPC values were always detected in February-March, followed by a sharp decrease in the late spring and slowly increasing values during the summer months.

Nevertheless, the graph also showed an overall increase in SPC values due to the accumulation of ionic constituents over time. The extreme winter conditions and a large temperature variation over the year were the main factors responsible for the cyclic variation of water quality at Mine 2. In winter, the formation of an ice cap locked pure water; hence the high electrolyte concentrations in the remaining water.
The absence of the tailings ponds in the system results in high water property instability since the tailings ponds were known to have a crucial role in water stabilization. The Eh-pH curve for Mine 2 system was plotted to determine where the reactions occur. Figure 15 shows that the lines between points 1 to 2, 3 to 4, and 7 to 8 are perpendicular to the water-oxygen line. This indicated that the oxidative reactions happened in the grinding circuit, scavenger flotation of copper, and tailing ponds. The decrease of pH in the tailing pond suggested the oxidation of compounds that acidifies the medium. Vongporm (2008) discussed that the oxidation of sulfide minerals by bacteria and oxidation of thiosalts would show the same effect. The redox reaction in the pond was vital in decreasing the amount of reduced compounds such as thiosalts in the process water. Without the tailings pond, the reduced compounds will tend to accumulate in the process as seen in the case of Mine 1 (Publication 1). After the full reticulation in 2015, COD which is an indicator of thiosalts concentrations (Kuyucak, 2014), started increasing and reached its peak around 2017. Such phenomena did not happen when the tailings were stored in the tailing ponds before the full recycling.
4.2.2 The complexity of water streams in the mine site

The differences in the compositions of the different water streams at Mine 1 were revealed with PCA analysis. Two PCs have been chosen to build the model, they explain almost 79% of the dataset variability (Figure 16). The remained PCs can be considered as noise. The scores projection of the PC1-PC2 plan showed a tendency of clustering between different water types. Generally, the clustering separated them into five main groups (Figure 16):

- Group 1: Waters from the processing plants (Plant 1 and 2) and feed to the paste plant (TPS), paste plant’s thickener overflow (PL O/F), the output of the industrial water tank (TAI out)
- Group 2: ETAM out, Mine’s clarifier underflow (U/F) and overflow (O/F)
- Group 3: Clean surface waters (P1, P2), and fresh water
- Group 4: Dirty surface water (P3)
- Group 5: CDM reservoir and feed to the industrial water tank (TAI in).

The water matrices differed substantially between the groups. For example, group 1 was characterized by high salinity, calcium, thiosalts, and pH. Those properties were directly linked to mineralogy and ore processing since the plant processed a massive sulfide ore at a basic pH. Meanwhile, group 3, the “clean water group”, was characterized by a relatively low concentration of all parameters. Group 4, the “dirty surface water” was characterized by low SPC, salinity, pH, but extremely high metal, magnesium, and sulfate contents. Group 5 had quite similar characteristics as group 2 but had a lower pH and higher metals, sulfate, and magnesium concentrations.

This example took into consideration just a few major streams that Mine 1 monitored regularly. In reality, the number of streams was higher, and several modifications and changes in the operations had happened frequently. That resulted in an even higher degree of diversification in terms of water quality of the plant.

![Figure 16: PCA analysis applied the major water streams of Mine 1 (dataset 2). Eigenvalues of the principal components (left), plot of loadings (middle), and scores (right) projected on the PC1 vs. PC2 factorial plane.](image)

4.2.3 Modification of the water circuit

The modification of the water circuit had a great impact on the plant water quality. It was illustrated by PCA results applied on dataset 1 from Mine 1 (Table 4).

The PCA loading and score plot along the first three PCs, which accounted for 86% of the total variability of the original dataset are shown in Figure 17. Four major changes implemented in the mine water circuits that significantly affected the process water quality from 2002 to 2018 were identified by PCA.
Main results

Figure 17: Scores (left) and loadings (right) along the first 3 PCs resulted from the PCA analysis applied on Mine 1’s dataset 1. The arrows indicated the major changes in the water circuits and operating set-point.

PC1, which captured the highest variation of the dataset, described the changes of water quality after the transition to the short water cycle (i.e. the full reticulation at observation 160) and the commissioning of a Fenton-HDS treatment plant (observation 680). The full reticulation completely changed the composition of the process water. It caused a dramatic increase in SPC, sulfate, COD of the system. The increase stopped and plateaued around the observation 380-400 (August-September 2016). The decrease in SPC, thiosalt, and sulfate from March 2018 (observation 730) conformed with the Fenton-HSD treatment plant’s commissioning which oxidized thiosalts and removed sulfate as gypsum.

The changes in the pH set point were described in PC2. Precisely, the pH set-point was changed twice. Among them, the 2nd change had more pronounced effects on process water quality. From May-June 2017 (around observation 600), the pH was set to be between 8 and 9, while the previous set point was between 9 and 10. As the pH was adjusted with lime, the variation of the pH set point affected the calcium level in the process water. Hence, a positive correlation can be observed between them as described in the loadings.

From March 2018 (observation 730), due to the operation of the Fenton-HSD, the calcium concentration and pH increased. Additionally, since Fenton-HSD removed sulfate from the system, the concentration of sulfate in the process water decreased significantly. The PC2 also captured a negative correlation between calcium and sulfate, probably due to the sulfate-calcium balance. However, the main mechanism and explanation are still unclear.

PC3 captured the variations in DO. The two major periods of high variation can be identified from the score plot: observation 0 to observation 160 and observation 600 to observation 750. The result indicated that process water was more oxygenated before the full reticulation. The second period of high variation in DO coincided with the 2nd change.
in the pH set-point. It suggested that the second modification of pH affected the DO concentration in the process water. Thus, a positive correlation between pH and DO along this PC was observed.

Those results indicated that any modification of the water circuit would significantly change in terms of the water quality and its characteristics.

More details about the effect of water circuit modification on the process water quality of Mine 1 can be found in Publication 1.

4.3 Challenge in evaluating process water quality

4.3.1 Choosing the sampling frequency

As said in Chapter 3.3.1, the optimal sampling frequency for Mine 2 was defined by applying variographic and statistical approaches on the HF dataset (Table 4).

The univariate variograms for the five properties presented in the HF dataset are shown in Figure 18. The sill values indicated that turbidity and Eh had higher variability compared to SPC, pH, and DO.

The variograms of pH, Eh, and DO displayed a typical increasing variogram shape with a common range of approximately 300-350 lags = 2-2.5 days. Such a result indicated that the current weekly sampling frequency practiced on-site is not sufficient to capture the variation of those three parameters.

The variograms of pH, ORP, and DO showed a typical increasing variogram shape while the variogram of SPC displayed cyclic behavior with a period of \( j = 380 = 3800 \text{ min} = 2.6 \text{ days} \). On another hand, the variogram of turbidity showed a large scale increasing trend over the monitoring period. This trend continued out of our study range. In this case, detrending was needed to remove the trend and therefore show possible cyclicities. The variogram of the detrended turbidity is found in Figure 19. It showed clearly a typical cyclic variation with the periodicity of \( j = 120-140 = 20-23 \text{ hrs} \). This frequency was clearly associated with the daily change of tailings discharge location in the pond. In addition, a very clear local minimum is observed at \( j = 380 \). This coincided with the periodicity observed in SPC. The turbidity de-trended variogram showed a range of approximately \( j = 100 = 1000 \text{ min} = 16.7 \text{ hrs} \) while a common range of approximately 300-350 lags (2-2.5 days) was observed for SPC, pH, ORP, and DO. This result indicated that turbidity had a much shorter range compared to other properties, hence required a higher sampling frequency. More results can be found in Publication 4.
Figure 18: Univariate variograms of the five properties of the HF dataset. A common range of approximately 300-350 lags (2-2.5 days) is observed for SPC, pH, Eh, and DO (A, B, C, and E). A shorter range of 100 lags (~17 hours) is observed for turbidity (D). (Figure from Publication 4)

Since Eh displayed the highest variability (i.e. highest sill value), the common procedure in the univariate variographic approach was to design the sampling protocol based on the variation of this property only. The standard deviation of sampling error (SDSE) as a function of the number of increments collected was calculated for Eh to get information on the sampling strategy. The results are shown in Figure 20.

The results suggested that two or three increments that were extracted systematically were already enough to reduce the SDSE to below 0.1 (i.e. 10%) (Figure 20). In terms of the sampling frequency, the range of the variogram indicated that the sampling should be done every 2.5 days systematically or more often if more resolved insights into the process variation is deemed of interest.

Figure 20: Univariate variograms of the Eh of the HF dataset (left). The corresponding sampling error is expressed as the standard deviation of the sampling error (SDSE, right)

However, as mentioned afore, this sampling protocol deliberately ignored the other properties. In this case, it did not take into consideration the higher variation of turbidity...
compared to Eh and the cyclic variations of SPC. Therefore, designing the process water sampling campaign solely on Eh will ultimately underestimate the overall global sampling variance for all the other properties that may not contribute as much as Eh to the total variance but which may be relevant in process control. That is why multivariate approaches are needed (Dehaine et al., 2016).

The multivariograms applied to the raw HF dataset, referred to as global multivariogram, and the scores for the first two PCs are shown in Figure 21. The figure also shows the corresponding sampling error profiles of SDSE as a function of the sampling mode and the number of increments collected.

The global multivariogram displayed a classic shape of an increasing variogram with a range around $j = 250 = 1.7$ days. The sill value is much higher than any of the univariate variograms (Figure 18). It was a known consequence of considering the correlations between the variables when computing the variogram (Dehaine et al., 2016). The range indicated that, in winter, the quality of Mine 2’s process water changed with a frequency of every 1.7 days. This value was coherent with the residence time of water in the tailings pond. It is worth noting that the residence time of water in the tailings pond is much shorter in winter than summer due to the formation of the ice cap that reduces the pond available volume. Therefore, in summer, the variation frequency of the Mine 2’s process water quality should be lower.

The three sampling modes displayed similar results, but the systematic mode still gave the lowest sampling variance. Figure 21 shows that an aggregate sample with only two increments can reduce the SDSE by 60% compared to spot sampling. A four-increments aggregate sample can reduce the SDSE by 80%. However, to reduce the SDSE to below 10%, at least 15 increments must be taken to make the final sample, which was impractical to be implemented on-site. Additionally, the global multivariogram did not capture cyclic variation observed on the SPC and turbidity individual variogram.

Hence, a better approach was to filter the noisy and non-significant components from the HF dataset before applying the multivariogram. For such a purpose, PCA was applied to the initial dataset to extracting the most important variation. The first two PCs were chosen since the variation expressed in the last three PCs was not significant (more details can be found in Publication 4). Applying the multivariogram to PC1 and PC2 scores (referred to as a multivariogram of PC1-2 in the text) decreased the multivariogram sill for the HF data by half (Figure 21, left bottom). Additionally, the nugget effect, which was quite significant in the global multivariogram, was reduced to near-zero with the multivariogram of PC1-2. In TOS, the nugget effect reflects the short-scale process variability and includes all of the sampling, analytical and sample preparation variances (François-Bongarçon, 2004). This result must be related to the nature of the dataset which only contains the most significant and important variance of the original dataset since PCA acted as a filter on the raw data to retain only relevant information on the global variability of the dataset. Hence, the multivariogram applied to the first PCs provides a more noiseless, summary of the structure of variability than multivariogram applied to raw data (Dehaine et al., 2016). The same reason explained why the difference between the random sampling mode and the two other modes was more significant in the multivariogram of PC1-2 than the global multivariogram. Moreover, the multivariogram of PC1-2 managed to capture the cyclic phenomenon attributed to SPC but did not capture the mega trend of turbidity.
The multivariogram of PC1-2 suggested a frequency of sampling of every 2.6 days. To reach a SDSE lower than 10%, the aggregate sample should be made of at least five increments (Figure 21, middle bottom).

4.3.2 Challenges in preparing and analyzing process water

This section aims to provide the results of the studies that were described in Chapter 3.3.2. The same results can be found in Publication 3.

Sample degradation

As a reminder, one of the objectives of this study was to find the answer to the question: Were the preservation methods proposed by the laboratory and practiced by on-site personnel sufficient to preserve the process water matrices until the analysis?

The variation of DO (in %) and sulfate of the water sample as a function of storage time at room temperature before the stabilization is shown in Figure 22. The level of DO decreased from 75% to 35% during 10 hours. As seen in the variation of a major physicochemical parameter such as DO, the water matrix clearly changed. Those results indicated that the long waiting time before preservation can strongly affect the water matrix. However, such a practice is still largely used on-site when the number of samples can be very high during the sampling campaign and the amount of personnel for sample preparation is limited.
Additionally, the samples can furthermore degrade during transportation due to the inappropriate method of preservation. Indeed, the pH measured in-situ was constantly higher than the laboratory measurements, with a magnitude of difference around 4 or 5 units (Figure 23). Several locations displayed a difference even higher than 60%. On average, the difference was 45%. It is worth reminding that since pH is logarithmic of free acidity, the magnitude of difference in terms of free acidity was from $10^4$ to $10^5$.

![Figure 23: pH measured in the laboratory vs. pH measured in-situ (Figure from Publication 3)](image)

Quality control of the analytical work via control samples and elemental balances

Control samples were sent for analysis together with the plant water samples to evaluate the quality of the results provided by the laboratory. The differences between the theoretical values and the laboratory results are reported in percentage and shown in Table 9. The percentage difference in results was calculated by dividing the absolute difference between the theoretical value and the laboratory value by the theoretical value.

For Mine 1, a low analytical error for all compounds/elements, except chloride, thiosulfate, and sulfite. The analytical errors were particularly high for chloride (difference of 172%), thiosulfate (difference of 94%), and sulfite (difference of 100%).

Table 9: Theoretical values and analysis results of the control samples (The analyses where the differences were significant are highlighted in orange)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mine 1</th>
<th>Mine 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample S1</td>
<td>Sample S1</td>
</tr>
<tr>
<td></td>
<td>TV mg/L</td>
<td>LR mg/L</td>
</tr>
<tr>
<td>TDS</td>
<td>6319</td>
<td>5517</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>661</td>
<td>655</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>535</td>
<td>1452</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2570</td>
<td>2827</td>
</tr>
<tr>
<td>K⁺</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>50</td>
<td>54</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1106</td>
<td>1134</td>
</tr>
<tr>
<td>S₂O₃⁻</td>
<td>351</td>
<td>681</td>
</tr>
<tr>
<td>SO₃⁻</td>
<td>275</td>
<td>109</td>
</tr>
<tr>
<td>S₄O₆⁻</td>
<td>616</td>
<td>767</td>
</tr>
<tr>
<td>Total S</td>
<td>1553</td>
<td>1433</td>
</tr>
</tbody>
</table>

(TV: theoretical value, LR: laboratory result, D: Difference, N/A: Not Applicable)

In the case of Mine 2, sample S1 indicated a high analytical error for TDS, calcium, and thiosulfate. In contrast, sample S2, which had a similar composition, indicated an error below 20% for all elements/compounds. The sample S3 results showed a higher error in sulfur compounds analysis (sulfate and thiosulfate) than the S2 sample values. As said previously, the only difference between S2 and S3 was that S3 contained a spiked amount.
of tetrathionate and sulfite in its water matrix. This result indicated that a high concentration of reduced sulfur compounds influenced the sulfate and thiosulfate analysis.

Additionally, balances of TDS and sulfur were calculated. The main hypothesis behind this task was that if the quality of the analysis was good, a good balance should be seen between (1) TDS measured and the sum of major compounds and (2) total sulfur measured and total sulfur calculated from compounds. Ideally, the difference with the value measured and calculated should be very close to 0.

**Figure 24** shows the TDS measured, the sum of major compounds as well as the difference between them for Mine 1 and Mine 2. The results showed that there was a significant difference between the TDS measured and the sum of major compounds for both mines. Generally, the balance is positive towards the sum of major elements. For Mine 2, different behavior of the imbalance in summer and winter was observed. In winter, the difference was relatively constant with an average value of around 15%. Whilst during summer it fluctuated more. The difference was particularly high for samples coming from the processing plants (location 10 to location 18), the output of the TSFB (location 6), and the tailings of the Ni circuit (location 23).

![Figure 24: Balance of TDS calculated for samples from Mine 1 (A) and Mine 2 winter survey (A) and summer survey (B). (Figure from Publication 3)](image)

The sulfur balance of both mines is shown in **Figure 25**. Location 13 to 18 of Mine 1 displayed a very high imbalance of sulfur. The value can reach more than 70%.

Interestingly, the imbalance of sulfur seemed to be higher for Mine 2 than Mine 1. For Mine 2, the average difference between values measured and calculated was around 30% in winter. Meanwhile, for Mine 1, this value was around 15% if locations 13 to 18 were excluded from the calculation. Additionally, the imbalance was more significant in summer than in the winter for Mine 2.
Main results

Figure 25: Balance of Sulfur calculated for samples from Mine 1 (C) and Mine 2 winter survey (A) and summer survey (B). (Figure from Publication 3)

Such results indicated an analytic problem. The higher sum of major compounds compared to the TDS measured indicated an overestimation of at least one major element. The control samples prepared for Mine 1 suggested that the problem might come from chloride and tetrathionate, which were overestimated.

In the case of Mine 2, since the curve shape between the imbalance of TDS and total sulfur compounds in summer was very similar, the overestimation of one of those sulfur compounds could be the reason for the imbalance in TDS. The high temperature in Mine 1 during summer could increase the concentrations of reduced sulfur compounds in the process water. Hence, the concentrations of sulfate and thiosulfate could be overestimated due to the matrix effects as shown in the control sample S3.

Effect of the water matrix on the analytical results

Different compounds (thiosalts and metals) were spiked in the process water (PW) and synthetic water (SW) matrices to investigate the effect of water matrices on the water analysis as described in Chapter 3.3.2. Figure 26 shows the differences between the analytical results of spiked waters and the theoretic values.

The addition of thiosalts to the synthetic water (SW) matrix caused an overestimation of potassium, magnesium, total sulfur, and chloride while no notable effect was observed when the same compounds were added in the PW matrix. Nevertheless, the addition of metals likely attenuated the interference of thiosalt on the SW matrix. The difference was reduced generally by half.

Inversely, the addition of metals increased the interference of thiosalt on the PW matrix. The difference now increased up to 40%. Those values were higher than the standard analytical errors claimed by the laboratory which were generally between 10-15%.
4.4 Control and monitoring of process water quality

To remind, for detecting faults in water quality, the input matrix from Mine 1 that contained 11 variables (pH, SPC, DO, calcium, total alkalinity, carbonate, bicarbonate, hydroxide, thiosalts, COD, and sulfate) and 638 observations from 2015 to 2018 was divided into a training set (observation 0-500) and a test set (observation 501-638). PCA model was built based on the training dataset. Afterward, each observation from the test set was projected into the PCA model to obtain the residual Q and Hotelling’s T².

**Figure 27** shows the residual Q and Hotelling’s T² calculated for observations from the test dataset. The 95% confidence limits defined the control region (the dashed line).

In practice, the water quality was out of control when at least two consecutive observations were out of the control limits (Sánchez-Fernández et al., 2018). Observations 3, 4, 5, and 6 of the test set satisfied this criterion. It is worth noting that observation 127 also had a high residual Q and Hotelling’s T² value. However, it should be considered more as an outlier than being out of control due to its singularity.

Contributions into residual Q and Hotelling’s T² were calculated to determine which variables are responsible for unusual residual Q and Hotelling’s T² behavior. The contributions to the Q statistics and Hotelling’s T² of samples 4 and 5 are plotted as an example.
in **Figure 28**. The Hotelling’s $T^2$ contribution showed sulfate, thiosalts, and calcium were out of the normal operating range. Sulfate concentration was abnormally high, while the concentration of thiosalts and calcium was low. The residual Q contribution plot indicated that for both observations, pH, DO, bicarbonate, and carbonate did not follow the variable correlations even though their values were within the normal plant range.

![Figure 28](image.png)

**Figure 28**: The contributions into the Hotelling’s $T^2$ and Q values for observation 4 and 5 of the test dataset (Figure from **Publication 1**).

The application of MSPC for identifying out-of-control parameters can be found in detail in **Publication 1**.

However, it is important to keep in mind that it is not just the plant normal range based on historical data that matters. Decisions on whether water treatment or other water quality management measures are triggered for process control should be based on not only the normal range, but also the tolerable range. The latter should be determined by rigorous experimentation because this range varies depending on specific mineralogy and water matrix, among others.

### 4.5 D-loop for predicting and creating process water for flotation response evaluation

#### 4.5.1 D-loop water matrix vs. plant water matrix

The water matrix created by the dissolution loop with Mine 1 ore was compared with the actual plant process water composition matrix. **Table 10** shows the comparison of composition between the final water from the dissolution loop (DWL) and the average values recorded on-site. The results indicated that the DLW composition came close to the in-situ plant water quality for the major elements except for calcium and sulfate. The concentration of those two compounds/elements in the DLW was much lower than the values observed on-site. The discrepancy of calcium concentration was likely due to the historical overdosing of lime in the concentrator to depress pentlandite in the copper circuit. Since lime addition affected the formation of sulfate (Schumann et al., 2009), the
concentration of sulfate was lower in the DLW. The concentrations of minor metal elements were found to be much lower in the DLW than in the in-situ plant water. It was a direct consequence that the test did not simulate the plant tailings pond, where oxidation reactions of sulfide took place, reducing the pH and increasing metal solubility. The higher amount of phosphorus in the plant water was originated from the decomposition of the P-containing collector used in the copper flotation circuit. Since there was no addition of collector in the D-Loop, such a result was expected. More results of the D-loop can be found in Publication 2.

Table 10: Comparison of composition between the final water from the dissolution with DW at 20°C (DW20_8) and the average value recorded on-site. The difference is shown in percentage.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unity</th>
<th>DLW</th>
<th>Plant</th>
<th>Diff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPC</td>
<td>μS/cm</td>
<td>2118</td>
<td>2650</td>
<td>-22</td>
</tr>
<tr>
<td>Cl</td>
<td>mg/l</td>
<td>390</td>
<td>440</td>
<td>-12</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>mg/l</td>
<td>420</td>
<td>620</td>
<td>38</td>
</tr>
<tr>
<td>K⁺</td>
<td>mg/l</td>
<td>52</td>
<td>53</td>
<td>-2</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>mg/l</td>
<td>81</td>
<td>160</td>
<td>-66</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>mg/l</td>
<td>67</td>
<td>66</td>
<td>2</td>
</tr>
<tr>
<td>Na⁺</td>
<td>mg/l</td>
<td>180</td>
<td>205</td>
<td>-13</td>
</tr>
<tr>
<td>Total S</td>
<td>mg/l</td>
<td>260</td>
<td>241</td>
<td>8</td>
</tr>
<tr>
<td>Si</td>
<td>mg/l</td>
<td>5</td>
<td>9</td>
<td>-57</td>
</tr>
<tr>
<td>Fe</td>
<td>μg/L</td>
<td>50</td>
<td>700</td>
<td>-173</td>
</tr>
<tr>
<td>Ni</td>
<td>μg/L</td>
<td>21</td>
<td>10</td>
<td>71</td>
</tr>
<tr>
<td>Cu</td>
<td>μg/L</td>
<td>2</td>
<td>3</td>
<td>-40</td>
</tr>
<tr>
<td>Co</td>
<td>μg/L</td>
<td>0.2</td>
<td>2</td>
<td>-163.6</td>
</tr>
<tr>
<td>P</td>
<td>μg/L</td>
<td>7</td>
<td>140</td>
<td>-181</td>
</tr>
</tbody>
</table>

4.5.2 Application of the D-loop for predicting the impact of recycled water on the flotation performance

This section aims to provide the results of the study that was described in Chapter 3.5.3. To ease the reading, the author would like to recall that the test hypothesis was that if the dissolution loop water (DLW) created by the D-loop due to its composition has a similar effect on the flotation performance in the batch flotation test as the process water, the flotation test results should be the same. Additionally, if the results of flotation with process water and DLW are similar, the D-loop and the water that it generated could be used for predicting the future impact of recycling water on flotation performance in greenfield cases.

The batch flotation tests were carried with onsite fresh water (FW), DLW, and plant process water (PW) and using Cu-Ni ore samples from Mine 2. All the tests were performed in duplicate to investigate the reproducibility of the approach. The process water was freshly collected from the feeding point to the flotation circuit in the plant in the morning before the test. The maximum aging time between the flotation test and the collection time was 90 minutes. Since the residence time was short, it was reasonable to assume that the process water composition was constant during the tests. More details about the procedure can be found in Publication 2.

The recovery-grade results for the batch scale Cu and Ni flotation tests are shown in Figure 29.
Main results

Figure 29. Recovery-grade curves for the Cu and Ni flotation performed with fresh water (FW), dissolution loop water (DLW), and process water (PW) (Figure from Publication 2).

The results showed that the copper flotation with fresh water (FW) gave the best recovery but the lowest grade. The flotation with process water (PW) decreased the recovery of Cu but increased the grade. The drop in the recovery can be up to 10% while the grade increased by almost 3%. The flotation with the dissolution loop water (DLW) indicated the same trend as with the PW.

Now, let assume that Mine 2 was a green case and the engineer would like to predict if recycled water can have negative effects on flotation performance. The flotation with the DLW predicted a drop in terms of recovery, around 15%. The flotation with PW confirmed such a prediction was very close to reality since the flotation with PW also decreased the recovery by 15%. However, the predicted increase in grade was higher than the reality, around 8% instead of 3%.

The flotation with DLW and PW gave similar results in terms of Ni recovery and grade. The grade and recovery of Ni increased significantly compared to the flotation with FW. These results supported two important findings:

- The potential effect of recycling water can be predicted with flotation tests using D-loop water. Even though this approach cannot yield an exact effect, it can point out the main tendencies.
- The flotations with fresh water and recycled water (or process water) give different results. It indicates that if the plant is planned to recirculate water, the metallurgical testing for plant design shall not be done using fresh water or local tap water but with dissolution loop water. Otherwise, the results can lead to an inappropriate design.
5. Discussion

5.1 Importance of understanding PW behaviors and characteristics

5.1.1 New challenges need new solutions

The first question this study sought to understand is why it is so challenging to evaluate, monitor, control, and predict mining process water quality and what pieces of information are missing in order to manage process water to optimize the process performance.

The results of this study show a lack of data concerning process water quality, its variation during the mineral processing operation, and its effect on the process performance under a specific ore type. Additionally, the traditional tools and approaches for examining and studying water quality currently used in mine-site seem not suitable for answering the new challenging tasks.

One of the main objectives of this thesis was to investigate the variation in water quality characteristics during mineral process operation. This work has shown that not all water quality characteristics are considered when designing a water management system serving process optimization purposes. Several important characteristics of the process water variation have not been identified and characterized before. Three major ones are:

- The water matrix can change fast, in a matter of hours.
- The variation of parameters that characterize the water quality is not independent.
- The range or frequency of variation is not similar for all variables. Some variables can change very fast, some much slower.

The two very different case studies presented illustrate the current approach in managing water in the mining industry. Common to both sites is that water management focuses on the overall water circuit (Chapter 4.2.2). The management plans aim to fulfill the environmental requirements set by the permitting government bodies (Publication 4). As permitting appears not to be very particular on the representativeness, sampling has been chosen to be most practical for the mine personnel, e.g. as one sampling per day.

Common drawbacks in both cases are that the processing plant’s water feeding point is usually included in the monitoring program, but no regular information about the properties of slurry quality within the process appears to be available. Water in the process proper is not analyzed regularly.

Firstly, the fast variation kinetics in water quality require either a high frequency of sampling or an online water monitoring system. Since information about water chemistry at critical process locations is not available, there is no possibility of obtaining any
systematic information about the variation of water quality inside the process and the nature of the reactions.

Secondly, the water matrix is a whole and unique unit. It is not characterized by one parameter but a set of parameters that might strongly correlate. Different factors can govern the correlations between the variables: thermodynamic law (e.g., pH vs. metals, Eh vs. DO), operating conditions, and seasonal variations (see Chapter 4.2). When there is a correlation between different compounds, the change in one variable indeed results or causes the change of other variables. Nevertheless, as observed in the two case study objects, only single variables are separately considered by on-site engineers for water quality control purposes. Additionally, the attention is put on the magnitude of the change without considering the correlation matrix. Such action is meaningless and even dangerous since a fault can be wrongly detected or overlooked (Publication 1).

Lastly, the different frequency of variation indicated that the sampling frequency should be customized for a specific water matrix or a group of components (Publication 4). Higher variation frequency might require a higher sampling frequency while the lower frequency of variations could be captured with a lower sampling frequency. Additionally, since water-related variables might be strongly correlated, a sampling frequency that considers the whole nature of the water matrix is needed. Otherwise, the error of sampling could be underestimated (Publication 4).

The mines should consider these findings in the future updates of their water management plans and schemes.

5.1.2 New possibilities for sustainable and better mining

Understanding the nature of process water quality variations is the first condition to prevent possible adverse effects and build a better and more sustainable mining operation.

In this thesis, three important driving forces behind the variation of water quality are pointed out: (1) tailings storage methods, (2) degree of complexity of the water management system, and (3) modification related to the water circuit or the process operating set point. That means any modifications related to those aspects should be carefully considered when keeping in mind that changes in terms of water quality should be expected and anticipated.

This study has shown that a change from a long water recycling loop to a short loop will result in a complete change of the water matrix. Muzinda and Schreithofer (2018) indicate that a long water cycle generally results in a cyclic variation of the water quality where the seasonal variation is the major contributor. This study confirms this observation through the two case study objects, but pointing out that this tendency will disappear if a short water cycle is taken into use. Then the variation becomes noisier, and out of thermodynamic equilibrium. Additionally, dissolved species tend to accumulate in the process water, and therefore, additional water treatment processes are required, which again affect the water quality. It appears that in the near future, short water recycling loops will be used more frequently due to environmental and water availability constraints. Knowing the characteristics mentioned above brings advantages in the design phase of the plant, the monitoring system and allows to create more room for future modifications if needed.

Moreover, the current driving forces for water closure are still the environmental regulations, and the ultimate goal of water management is to ensure water balance. Closing
the water circuit is generally considered a costly modification due to the need to implement process water quality stabilizing solutions. The knowledge of process water characteristics will allow to perform the closure with minimal cost or even create added value to the products. Additionally, it is now possible to manage water to ensure both water quality stability and water balance. This approach is more challenging compared to solely ensuring water balance and requires further investigations. However, it could simply start with the idea that since the water quality of streams can differ substantially, it might be appropriate and important to isolate waters from different circuits.

5.2 The urgent target: water database for operation purposes

5.2.1 What did we learn from the current database?

Both mine sites concerned in this study currently have water database. However, they are not set up nor used for operating purposes. Mine 1 water database has a higher frequency of sampling than Mine 2 (daily vs weekly). However, only 11 parameters are included in the monitoring scheme at Mine 1. Among them, several parameters are strongly correlated. Unfortunately, not all parameters of interest are included. Some components which are essential in linking the water quality to the plant performance are not included. They are variables such as Eh, the concentration of metals, salinity (sodium, potassium, chloride, magnesium, and other elements), speciation of the thiosalt compounds, organic compounds, residual reagents, suspended solids, and bacteria. Therefore, the linking of water quality to plant performance was impossible. Since the importance of those parameters on the flotation performance is emphasized in the literature, (Levay et al., 2001; Muzinda and Schreithofer, 2018; Ikumapayil et al., 2010; Farrokhpay and Zanin, 2011; Senior and Trahar, 1991; Rao and Finch, 1989) they should be included in the dataset to gain a comprehensive understanding of the water quality effects on flotation performance.

Mine 2 datasets are purely built for fulfilling the environmental regulations. The current sampling procedure for water in Mine 2 is a weekly sampling. That means the operator assumes that the water quality will change with a frequency lower than one week. The individual variograms for the five properties of the HF dataset confirm that such an assumption is not accurate. The range of some variograms is around 3.5 days, indicating a frequency of variation much higher than one week. Such results indicate that the environmental water database cannot be used for operating purposes since it does not capture the high variation of the process water.

Additionally, the current practice in both mines is spot sampling. For some compounds/elements, spot sampling can generate a very high sampling error. Therefore, such a sampling method is not suitable for providing a representative sample for operating purposes.

Moreover, due to the matrix interference and the unstable nature of mine process waters, standard generic analysis methods usually applied for environmental and drinking water samples will likely not be applicable for the analysis of mine process waters. Indeed, Chapter 4.3 and Publication 3, highlighted the low quality of part of the analysis results and the inappropriate methodologies proposed by certified laboratories for preserving and analyzing the complex and unstable mining process waters. The results showed difficulties in providing satisfactory results when analyzing control samples and
a substantial imbalance in TDS and sulfur compounds. Several potential causes associated with the poor quality of the analysis results could be outlined: (1) the preservation methods are not suitable for preserving elements of interest in mining process water, and (2) standard generic methods developed for environmental and drinking waters are not suitable for analyzing mining waters which are extremely mine-specific. These shortcomings are illustrated between in-situ and laboratory pH measurements. The differences were even higher than 60% in some locations within the process. On average, the difference was 45%. Since pH is considered as a proxy for water quality, any change of pH indicates a change in the water matrix. The results suggest that preserving samples at 4 °C is not sufficient to prevent degradation of the process water. It should be kept in mind that in order to have reliable analytical results, the sample must be preserved in a way that its initial properties are maintained until the analysis. Otherwise, the readings will be meaningless.

Furthermore, unsatisfactory analytical results of the control sample were observed when the latter was sent together with the plant water samples (Mine 2, control sample S1, Table 9). If the laboratory standard procedure for analysis causes such a result, a high difference should have been observed in both control samples S1 and S2 for Mine 1 and not only in specific sample S1, as is the case. This observation may support the hypothesis that the problem of unsatisfactory analytical results of some elements in control samples is more likely due to errors in delivering consistent analysis results from the analytical laboratory than the analysis procedure per se. Therefore, it is appropriate to question the sample handling procedures and the quality control of the analytical work performed by certified laboratories along with the suitable analytics methods.

5.2.2 Recommendation for improvement

Application of multivariate variogram to design sampling procedure

In order to capture the variation of process water quality and to provide a sample with better representativeness, the mine sites should change their traditional practices for water sampling. The lessons obtained from the two case study objects are that it is very common that mine-site practices weekly or daily sampling for water monitoring. Despite its practicability, such an approach is not an engineering approach since the frequency of sampling needs to be decided by the nature of the process itself, not by an existing tradition. Those traditional practices can fail to capture the water variation and the representativeness of the sample should be questioned as shown in Publication 4 and Chapter 4.3.1.

Moreover, process water quality is very mine-specific. Its signature depends on the ore, reagent suite, operating practices, water source availability, water management, and the mine’s climate. Since the basic aim of a sampling procedure is to capture the intrinsic heterogeneity characteristics of the process (Esbensen et al., 2007), there is no universal sampling procedure that is validated for all mines. Therefore, before performing any major sampling campaign, an experimental sampling error evaluation is needed.

Additionally, the variability given by the variographic analysis is valid for a certain time only. Its property can vary as different ores are mined, or modifications are made in the water circuit. Therefore, it is unrealistic to apply one sampling procedure over the mine’s total lifetime (Marques and Costa, 2014).

Designing water sampling in mining is a decision-making procedure. It needs to be based on a combination of variographic approaches, statistical analysis, and constraints
Discussion

Details of the decision-making process for water sampling in mining can be found in Publication 4. The procedure contains 4 major steps (Figure 30): sampling (to obtain the dataset for the variographic modeling), modeling, defining criteria provided by each modeling pathway, and final decision.

![Figure 30: Decision-making procedure proposal for water sampling in mining.](image)

Before any design, a set of predefined criteria should be set up in order to make the sampling procedure applicable and feasible on-site. The pre-defined criteria should contain the sampling objective, the practical constraints (e.g., possible time window for sampling, number of personnel), economic constraints (e.g., laboratory cost for water analysis), environmental constraints (e.g., minimum sampling frequency defined by the environmental regulations), etc.

The sampling design procedure starts with data collection. Data could be obtained by a systematic sampling campaign as described in Chapter 3.3.1, or by implementing probes in the stream, or from historical data on-site. Those data, after “cleaning” (e.g., remove outliers), could be used for modeling tasks. The objective of the modeling is to extract different hidden variation features of the data. For that different variographic and statistical approaches are available (see Publication 4, Discussion section for more details). With the results obtained from the modeling, different sampling choices, as well as their pros and cons can be defined. And finally, a tailored water sampling procedure satisfying all criteria could be obtained based on the results from step 3 and the pre-defined criteria.

It is worth noting that variographic design can help to provide a representative sample. However, due to the high instability of the water (Chapter 4.1 and 4.3.2) the sample should be properly preserved and stabilized before sending for analysis.

Pre-survey to improve the preservation and analysis procedure

The results presented in Chapter 4.3.2 has clearly demonstrated that standardized procedure for preserving and analyzing water provided by analytical laboratory (even if certified) are not necessarily applicable for mining and mineral processing waters. Those
procedures are not taken into account the complexity and the numerous unstable compounds present in those waters that can cause particular challenges for sample preservation and analysis.

The results showed that sulfur compounds are one of the most challenging to preserve due to their high reactivity. Speciation might change while the sample is transported from the site to the laboratory even though preservation methods that were found in the literature were applied. Due to their instability, thiosalts analysis should ideally be done on-site (Miranda-Trevino et al., 2013). Titration is the most commonly used on-site suitable method for the total concentration of thiosalts compounds (Makhija and Hitchen, 1979). However, if no on-site analysis is available, samples should be preserved via filtration and fast freezing (Miranda-Trevino et al., 2013). The thawing process must be done just before the analysis in a controlled thermostated bath.

Moreover, not all laboratories can analyze all thiosalts speciation (e.g. the laboratory contracted by Mine 2 can only perform thiosulfate analysis). An accurate analysis of different thiosalt speciations is especially important, as the presence of different thiosalt species can negatively affect the froth stability and flotation performance in sulfide ore processing (Biçak et al., 2012; Öztürk et al., 2018; Whaley-Martin et al., 2020).

Additionally, some thiosalt analysis standards required the use of some eluent that might modify the solution pH (ref. SFS-EN ISO 10304-3). It is worth notifying the laboratory personal that the pH adjustment can only be done right before the analysis since it is shown in the literature that the thiosalt speciation changes with pH (Miranda-Trevino et al., 2013; Vongporm, 2008; Wasserlauf and Dutrizac, 1984).

Matrix interference is one of the major factors that analytic methods usually applied for environmental and drinking water samples will likely not be applicable for mine process water analytics. Additionally, since mining waters are also mine-specific, there is probably no standard analysis procedure that fits all the mining waters. It means that the sample preservation and analysis procedure need to be customized on a case-by-case basis.

The afore discussion highlights the importance of having a pre-study before implementing a regular sampling program or performing extensive sampling surveys. Such a pre-study should be done in collaboration with the laboratory to identify the compounds/elements that might cause the deterioration of the samples between sampling and analysis. Proper preservation and analysis methods should be defined and implemented so that the quality of the obtained results could be ensured. This approach warrants that the economic and personnel efforts spent for such campaigns bring reliable results.

5.3 What would be the future of water management in mining?

5.3.1 From process water to operating parameter: still a long road

One of the main initial targets of this thesis is to explore a possible way to turn process water into a set of operating conditions that, similar to the reagent dosing or any other traditional operating parameters, can be modified by the metallurgists scientifically. Hence the impact of water quality of flotation would be minimal or even improving the process performance. The study results point out that such a procedure is extremely complicated, and there is still a long road to go.
As discussed previously, one condition for process water to be considered as an operating parameter is that its effect on the flotation performance must be well defined. However, such a goal is very challenging to achieve as the variation of water quality and its impact on the flotation results from an ore-water quality-operating conditions-performance feedback loop (Figure 31). Any attempt to isolate water from that feedback loop and investigate its effect solely on flotation performance might be useless from an industrial point of view.

![Figure 31: Complex interactions between different groups of variables that are present in the flotation system](image)

Indeed, in mineral processing plants, the final objective of the operators is to maintain the recovery and quality of the products in terms of grade and impurities. Most of the time, the parameters they can change are the operating condition parameters. The changes in operating parameters contribute to the change of the water matrix, as shown in the variogram of calcium and phosphorus of Mine 2 (Figure 13). The half-year cyclic variations of those operating-related parameters directly result from adjusting operating conditions to seasonal variations (Publication 4).

Separately, the ore quality is known to influence the performance of the flotation. It also dictates the reagents regime (i.e. operating condition), as well as influences on the water quality via the dissolution and oxidation during milling and flotation. That means the variation of mineralogy results in changes in operating conditions and water quality. The water quality, in return, can influence the mineral surface and froth stability, hence the performance. Additionally, the water quality can affect the dissolution of the ore. As observed in the development of the dissolution loop test, the kinetics decreased as a function of the number of cycles (Publication 2). That means the relation between ore dissolution and water quality is a two-way relationship. Such a double relationship is also true for water quality and flotation performance. The success of the flotation is partly influenced by water quality, and in return, the remaining flotation reagents affect the water matrix. Such a feedback loop is one of the responsible reasons for the high variation of water quality. It also indicates that the definition of “good quality water” for the process performance might change with the ore type. Such interactions cast doubts on our current approach to study the effect of water quality on the floatability using pure minerals, or one ore type and synthetic water.

Moreover, both mines concerned in this study did not have a pre-defined sampling plan or in-situ measurement infrastructure (sensor and water balance) to do any detailed surveys. An obtained water balance can only be applied for the whole mine. However, it cannot be broken down to the level of the mineral processing plants. The lack of an intensive water monitoring system in both plants is attributed to their assumption that the process water quality is meta-stable. Thus, any variation which may happen will be only observed in a medium or long-range. However, since the dissolution of the ore during the milling and flotation continuously changes the water matrix, there is no reason that water quality does not have a similar frequency of variation as the ore (Chapter 4.3.1).
The lack of an appropriate monitoring system and database aggravates the difficulty to transform water quality into an operating parameter.

Moreover, assuming that “good” datasets exist, the question becomes how to handle such high-dimensional, high-frequency datasets, interpret them, and provide adequate control actions for the flotation circuit. That is not an easy task owing to the number of variables involved, the number of observations, and the non-linear and dynamic nature of the process (Bonifazi et al., 2002). Advanced mathematical techniques such as machine learning and neural networks could help deal with a large dataset and provide a pattern in non-linear relationships (Jahedsaravani et al., 2014). However, not all mineral processing engineers have enough mathematical background knowledge to apply those techniques, and vice versa, not all data analysts have mineral processing and process background to interpret the physical meaning of the results.

5.3.2 From synthetic/distilled water testing approach to D-loop water

Chapter 2.1.3 discussed why using synthetic and distilled water to study the effect of water quality on process performance was not an ideal approach. With the dissolution protocol, it is now possible to create a water matrix similar to the plant water matrix. It could be used as a baseline for studying the effect of particular elements/components on the flotation performance. Such a tool is crucial in the case that access to plant process water is impossible (f.ex. greenfield cases).

Nevertheless, it is worth noting that the basic dissolution loop protocol deliberately ignores events that could affect the process water quality such as changes in ore types, water blending, bacterial activities, and seasonal variation. Therefore, discrepancies are observed between the DLW and the real process water, particularly in terms of minor elements such as metals. Compared to the actual plant process water circuit, the dissolution loop is still a simplified process. It could not fully mimic the complex interactions between ore, water, and operating conditions that affect the quality of process water in the true plant. Depending on the objective of the test, the basic protocol can be further extended by including and simulating different conditions of interest (f.ex. bacteria can be added during the dissolution to investigate the bacterial effect on the quality of the future process water).

5.3.3 From the univariate approach to multivariate models

Water management in the mining industry tends to employ univariate approaches as the main pathway. Such approaches are observed in all activities related to mining water such as testing plan, monitoring, prediction, and treatment. Nevertheless, the univariate approach cannot reflect the whole complexity of the water system due to thermodynamics and correlation relationships between variables. Single variable results are always affected by other variables in unknown ways. The interpretation becomes uncertain and even faulty (Publication 1, 2, and 4). The water matrix complexity and the correlations between the variables require a multivariate approach. The whole system must be considered to provide meaningful testing plans (see Chapter 5.3.2), models, interpretations, and decisions. The multivariate approach gives more in-depth insights into the water matrix changes and effects on flotation. It gives tools to manage the water property matrix to ensure its stability and provide an effective way to control the flotation circuit.
This study has highlighted the possibility of using the multivariate approach to monitoring the water system. The methodology could also be extended in other aspects of water management (e.g., exploring water quality, predicting water quality variation, controlling the flotation performance).

This work demonstrated the use of Multivariate Statistical Process Control (MSPC) on historical data to build a monitoring system for detecting changes and alerting plant personnel when the water quality reaches a certain threshold. However, it is worth noting that the threshold for water quality might change with the ore type. It is unrealistic to expect that there is one water matrix that works for all ore types. Such a statement enhances the need to approach the challenge by using big-data-driven solutions. Advanced machine learning methods, applied on suitable datasets, could predict the behavior of one ore type as a function of water matrices based on historical knowledge.

In the future, MSPC should be combined with mine site water balance and thermodynamic calculations to provide better management of site water. Precisely, MSPC could be used to alert a malfunctioning of the process water system or when water quality shifts from the normal operating range. When it happens, a water balance combined with thermodynamic calculations should be simulated by the computer to investigate the possibility of blending the process water with other streams to counterbalance. If the returned results are such a simple strategy would not work, then the water treatment would be initiated. The program will automatically provide the amount of water that needs to be treated, treatment methods, and blending strategy after treatment. With such an approach, the water quality and water balance could both be maintained in a control range automatically. It would decrease the error made by operators when randomly blending different water sources, which often leads to inferior water quality in mineral processing operations and therefore negatively affect the flotation process performance. However, currently, most of the mine water and elemental balance is still absent or incomplete. Additionally, the platform that allows the integration of MSPC, water balance, and thermodynamic calculations all together is still missing.
6. Conclusions

The work was based on four datasets obtained and collected from two mines with very different processes and water management systems (Table 4).

The variogram analysis is used to study the variability in the water property matrix and to investigate the origin of the variations. Such knowledge is crucial for designing tasks related to process water management, such as sampling, laboratory testing, water blending, and water treatment. The results showed that mining process waters possess an extremely complex variability. The variations of all parameters can be both correlated and independent, depending on the factors that govern the variations. The range and frequency of variations are not similar for all variables. Unstable variables or operation-related variables can change very fast. Meanwhile, stable and season-related variables can change much slower. Such results confirmed the hypothesis of a multidimensional and dynamic water property matrix.

PCA turned out to be a useful tool to characterize and analyze large datasets, hence an effective tool to study the water property matrix. The PCA loading vectors provided meaningful information about how the studied variables related to each other (i.e., the correlation between variables). The obtained score vectors contained the information on how different observations related to each other (i.e., the trends of variations over time). The results showed that the studied water matrices posed a multivariate challenge. They were characterized by a large number of strongly correlated parameters. The relevant complex features of different water matrices could be captured by advanced mathematical and statistical methods, as was hypothesized.

The variogram work confirmed that the sampling frequency for process water must be tailored and customized based on the anticipated water composition. The sampling protocol depends on composition variability caused by the nature of the process and the ore. Consequently, a generic standard practical sampling procedure defined arbitrarily for environmental reporting is not the most optimal solution to characterize process water.

As discussed in the thesis, the variogram and PCA refinement could be used to develop a sampling plan which can capture the overall variation of the whole water matrix. It could also find hidden trends and patterns of variation that are not visible with the raw data. Additionally, a customized sampling plan can increase the reliability of the analysis results by providing a representative sample. The results confirmed that, in this study case, the SDSE associated with spot sampling is relatively high. However, with a simple two-increment sample, the SDSE could decrease by 60%, and with a four-increment sample by 90%. These values are based on the variability of only five physicochemical properties that we could monitor with high frequency. In reality, other chemical properties should be added to the monitoring program. Therefore, the final SDSE would be
higher, and the number of increments needed to decrease the SDSE would increase accordingly.

In this study, methods for preserving and analyzing process water were challenged. The results were alarming: (1) even certified laboratories are not necessarily aware of the complex and dynamic system they are dealing with. (2) The traditional analysis methods developed and standardized for monitoring effluent and drinking water are not suitable for characterizing process water. The ions of interest and background matrix are not the same. Using generalized standard methods without optimization to the prevailing conditions may cause high uncertainty in analysis results. This uncertainty could be critical to the planning and execution of any changes and improvements in water management or ore beneficiation. These findings are very significant as they raise the alarm for all mines to revise their procedures for preserving and analyzing process water no matter if the analysis procedures are performed internally or externally.

This study developed an integrated decision-making process to design water sampling in mining under the context of improving process performance. Such a procedure, combined with the methodologies for preserving and analyzing process waters should be used in mining operations worldwide as standard procedures for designing process water evaluation protocols to obtain reliable results.

Additional statistical parameters such as Q residue and Hotelling’s $T^2$ obtained from the PCA model were shown to be useful in detecting process drift outside its normal statistical behavior and identifying the possible causes of the drift, hence monitoring the water quality. The two parameters allowed to monitor both the operating range of the inputs and the correlation between the variables. Compared to a univariate approach for process monitoring, this approach was more advantageous since it offered a possibility to monitor the whole thermodynamic state of the studied water matrices.

A unique protocol, named D-loop, to produce water that mimics the water found at processing plants was developed during the work. The results obtained showed the final water composition to be close to the in-situ plant water quality in terms of major elements and some of the minor elements in the studied system. It appears that for a given ore the D-loop is capable of producing a water property matrix mimicking reasonably well the property matrix found at plants processing the said ore. The D-loop makes it possible to perform multivariate studies of water effects on flotation on the laboratory scale. It is more realistic than making tests with simplified artificial water property matrices or undefined property matrices like tap water. The D-loop allows also dynamic studies, even seasonal variation studies. Furthermore, different technologies for recycled water purification can be evaluated. Even though the exact variation in grade and recovery cannot be forecasted, the direction of the changes caused by the water quality can be foreseen. Pending further validation, D-loop may become a tool to complement the traditional processing plant design and water treatment facility selection and dimensioning.

This thesis points out that turning process water properties into operating parameters appears an extremely challenging task due to the lack of appropriate tools to deal with process water property matrices that are complex, dynamic, and mine-specific. Those properties are the direct consequences of the ore-water-performance feedback loop in the plant, tailings storage methods, water circuit complexity, external parameters such as local climate variations or operating practices, and operating set points. Such characteristics make process water differ greatly from the discharged effluents.

This study has shown with two case study objects the little known dynamic nature of the process water. The used statistical tools have shown to be able to capture much of
such variations. However, the lack of appropriate datasets became evident. The work was restricted to the variables available in the four datasets, as no economic means were available to perform new sampling campaigns. Therefore, some variations of the water property matrices may not have been identified.

The identified complexity calls to rethink the role of the water as an important component in improving resource efficiency; both in saving fresh water by enhanced water reuse and better recovery of valuable constituents of an ore.
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Conclusions

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Due to the potential adverse effects of recycled water on the performance of mineral separation processes, water management in mining is now shifting focus to not only fulfil the environmental regulations but also to improve process performance. The dynamicity and variability in terms of quality of recycled process water bring challenges in the recovery and the quality of the final products. By turning water quality into operating parameters, its properties could be controlled and modified to hopefully provide added value to the process outputs.

This thesis aims to explore the challenges and to fill the gaps for transforming water quality into a set of operating parameters in mineral processing. The underlying idea is to investigate and develop tools that are needed for making suitable water quality for each processing step. This thesis focuses on three main cornerstones that are relevant for managing water in a context related to operating performance: (1) procedure for collecting process water data, (2) data analysis and monitoring methods, (3) procedure for predicting process water variation and laboratory testing method for investigating the effect of water matrix on process performance. The traditional methods for those mentioned aspects developed for effluents (environmental purposes) have neglected to account for the three major characteristics of recycled process water: dynamic, complex and mine specific, a shortcoming this thesis addresses. This thesis asks to what extent traditional methods for managing water for environmental purposes are applicable for