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Assessing the Evolution of Mine Water Quality With Empirical 'First-Flush' Models

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ABSTRACT

Coal mining activities can leave an extensive network of abandoned underground workings that gradually flood after operations cease. This rising mine water, with low pH and high sulfate, acidity, and metals can lead to uncontrolled releases of harmful acid mine drainage to the environment. Treatment plants are used to extract and treat the mine water to maintain its elevations below suspected discharge zones. Accurate predictions of long-term water quality is highly challenging due to the complexity and volume of the underground workings. As numerical models can be expensive and require considerable effort to effectively implement, empirical models that are based on Younger's 'first-flush' phenomenon, where mine water concentrations peak shortly after flooding and then exponentially decline, may provide suitable long-term predictive modeling. The objective of this study was to assess the robustness of 'first-flush' empirical models for describing and predicting mine water behavior at large, complex mine pools in The Sydney Coalfield (Nova Scotia, Canada). Numerous mine pools in the coalfield flooded at various times over 100+ years, allowing long-term mine water evolution to be studied in various pools of different ages. Analysis of extensive historical data from the older pools demonstrated that the evolving mine water quality, both overall and within each stratified layer, followed the 'first-flush' phenomenon. 'First-flush' trends were consistent across differing depths, water quality parameters (acidity, sulfate, iron), and concentration ranges. Two newer mine pools, which recently flooded in 2012, rely on a new active treatment plant to manage mine water levels below discharge points. Using behavioral conditions observed in the older mines, such as decay rate, 'first-flush' based empirical models were calibrated and validated to early mine water quality data collected at the treatment plant bi-weekly between 2012 and 2021. They were then used to predict future mine water quality and estimates of long-term treatment requirements and related expenses.

Keywords

Mine water, abandoned mine workings, acid mine drainage, predictive modeling, first flush

SUMMARY FOR LAY AUDIENCE

Closed and abandoned mine tunnels underground can often fill-up with contaminated water that can damage the environment and ecosystems if it is allowed to escape. To prevent this from happening, mine water treatment plants are often constructed to pump out and treat this contaminated water so it does not fill-up the mine tunnels and spill over into the environment. These treatment plants are expensive infrastructure projects, often requiring millions of dollars to construct and operate. It is important to understand the long-term behavior and changes that happen to this mine water so that the treatment infrastructure can be designed and operated as good as possible. However, modeling these flooded underground mine workings is a very expensive and difficult task because of the size and complexity of these systems. Numerical models are often used in these situations as they can model in detail the physical and chemical processes that take place. However, numerical models often require data about the exact layout of the mine workings, which may be unknown or unreliable. In addition, they can be expensive to develop and take considerable time and effort. Empirical models are more simple and less expensive and they are based only on analyzing the quality of the water after it was collected from the mine workings. Empirical models take a 'higher-level' approach to predict the water quality, going off of actual water data, changes and trends, instead of trying to model all the details and processes that make the water change.

This study collected and analyzed mine water sampling data from the historic Sydney Coalfield that is located in Nova Scotia, Canada, and a easy-to-use and low cost empirical model was developed to understand how the mine water changes over time. It was found that: (i) empirical models can accurately predict the behavior and changes in the mine water, and (ii) water quality is expected to get much better over the coming decades, which will result in less expenses in the treatment operations. The results of this study provide critical information needed for the planning and management of mine water treatment infrastructure, which can be used to protect the environment.

CO-AUTHORSHIP STATEMENT

The candidate is responsible for the collection and analysis of field data, as well as writing the drafts of all chapters of this thesis. Dr. Christopher Power provided the initial motivation for this research, assisted with fieldwork, provided suggestions for data analysis, and provided revisions for improvement of the thesis. The co-authorship breakdown of Chapter 3 is as follows:

Authors: Patrick Merritt, Christopher Power

Contributions:

Patrick Merritt conducted collection and analysis of field data, model development, and interpretation of the results to prepare a draft of the chapter. Christopher Power supervised field data collection, analysis, provided insight and interpretation of results, and reviewed the draft chapter.

ACKNOWLEDGMENTS

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1 INTRODUCTION

1.1 RESEARCH BACKGROUND

During the operating life of underground coal mines, the workings are commonly dewatered to provide the necessary dry working conditions. When mining activities cease, the dewatering pumps are turned off and this complex network of open workings will begin to flood. The mine water that is gradually rising in the workings will interact with oxygen and exposed metal sulfides (often pyrite) and cause a complex sequence of reactions that will generate toxic acid mine drainage (AMD). AMD is released when the mine water elevation rises to that a discharge point, such as an outcrop, airshaft, or other access points. From destroying the bicarbonate buffering system that leads to a significant drop in pH (Hoehn & Sizemore, 1977) to the precipitation of iron hydroxides in stream beds (Banks et al., 1997) and to the loss of biodiversity (Grande et al., 2005; Ojonimi et al., 2019), uncontrolled AMD releases can be catastrophic to the receiving environment.

While sealing discharge points would be the most desirable method for preventing or controlling the release of AMD from underground workings, it is extremely challenging. There may be numerous hydraulic connections between the workings and the surface, and many of them could be unknown, such as randomly distributed bootleg workings (Forrester & Noble, 2010). An alternative approach is to maintain the elevation of mine water below expected discharge points. The mine water is continuously pumped out of the workings and into treatment plants constructed adjacent to the workings. Treatment plants can be active or passive, depending on the quality of the water and the pumping rate needed to maintain target water elevations (Trumm, 2010).

Modeling the evolution of mine water quality within flooded mine workings can provide valuable insight into both the design and long-term requirements and expenses of mine water treatment plants. Mine workings are extremely heterogeneous by nature and are typically characterized by their sheer scale, depth, and the complex, sometimes random and unknown distribution, and the intersection of the mine shafts. Furthermore, the mining process, such as room and pillar or longwall, involves the deliberate collapse of the tunnel roofs, which results in a highly tortuous and unrevealed pore structure. Numerical models have been used to simulate mine water flow and

chemistry in mine workings(e.g., Vandenberg et al., 2016; Kuchovský et al., 2017; Tomiyama et al., 2020), but they require incredible investment and effort to recreate the complexity and heterogeneity of larger systems. For example, mine workings have been represented by homogeneous pipe networks or ponds (e.g., Banks, 2001; Hamm et al., 2008; González-Quirós & Fernández-Álvarez, 2019), which becomes onerous at larger scales or in complex workings.

Empirical models are simpler, typically taking a larger-scale, almost watershed level approach to predicting mine water quality, rather than trying to describe the exact nature of the system. It has been shown that these empirical models can be representative of actual mine water quality and its expected behavior while requiring significantly less investment than numerical models(Younger, 2016). These models have been ascertained through examining decades of historical mine water quality and trends that have been observed in minefields worldwide. Younger (2000) examined the long-term behavior of mine water in numerous coal mines in the UK and derived the 'First Flush' principle which indicates that contaminant concentrations in the workings peak shortly after flooding and then decrease exponentially, before eventually reaching asymptotic conditions. This principle has been used to describe evolving mine water quality in flooded mine workings worldwide, including South Africa (Huisamen & Wolkersdorfer, 2016), the USA (Mack et al., 2010; Mountjoy et al., 2018), and Poland (Gzyl & Banks, 2007). Based on this established behavior, three models have been developed to predict the evolution of mine water quality over the long-term (Gzyl & Banks, 2007; Perry & Rauch, 2012). While these models have been developed and validated to complete long-term mine water quality, they have yet to be applied for future mine water quality predictions.

This thesis focuses on the evaluation and application of empirical 'first-flush' models to represent evolving mine water quality of flooded mine pools in the Sydney Coalfield in Nova Scotia, Canada. In 2012, an active treatment plant was constructed in New Victoria (NV) to control the water level in two mine pools – the Sydney Mines (SM) mine pool and the New Waterford (NW) mine pool – to prevent AMD discharge. Due to the high contaminant loadings currently entering the plant, it experiences high operation and maintenance (O&M) costs. It is of great interest to the plant operator – Public Services and Procurement Canada (PSPC) – to ascertain how the quality of the mine water influent (and contaminant loading) will evolve over time. This information can then be used to improve projections of the treatment timeframe and O&M expenses.

1.2   RESEARCH OBJECTIVES

The overall goal of this thesis is to assess the robustness of empirical 'first-flush' models for representing the evolution of mine water quality in flooded underground coal mines, and how these models can be used to predict long-term mine water quality and associated operating expenses at the New Victoria treatment plant in The Sydney Coalfield in Nova Scotia, Canada. As part of this goal, the following objectives were addressed:

1) Assess the viability of empirical 'first-flush' models for representing the evolution of mine water quality across the entire Sydney Coalfield and within the SM and NW mine pools.
2) Apply the most appropriate empirical model to predict the long-term quality of mine water influent being pumped into the New Victoria treatment plant, and the associated plant operating expenses.
3) Assess the feasibility of new approaches for optimizing mine water treatment in the SM and NW mine pools and reducing operational expenses.

While this research was performed in mine workings in the Sydney Coalfield, the findings are expected to be beneficial to the management of other flooded underground mines and operation of mine water treatment plants.

1.3   THESIS OUTLINE

This thesis is written in an "Integrated Article" format. A brief description of each subsequent chapter presented in this thesis is as follows:

- Chapter 2: summarizes the scientific literature relevant to mine water management and predictions of long-term mine water evolution in abandoned workings. The formation mechanisms of AMD in underground mine pools are discussed, along with mine water hydrodynamics and geochemical behavior. The various modeling approaches for predicting long-term mine water quality are presented, along with a detailed summary of The Sydney Coalfield.
- Chapter 3: details the evaluation of empirical models for representing mine water behavior in flooded underground mine workings, and the application of these models to predict long-

term mine water quality, and operating and maintenance (O&M) expenses, at the New Victoria mine water treatment plant in The Sydney Coalfield in Nova Scotia, Canada.

- Chapter 4: summarizes the findings of this research and suggests recommendations for future work.

- Appendices: provides supplemental information for the work presented in Chapter 3. This information includes summaries and results from several tests that were completed during the development of an 'in-house' mine water analysis laboratory at the New Victoria treatment plant.

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2 LITERATURE REVIEW

This chapter summarizes the scientific literature relevant to mine water management approaches for preventing and/or controlling acid mine drainage (AMD) release from flooded underground mine workings. This review first focuses on the generation of AMD and the adverse impacts that uncontrolled releases have on the receiving environment. The review will then examine the hydrodynamics and chemistry in mine pools, including mine water rebound and the temporal evolution of mine water quality. Finally, the legacy and characteristics of The Sydney Coalfield will be presented, followed by a summary that identifies research gaps and opportunities.

2.1 MINE OPERATION AND FLOODING

2.1.1 MINING OPERATIONS

In underground coal mining activities, two styles have commonly been used: 'room and pillar' and 'longwall'. Room and pillar mining involves extracting mineral resources from a seam in what is typically a grid pattern. The minerals are extracted in strips leaving behind pillars to support the roof structure (Bullock & Hustrulid, 2001), with the open areas typically referred to as stopes. The size of the pillars is typically dictated by concerns regarding stability and surface subsidence (Darling, 2011). An illustration of the room and pillar mining process is presented in Figure 2-1.
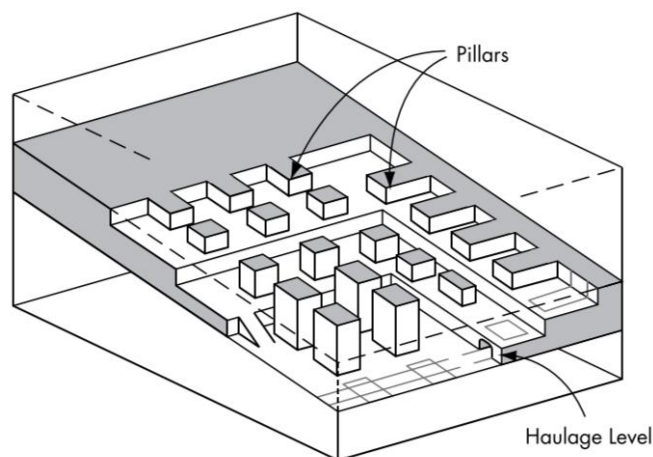
Figure 2-1: Illustration of the room and pillar mining process (source: Darling, 2011)

These pillars, while providing essential support to the roof structure of underground mines, are also incredibly valuable, often being composed of the minerals being extracted. When mining in

an area ceases, these pillars are often extracted in a process known as retreat mining (Darling, 2011), which is illustrated in Figure 2-2. While more economically productive, this process can be dangerous and result in significant loss of life. Despite significant recent advancements in this process (Lind, 2002; Darling, 2011; Mark & Gauna, 2017), longwall mining remains a significantly safer and popular method for coal extraction (Gallagher et al., 2000).
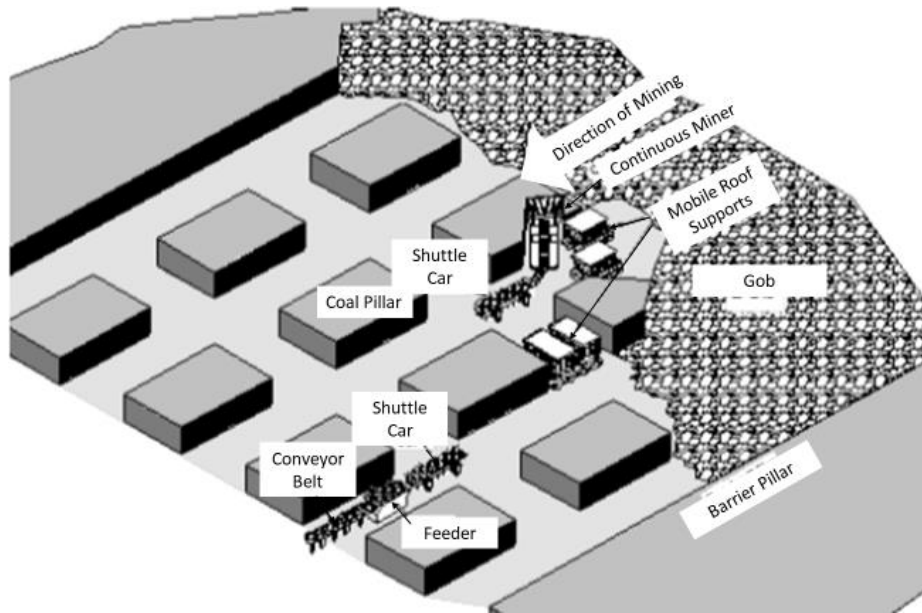
Figure 2-2: Illustration of the room and pillar retreat mining process, where initial support pillars are extracted after mining in the area has ceased (source: (Darling, 2011).

Longwall mining extracts resources in a back and forth motion along a straight line at the coal face. Unlike room and pillar mining which involves mining into the coal seam, longwall mining uses pilot tunnels to start at the edge of a seam and works its way back towards the main shaft. As the machinery advances back through the coal seam, the roof structure is allowed to collapse behind the working face (Bullock & Hustrulid, 2001). Figure 2-3 illustrates the longwall mining process. While this method allows for significantly higher extraction rates than room and pillar, the collapsed areas do not provide substantial support and can cause land subsidence if the method is used at shallow depths.

Despite their differences, both methods leave behind highly complex networks of underground workings and gob areas, and accurately understanding of hydrodynamical and hydrogeochemical

processes occurring within these systems is highly challenging. As a result, it is extremely difficult to develop models that can accurately simulate water flow and water quality in underground workings (Sahu et al., 2009).
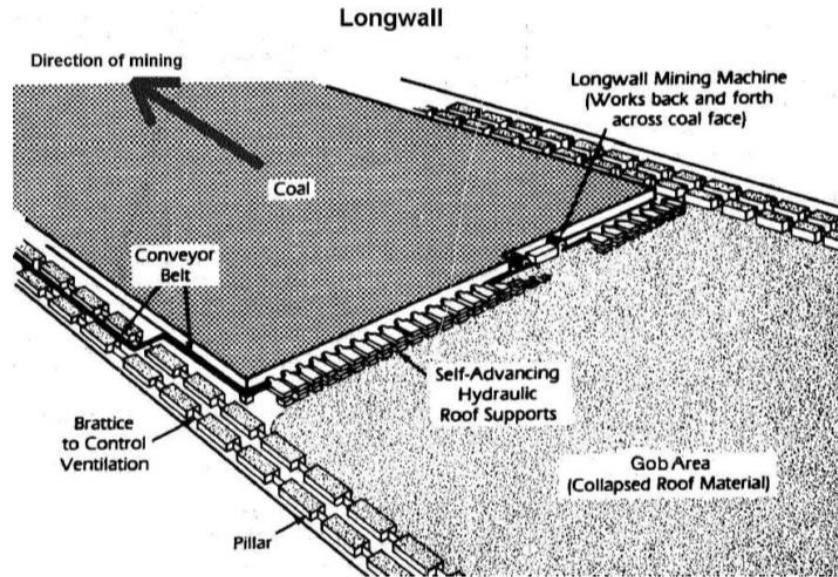
Figure 2-3: Illustration of the longwall mining process, where machinery moves back and forth at the coal face. As the machinery advances upwards through the coal seam, the roof structure is allowed to collapse (source: Nalbantov et al., 2010)

2.1.2 FLOODING

The intersection between mine workings and the surrounding groundwater is common when mining below the ground surface, causing groundwater recharge to the workings (Morton & van Mekerk, 1993). In open-pit excavations or workings with significant hydraulic connections to the surface, precipitation can also play a significant role in water ingress to mine workings (Álvarez et al., 2018). During active mining, water is removed via pumping to ensure dry working conditions for mining to continue. When mining activities have ceased and the colliery is closed, the pumps are turned off and the workings can gradually flood in a process known as mine water rebound (Gandy & Younger, 2007). Not only will the colliery be submerged in water, but high AMD generation will also occur as the previously dry workings that were undergoing oxidation will now interact with the rising water (Younger & Thorn, 2006).

2.2 ACID MINE DRAINAGE

2.2.1 SOURCES

AMD is the result of chemical reactions between sulfidic minerals, such as pyrite or chalcopyrite, oxygen, and water. AMD is typically associated with the mining of coal and other minerals such as gold, copper, and nickel (Akcil & Koldas, 2006; Ojonimi et al., 2019). The chemical reactions associated with AMD generation from mining activities can also occur naturally in rock minerals and is typically referred to as acid rock drainage (ARD) (Joeckel et al., 2005).

Flooded mine workings are a significant source of AMD. The introduction of the water recharging the mine workings is the initial catalyst for AMD generation. After being exposed to air and then water, oxidation of metal sulfides (often pyrite, which is iron-sulfide, FeS_2) within the tunnels of the open mines generates acidity. This contaminated water (or acid leachate) is highly acidic with a reduced pH and contains toxic metals such as iron (Fe), manganese (Mn), and aluminum (Al). As this water continues to rise, it can discharge at the surface and have a detrimental impact on the environment (Acharya & Kharel, 2020). AMD generation can occur as soon as mining begins and can continue long after mining has ceased (Johnson & Hallberg, 2005), thereby causing long-term contamination problems. In addition to underground mine workings, AMD can also occur at open mine pits, tailings ponds, and waste rock piles (WRPs) (Amos et al., 2015; Qureshi et al., 2016)

2.2.2 PYRITE OXIDATION

Pyrite oxidation is considered the dominant reaction that generates AMD. The AMD generation process has been extensively studied, and detailed reviews are provided by Banks et al. (1997) and Akcil and Koldas (2006). In general, the process can be described by the following set of equations, beginning with the cathodic reaction in Eq. (2-1), where pyrite (FeS_2) interacts with water (H_2O) and oxygen (O_2), oxidizing disulfide and releasing protons, sulfate, and ferrous iron:

$$2FeS_2 + 2H_2O + 7O_2 = 2Fe^{2+} + 4SO_4^{2-} + 4H_{(aq)}^+ \qquad \text{(2-1)}$$
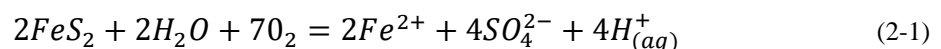
In the presence of an oxidizing environment, characterized by sufficient O2, a pH greater than 3.5, and bacterial activity, ferrous iron can be converted to ferric iron through Eq. (2-2):

$$4Fe^{2+} + 4H^+_{(aq)} + O_2 = 4Fe^{3+} + 2H_2O \qquad (2\text{-}2)$$
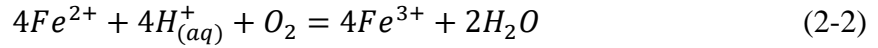
If the pH is between 2.5 and 3.5, ferric iron can precipitate out of solution as ferric oxyhydroxide (Fe(OH)₃) via Eq. (2-3), releasing even more protons and further decreasing pH:

$$Fe^{3+} + 3H_2O = 4Fe(OH)_{3(solid)} + 3H^+_{(aq)} \qquad (2\text{-}3)$$
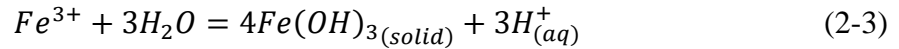
If the Fe^{3+} does not precipitate, it can cause further pyrite oxidation through Eq. (2-4):

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+_{(aq)} \qquad (2\text{-}4)$$
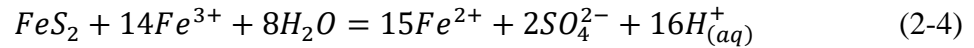
This complex series of chemical reactions can be integrated into Eq. (2-5) to describe the overall oxidation process of pyrite to release sulfate and protons:

$$4FeS_2 + 14H_2O + 15O_2 = 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+(aq) \qquad (2\text{-}5)$$
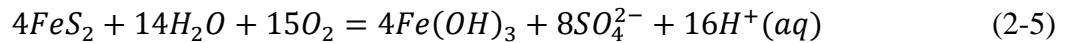
These reactions occur similarly for many other metal sulfides, with the notable exception of sphalerite (zinc sulfide, ZnS), which is unlikely to severely decrease pH as its oxidation does not directly release protons (Banks et al., 1997) as can be seen in Eq. (2-6):

$$ZnS + 2O_2 = Zn^{2+} + 4SO_4^{2-} \qquad (2\text{-}6)$$

2.2.3 ROLE OF MICROORGANISMS DURING OXIDATION

Bacteria can use both direct and indirect methods to participate in the pyrite oxidation process (Silverman & Lundgren, 1959; Silverman, 1967). The direct contact method involves the bacteria, including *acidthiobacillus ferrooxidans* (formerly referred to as *thiobacillus ferrooxidans*), *ferrobacillus ferrooxidans*, and other related species, acting as the primary oxidant, which involves being in direct contact with the mineral in an aerobic environment. The indirect method involves ferric iron ions acting as the primary oxidant and being reduced to ferrous iron, with the bacteria then re-oxidizing the iron back to the ferric state, propagating the oxidation reactions. (Gleisner et al., 2006) also discusses how both the direct and indirect methods occur but indicates that the indirect method is likely dominant.

2.2.4 AMD CHARACTERISTICS

AMD is typically characterized by a low pH, high acidity, and high concentrations of sulfate, metals such as iron, aluminum, and manganese, and various other heavy metals (Akcil & Koldas, 2006). While AMD is generally considered acidic, it can also be net-alkaline (Cairney & Frost, 1975; Banks et al., 1997; Younger, 2001). Net-alkaline AMD generally occurs in mines containing limestone and is usually less environmentally damaging than its acidic counterpart (Akcil & Koldas, 2006). However, even with these minerals, neutral pH is not a guarantee (Younger & Thorn, 2006). Mine water in underground mines can also have high salinity due to highly saline recharging groundwater, which can occur at mines near coastal waters (Banks et al., 1997).

When analyzing mine water samples for acidity, a measurement of the standard hot acidity (can also be referred to as modified acidity, hot peroxide acidity, or net acidity) produces more meaningful results than the standard acidity titration measurement (Cravotta & Kirby, 2004). Analysis with hot acidity gives good indications of pH decreases following oxidation of iron and manganese, as well as the quantity of alkalinity needed to neutralize a mine water sample. Hot acidity can also be accurately calculated if other water quality parameters are available such as pH, alkalinity, iron, manganese, and aluminum concentrations. Park et al. (2015) developed the following equation for calculated net acidity:

$$Net\ Acidity\ = 50 * \left(2 * \frac{[Fe]}{55.85} + 3 * \frac{[Al]}{27} + 2 * \frac{[Mn]}{54.94} + 10^{(3-pH)}\right) - alkalinity \quad (2\text{-}7)$$

2.2.5 AMD RELEASE AND PREVENTION

In the context of underground mine workings, AMD is released when the water elevation inside a colliery rises to that of a discharge point such as an outcrop, air shaft, or other access points (Adams & Younger, 2001). After reaching the discharge elevation, AMD-impacted water will escape from the workings and release into the environment and find its way into nearby surface water bodies and/or groundwater aquifers. *Figure 2-4* presents a conceptual model of AMD release from vertical shaft workings and slope-mined workings.
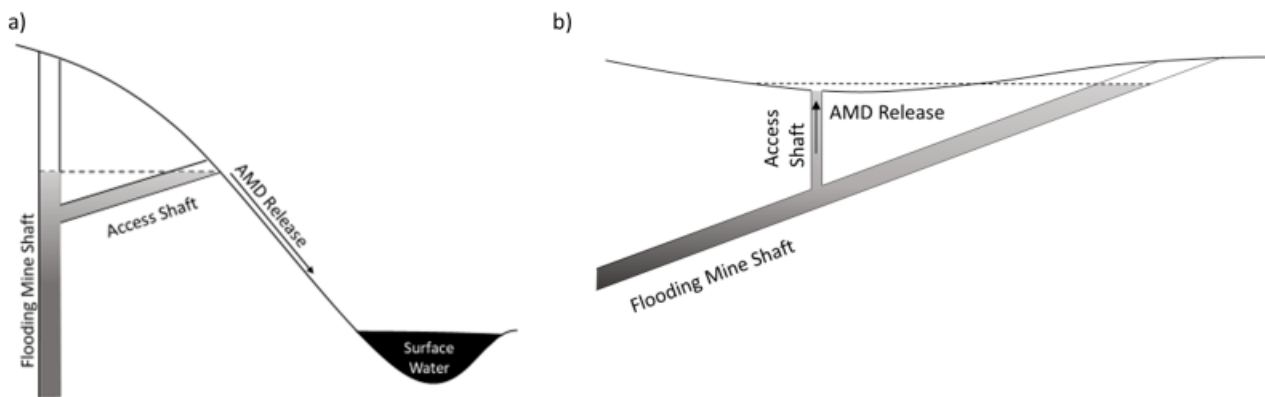
Figure 2-4: Conceptual illustration of AMD release from a) vertical shaft workings, and (b) slope-mined workings

Several strategies exist that aim to prevent and/or control AMD release from its various sources. Following the cessation of mining, workings can be rapidly flooded and kept submerged to prevent further ingress of oxygen which is essential for pyrite oxidation (Kefeni et al., 2017; Park et al., 2019), while mine tailings and waste rock piles can be sealed from the atmosphere with engineered cover systems (Power et al., 2017; 2018). Figure 2-5 outlines several preventative strategies that are used to prevent/control AMD.
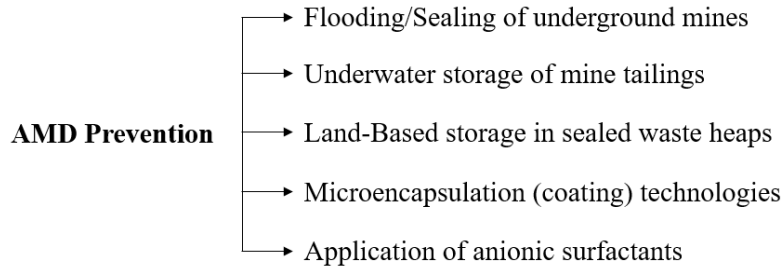
Figure 2-5: AMD prevention strategies (modified from Johnson and Hallberg, 2002)

While flooding and sealing open mine shafts is the primary method for preventing or controlling AMD from underground workings, it is extremely challenging due to the number of possible connections to the surface. Some of these connections are unknown, such as through randomly distributed bootleg mine workings (Forrester & Noble, 2010). An alternative approach is to maintain mine water elevations below expected discharge elevations. The mine water is continuously pumped from the mine pools and treated at active or passive treatment plants, which will be described below in Section 2.2.7.

2.2.6 ENVIRONMENTAL IMPACTS

AMD release to the environment can have many adverse impacts, which can be categorized into five broad categories: chemical, physical, biological, ecological, and socioeconomic (Gray, 1997; Acharya & Kharel, 2020). These impacts are summarized in Figure 2-6.
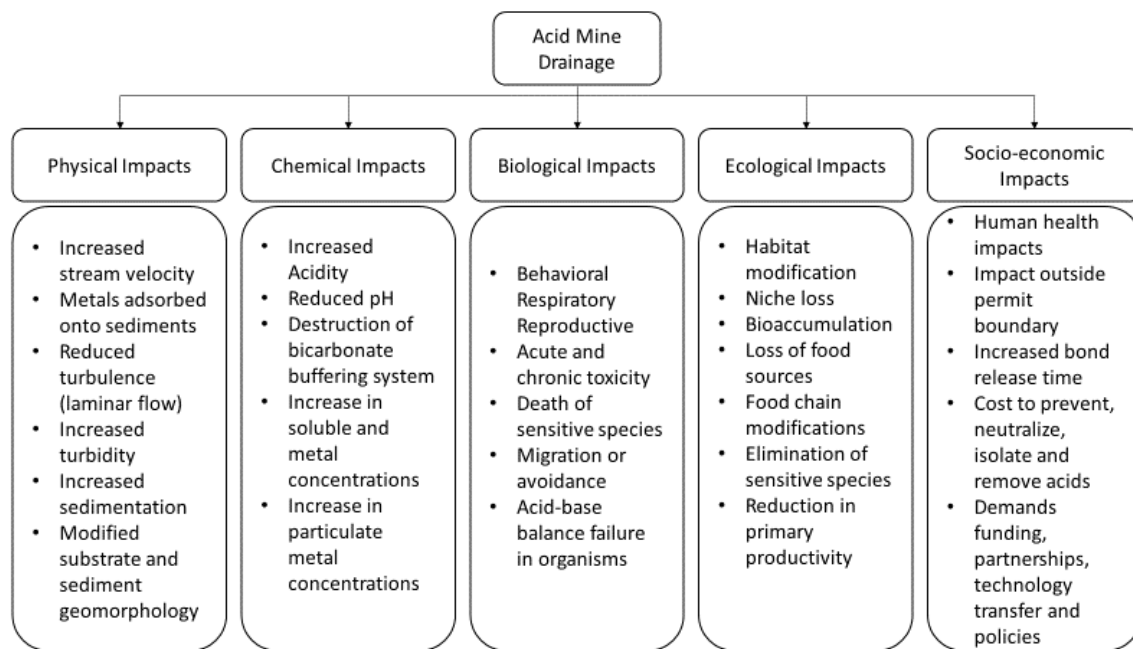
Figure 2-6: Adverse environmental impacts of AMD (modified from Acharya and Kharel, 2020)

While many impacts are listed in Figure 2-6, some impacts should be specifically highlighted, including the destruction of the bicarbonate system caused by AMD released into water bodies. Hoehn and Sizemore (1977) noted that when AMD interacted with a stream in Virginia, USA, alkalinity was almost eliminated and pH dropped significantly. Luís et al. (2011) noted a decrease in biodiversity, with a shift towards microorganisms more tolerant of the acidic conditions found in AMD impacted streams. Brake et al. (2001) also noticed the complete absence of macroscopic life in the Little Sugar Creek in Indiana, USA, after it was impacted with AMD.

The precipitation and sedimentation of iron (III) hydroxide ($Fe(OH)_3$), often referred to as Yellow Boy, is also known to harm aquatic life via toxicity and the smothering of benthic organisms (Hoehn & Sizemore, 1977; Banks et al., 1997; Ojonimi et al., 2019).

2.2.7 AMD TREATMENT

Treating AMD-impacted water that is extracted from mine pools often involves the construction of dedicated treatment systems. These systems can range from small passive systems to large-scale active treatment plants (Trumm, 2010). Passive systems can utilize natural processes to provide treatment (Kaur et al., 2018), resulting in significantly lower capital and operating costs. They are

used in mine systems with low flow rates and reasonable water quality. Passive systems utilize either oxidizing or reducing conditions to treat AMD. Oxidizing systems cause iron to transition from ferrous iron to ferric iron, allowing it to precipitate out as iron hydroxide while reducing systems involve reducing iron and sulfate into pyrite (FeS_2), iron sulfate (FeS), and hydrogen sulfide (H_2S), and removing dissolved iron and sulfate species from the mine water (Trumm, 2010). Oxidizing strategies are typically open to the atmosphere and include open limestone drains, limestone leaching beds, and aerobic wetlands. Reducing strategies are typically anaerobic and include anoxic limestone drains, anaerobic wetlands, and reducing and alkalinity producing systems (RAPS).

Active systems can treat mine systems with high flow rates and poor water quality. Typical systems utilize alkalinity addition, raising the pH and allowing for the precipitation of metals (Aubé & Zinck, 2003; Cravotta, 2010) However, these systems result in high operating expenses related to purchasing alkalinity-amending material, such as lime, and the disposal of resulting sludge (Skousen et al., 2019).

While many factors need to be considered, the selection of either a passive or active system mainly depends on the mine water quality. Figure 2-7 presents a flow chart by Trumm (2010) that can be used to select the appropriate treatment type. As mine water quality can improve over time, it may be possible to transition from an active system to a passive system; however, no studies were found during this review that assessed when this transition is possible and benefits and problems associated with it.
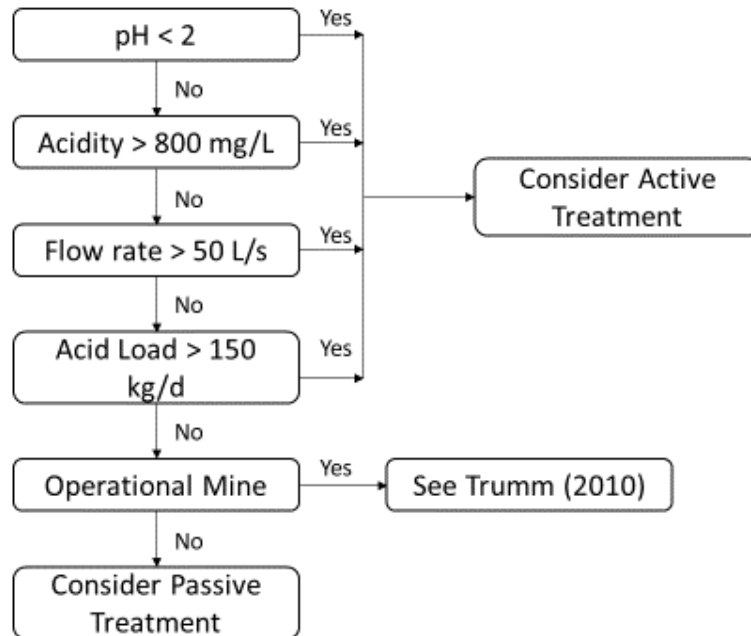
Figure 2-7: Schematic of the selection process for treatment type (adapted from Trumm, 2010)

2.3 HYDRODYNAMICS AND HYDROGEOCHEMISTRY

Due to the high complexity and unknowns in abandoned underground workings, understanding the hydraulic and hydrogeochemical processes is a major challenge. A summary of the literature relevant to these processes is provided in the following sub-sections.

2.3.1 HYDRAULIC BEHAVIOR

The flow of water through underground workings is extremely complicated. The flow can be Darcian or non-Darcian, or both in the same workings (Wolkersdorfer, 2008b). The nature of these systems allows for areas of different hydraulic conductivities, where main shafts/roadways can allow for the rapid movement of water, and collapsed gob areas can have very low hydraulic conductivity, even resulting in short-circuiting of low conductivity workings (Mack et al., 2010). This non-uniform behavior has caused many to describe mine systems as being similar to Karst-type aquifers (Younger, 2000; Elliot & Younger, 2014; Álvarez et al., 2018).

2.3.2 MINE WATER QUALITY

The quality of mine water in underground workings goes through various stages over time. During flooding, the rising mine water interacts with oxidized metal sulfides (pyrite) to generate AMD through the mechanisms discussed earlier. This leads to a significant deterioration in water quality, which is characterized by low pH, high acidity, and high concentrations of sulfate and metals such as iron, manganese, and aluminum. While the submerged workings reduce pyrite oxidation (SOURCE?), unflooded workings near the ground surface (the coal seam crop line) will continue to generate small amounts of acidity. Over time, a gradual improvement in mine water quality can occur, as first noted by Cairney and Frost (1975), and then extensively studied by Younger (2000; 2002). For instance, when the low-quality mine water is pumped from the workings, it is replaced by infiltrating surface water and groundwater, thereby flushing the workings, and gradually improving the water quality.

Younger (2000; 2002) used extensive monitoring data from numerous coal mines in the UK to investigate long-term mine water behavior and derive what is referred to as the 'First Flush' principle. This principle demonstrates that contaminant concentrations peak shortly after mine workings have flooded, and then decrease exponentially, before eventually reaching asymptotic conditions after a period equal to approximately four times the duration of the initial flooding. This can be written as:

$$t_f = (3.95 \pm 1.2)t_r \; , \qquad\qquad (2\text{-}8)$$

where t_f is the duration of the first flush, and t_r is the initial time for the workings to flood. This principle is illustrated in Figure 2-8. Younger (2002) noted that the asymptotic concentrations of certain key solutes such as iron could be estimated as between an eighth, to a tenth, of peak concentrations.
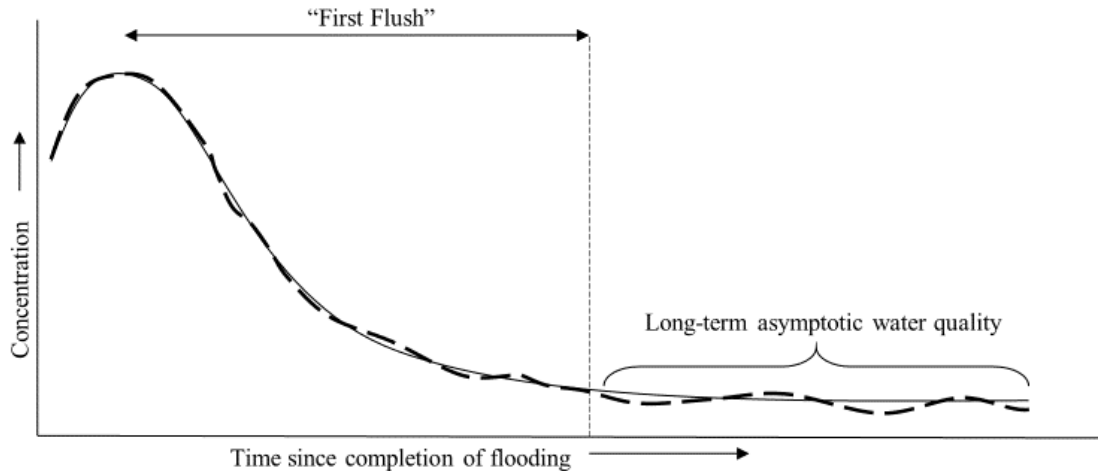
Figure 2-8: Illustration of the 'First Flush' principle (modified from Younger & Banwart, 2001)

This First Flush concept is a commonly accepted representation of the temporal evolution of mine water quality, and has been applied around the world in a wide range of scenarios, from open cast coal mines in South Africa (Huisamen & Wolkersdorfer, 2016), above- and below-drainage coal mines in West Virginia (Mack et al., 2010), and flooded underground coal mines in Poland (Gzyl & Banks, 2007).

2.3.3 MODELING MINE WATER BEHAVIOR

Several modeling approaches have been employed to represent water flow and quality within flooded mine pools. Many studies have modeled mine pools as pipe networks (e.g., Burke & Younger, 2000; Banks, 2001). Sherwood (1997) developed a lumped parameter model that defines areas of interconnected mine workings as 'ponds' that are connected through a system of pipes representing major roadways in the workings. Hamm et al. (2008) used the USEPA's EPANET, a modeling package typically used for water distribution systems, to simulate a single mine colliery (the Saizerais iron mine in France) as a series of pipes. Rapantova et al. (2007) utilized FEFLOW, a software package designed to model fluid flow, contaminant transport, and heat transport processes in the subsurface to simulate mine water flow through the Olsi-Drahonin uranium mine in the Czech Republic. This model assumed recharge only occurred through precipitation. Betrie et al. (2014) employed the geochemical model, PHREEQC, to simulate ion and anion concentrations that are produced through pyrite oxidation, while Croxford et al. (2004) used PHREEQC to determine alkali dosing rates and for quantifying sludge volume production

necessary for designing treatment schemes. Winters and Capo (2004) integrated groundwater flow equations with a GIS-based model to determine residence time and recharge rates; however, this type of approach has limited application due to the non-Darcian nature in realistic, complex mine pools (Younger, 2016).

Empirical models of mine water behavior can be the most appropriate approach for complex mine workings, as they are based on actual measurements and trends of water quality. Gzyl and Banks (2007) investigated extensive data that was collected over time from two flooded sections at the Siersza mine in Poland, confirming that mine water quality was following the First Flush principle. Exponential curves were fitted to sulfate measurements to predict the time it would take to reach 90% completion of the first flush (assuming $t_{90} \approx t_f$ from Eq. (2-8)), and the following equation was developed:

$$C = C_v * \exp(m * t) + C_b \,, \tag{2-9}$$

where C_v is the peak, or in this case, the initial concentration at $t=0$, C_b is the background (asymptotic) concentration, which was estimated as 90% of C_v, and t is time. It should be noted that this equation starts at the peak concentration of the 'First Flush' curve and only models the subsequent decay over time.

Gzyl and Banks (2007) estimated that it would take approximately 10-20 times the initial flood time (t_r) to reach asymptotic concentrations, which far exceeds that of Younger (2000; 2002) who predicted four times. This discrepancy in the flushing time may be due to several factors, such as whether the inflow rate is dependent on the hydraulic head difference between the workings and the surrounding groundwater table. Gzyl and Banks (2007) suggest that if inflow is not head-dependent, then the flushing time may be lower, and if the inflow is head-dependent, then it will be greater, as the head gradient will decrease as the mine floods to equilibrium. Also suggested was that higher elevation workings may cause more rapid flushing than lower elevation workings, with different exponential decay curves applicable to different depths.

A similar empirical approach was applied by Perry and Rauch (2012) to five mine pools in West Virginia, USA. However, in contrast to Gzyl and Banks (2007), a two-phase model was developed with different decay constants. The first phase describes a steep, initial decline in concentration, and the second phase describes a long-term, significantly slower decline. This two-phase model is described in Eqs. (2-10a) and (2-10b):

$$C = C_{v,1} * \exp(m_1 * t) \ when \ t < t_{transition} \tag{2-10a}$$

$$C = C_{v,2} * \exp(m_2 * t) \ when \ t \geq t_{transition}, \tag{2-10b}$$

where $C_{v,1}$ is the initial (peak) concentration, $C_{v,2}$ is the concentration at the transition between the first and second slopes, m_1 is the initial steeper slope, m_2 is the long-term, shallower slope, $t_{transition}$ is the time where the model changes from the first phase to the second phase, and t is time. Perry and Rauch also developed a simpler single-phase exponential model of the form:

$$C = C_v * \exp(m * t), \tag{2-11}$$

where C_v is the initial concentration at $t=0$, m is the slope, and t is time. The Perry and Rauch (2012) model did not consider the long-term asymptotic water quality suggested by Younger (2000; 2002) and Gzyl and Banks (2007). Also, each of the parameters studied (e.g., total acidity, iron, aluminum, sulfate, and total dissolved solids) had different decay rates (Perry & Rauch, 2012). The decay rate may not only be dependant on chemical conditions, but also on physical conditions, such as whether the workings are completely flooded, or how effectively the mine pool is flushed.

2.3.4 MINE WATER STRATIFICATION

Flooded underground mine workings can contain large bodies of stagnant water (Adams & Younger, 2001). The stagnancy of these bodies commonly leads to the development of stratification within the workings, where water quality decreases with depth, with better quality water layered above poorer quality water (e.g., Ladwig et al., 1984; Younger et al., 2001; Nuttall & Younger, 2004; Chudy et al., 2020).

Mine water stratification has been observed by many studies, with stratification frequently developing in systems with vertical shafts and remaining stratified for long periods when left undisturbed (Wolkersdorfer, 2008a; Zeman et al., 2008). However, stratification can be destroyed, such as when the shafts are pumped and causing agitation within the previously stagnant water (Nuttall & Younger, 2004; Wolkersdorfer et al., 2016). It should be noted however, that stratification will typically redevelop after pumping has ceased.

The aforementioned studies have all examined vertical-shaft mine systems, where the shafts behave similarly to water columns. Few, if any, studies have looked at the development of stratification in mines that have inclined adits instead of vertical shafts, such as the collieries within the Sydney Coalfield in Nova Scotia, Canada (Kwong et al., 2006; Shea, 2009). Wolkersdorfer et al. (2016) briefly discuss the presence of stratification in the 1B Mine Pool in the Sydney Coalfield. CBCL (2017) noted that the Gowrie mine in the same coalfield had shown the presence of stratification in 1912, which was just 11 years after flooding. No studies exist that assess the stability of stratification in these inclined adits, and how they differ from the vertical-shaft systems, where studies are more plentiful.

2.4 THE SYDNEY COALFIELD

2.4.1 HISTORY

The Sydney Coalfield is located on Cape Breton Island in Nova Scotia, Canada. It was formed approximately 300 million years ago during the Pennsylvanian Age and is composed almost entirely of bituminous coal with a total sulfur content estimated between ~2.5 to 6% (Hacquebard, 1993; Zodrow, 2005)

Figure 2-9: Site maps showing the location of the Sydney Coalfield in Nova Scotia, Canada

The first organized coal mining occurred in the 1720s to supply fuel for the construction of the nearby Louisbourg Fortress. Following the conclusion of the Seven Years War (1756-1763), Britain claimed ownership of Cape Breton, and from 1826-1850, the mineral rights were leased to the General Mining Association (GMA). In 1857, the GMA returned the mineral rights to the Province of Nova Scotia, who in the 1890s, sold much of them to the newly formed Dominion Coal Company, and several smaller mining outfits. Mining continued heavily until the mid-1940s when demand for coal began to decline. In 1967, the operation of all mines was taken over by the Cape Breton Development Corporation (CBDC, or DEVCO), a crown corporation established to manage the remaining active mines, phase out coal mining, and develop new economic

opportunities (Parsons et al., 2012). However, this approach changed during the energy crisis of the 1970s where rising oil prices resulted in a heavier, albeit temporary, investment in coal.

In 1987, the Enterprise Cape Breton Corporation (ECBC) was formed to broaden the economy of the island and reduce dependence on the coal industry (Jackson, 2003), and the last mine closed in 2001. CBDC was officially dissolved in 2009, with all assets and liabilities transferred to the ECBC (Ayers, 2010). In 2014, ECBC was dissolved, and its responsibilities were assumed by the Atlantic Canada Opportunity Agency (ACOA), except for remediation efforts, which were assumed by Public Services and Procurement Canada (PSPC) (King, 2014).

2.4.1.1   COALFIELD DESCRIPTION

During almost 300 years of active mining, over 2.4 billion tonnes of coal from 11 different seams were extracted from the coalfield and sold to market (Shea, 2008). The result was ~2500 square kilometers of underground mine workings starting from the coastal communities along the north-eastern part of the island and extending out below the Atlantic Ocean. The outlines of these workings are shown in Figure 1-10.
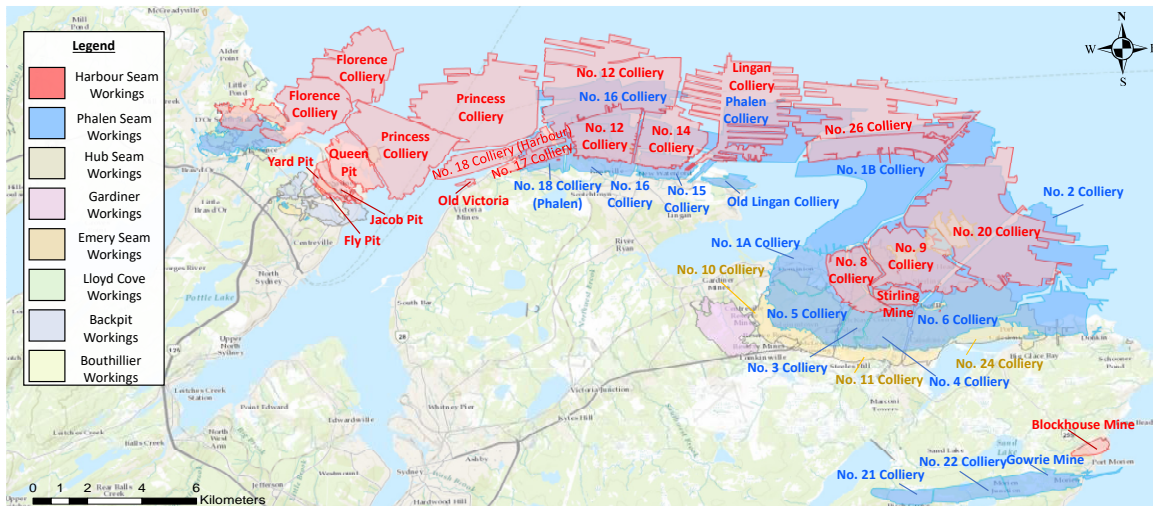
Figure 2-10: Map of the Sydney Coalfield showing outlines of the three largest mine pools – New Waterford (NW), Sydney Mines (SM), and 1B – and surrounding workings

25

Many of these workings are hydraulically interconnected, sometimes even between separate coal seams. This has created several larger 'mine pools', each consisting of multiple interconnected collieries. Three of these mine pools – New Waterford (NW), Sydney Mines (SM), and 1B – represent the largest collections of interconnected workings in the coalfield. A total of ~450 million tonnes of coal was extracted, leaving behind ~190 million cubic meters of void space that is available for AMD generation. Table 1-1 lists these major mine pools and their associated collieries.

Table 2-1: Major mine pools in the Sydney Coalfield and their associated collieries

Mine Pool	Collieries
New Waterford	• Dominion No. 12 • Dominion No. 14 • Dominion No. 16
Sydney Mines	• Princess • Florence • Queen Pit
1B	• Lingan Colliery • Phalen Colliery • Dominion No. 1A, 1B, 2, 5, 9, 10, 20, 26

Following the cessation of mining in 2001, CBDC (and later, ECBC) in partnership with Public Works and Government Services Canada (PGWSC was later renamed to Public Services and Procurement Canada, or PSPC as mentioned above) initiated the Former Mine Site Closure Program worth approximately $140 million. This program was meant to rehabilitate the over 700 properties and 1000 square kilometers associated with or impacted by previous mining activities. This included covering waste rock piles and dealing with mine water discharge, erosion, soil contamination, mine openings, and various impacts to ground and surface water (ECBC, 2013). Part of this remediation effort was the construction of the New Victoria mine water treatment plant in late 2012.

2.4.1.2   NEW VICTORIA TREATMENT PLANT

In 2005, boreholes were drilled into the flooded shafts of the NW and SM mine pools to measure the water levels. In 2008, additional boreholes were drilled into the Dominion No. 12/14 and No. 16 collieries within the NW mine pool. Water levels measured in these boreholes indicated that the mine water would soon reach discharge elevations and AMD would escape to the environment. To buy more time, the Dominion No. 12/14 and No. 16 workings were connected via a borehole, which allowed Dominion No. 16 to flood with the rising water from Dominion No. 12. This connection, which is illustrated in Figure 2-11, provided the owner, PSPC, more time to design and construct a new treatment plant and manage the mine water levels below discharge elevations.
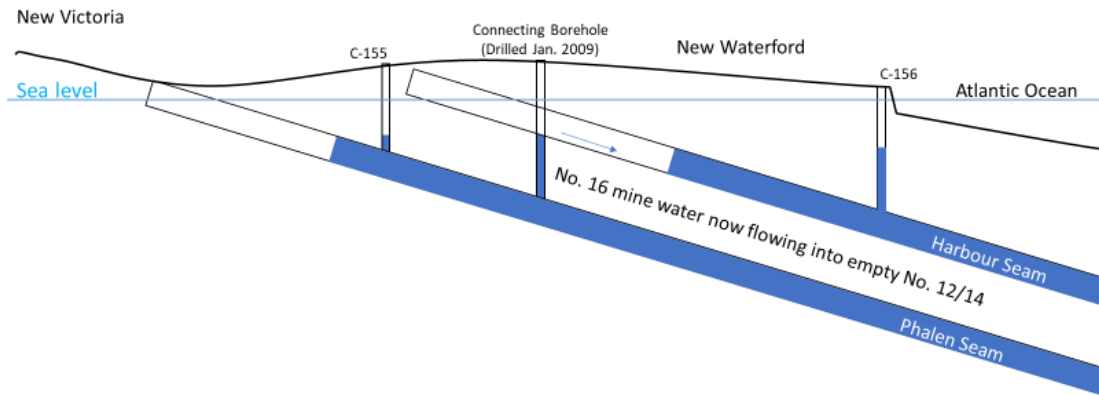
Figure 2-11: Cross-section showing the connection between the No. 12/14 and No. 16 workings (modified from Shea, 2012)

During the design process, several treatment schemes were considered. The first major design option involved constructing a treatment plant for each of the NW and SM mine pools, located on opposite sides of the Sydney Harbor, while the second option involved treating both mine pools from one treatment plant. For the second option, additional scenarios were considered, including the location of the combined treatment plant, and strategies to make connections from each mine pool to the combined plant.

At the conclusion of the design process, the combined treatment scheme was selected, with a single treatment plant constructed in New Victoria. The treatment plant would include a high-density sludge (HDS) system utilizing aeration, hydrated lime dosing for alkalinity addition, and a settling pond and reed bed for polishing. The location of the combined treatment plant in New Victoria,

along with a conceptual cross-section is shown in Figure 2-12. The treatment plant was designed to allow for a peak flow of 500 US gallons per minute (GPM).
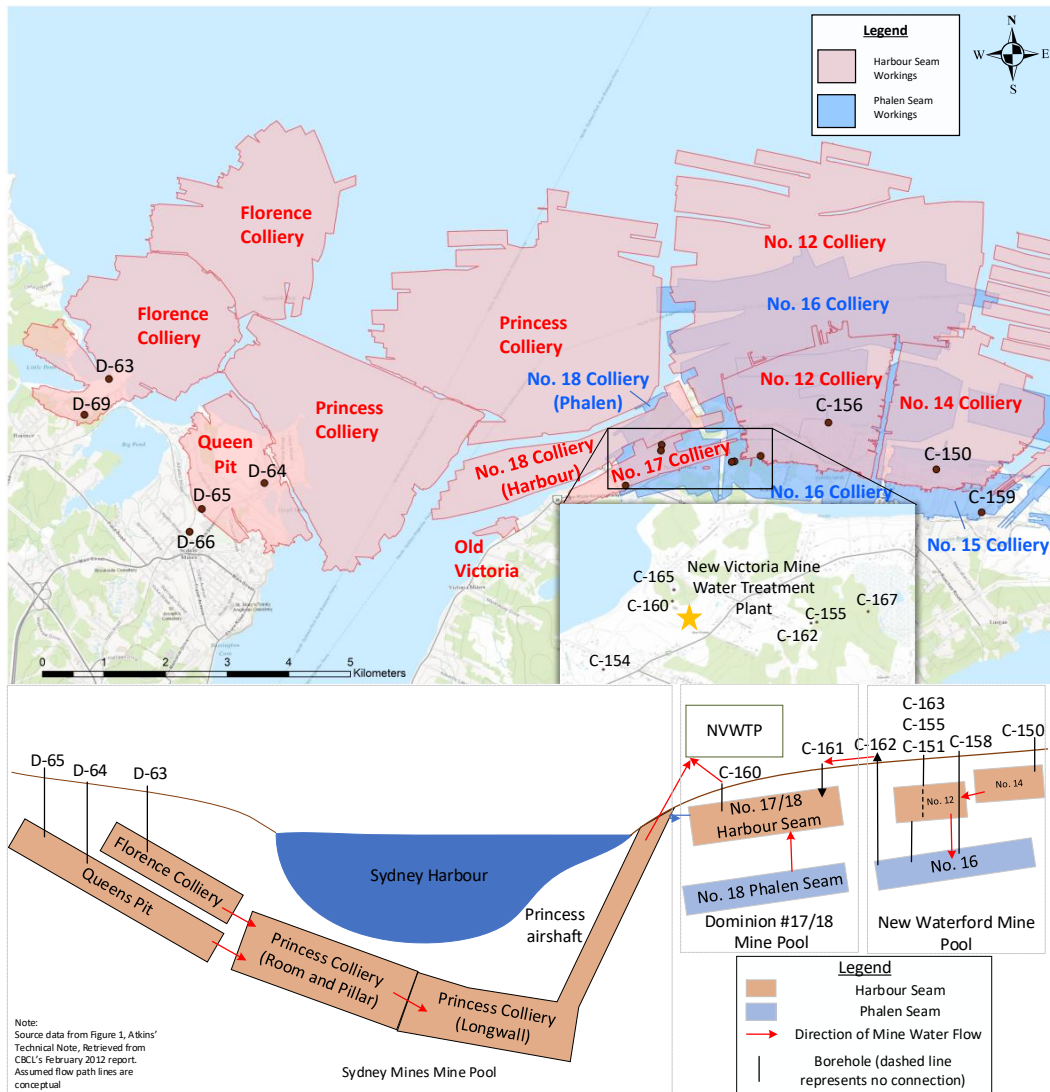
Figure 2-12: Site map of the New Waterford and Sydney Mines mine pools with a conceptual cross-section, indicating the location of the New Victoria mine water treatment plant

The placement of this combined treatment plant required the utilization of several boreholes and the complicated interconnection of the Dominion No. 17/18 and Dominion No. 12/14 workings to affect the entire NW mine pool. The SM mine pool system is more straightforward than the NW mine pool, allowing for the entire system to be treated from an underground tunnel that connects the SM mine pool to the area around the treatment plant.

Figure 2-13: Aerial view of the New Victoria mine water treatment plant

In 2018, PSPC hired an environmental consultancy firm (CBCL Limited) to evaluate the current performance of the treatment plant and estimate future O&M costs, as well as predicted capital expenditures. The resulting liability estimate report found that while the plant had been designed for a modified acidity loading of 10,400 mg/L, the plant is not able to meet that requirement due to higher than expected lime consumption and issues with lime dosing equipment not meeting required rates (CBCL, 2018). Despite this, the New Victoria treatment plant is still meeting current treatment objectives.

2.5   SUMMARY & DATA GAPS

This chapter outlined the generation, treatment, and environmental impacts of AMD, several First Flush modeling approaches used in the design of mine water treatment infrastructure, and the complex hydrogeological processes they approximate.   While the treatment and modeling of complex mine systems have been studied in detail, there is still significant uncertainty when it comes to forecasting contaminant loading due to the complex, interconnected nature of large mine pools and the inherent difficulty in tracking the flow of water through underground systems. Several empirical models of mine water quality over time have accurately represented temporal mine water evolution at specific mines; however, these models have not been compared, and there have been few if any, studies on their application to coalfields other than where they were developed.

There is a need to compare the effectiveness of different modeling approaches for forecasting contaminant concentrations over time and their application to predicting the future performance of mine water treatment systems. Chapter 3 of this thesis presents a study focused on the New Victoria mine water treatment plant in the Sydney Coalfield in Nova Scotia, Canada, and the two mine pools that it manages. Three empirical models are applied to sampling data from the treatment plant, as well as the wider Sydney Coalfield. Following detailed comparisons of each model, the most appropriate model was then used to estimate the evolution of mine water quality and predict future plant operational and maintenance expenses.

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3 ASSESSING THE EVOLUTION OF MINE WATER QUALITY WITH EMPIRICAL 'FIRST-FLUSH' MODELS

3.1 INTRODUCTION

Environmental contamination by acid mine drainage (AMD) from abandoned underground coal mine workings remains a major and persistent problem worldwide. Upon the cessation of mining activities and closure of the colliery, the de-watering pumps are turned off and groundwater rebound occurs, gradually flooding the open workings (e.g., Gandy & Younger, 2007; Álvarez et al., 2018). The rising mine water and oxygen in the void space interact with the exposed metal sulfides (often pyrite, FeS_2), causing a complex sequence of oxidation-reduction reactions that generate AMD (Nordstrom et al., 2015; Acharya & Kharel, 2020). Characterized by low pH and high concentrations of acidity, sulfate, heavy metals and other toxic elements (INAP, 2014), AMD emanating from abandoned workings can severely impact environmental receptors such as streams, rivers, and aquifers (e.g., Luís et al., 2011; Ojonimi et al., 2019).

AMD is released to the environment when the mine water elevation inside the workings rises to that of possible discharge points (Adams & Younger, 2001). While sealing of the open workings is usually the most desirable method for preventing and/or controlling AMD release, it is highly challenging. A large number of natural and man-made hydraulic connections can exist between the workings and the surface, including outcrops, air shafts, and discovered and/or undiscovered bootleg workings (e.g., Forrester & Noble, 2010; MacLeod, 2010). An alternative approach is to maintain mine water elevations below that of discharge points by continuously pumping mine water out of the workings and into treatment plants constructed specifically over the workings (e.g., Johnston et al., 2008; Wolkersdorfer, 2011).

Mine water treatment plants can be passive or active, depending on the quality of the mine water influent and pumping rate to achieve target water elevations (Trumm, 2010). Passive systems, which use sulfate-reducing bacteria or limestone, or both, to neutralize acidity and precipitate metals, are relatively low-cost but are limited to low contaminant loadings (Park et al., 2019; Skousen et al., 2019). Active systems use power and chemical additives (e.g., hydrated lime) to manage much higher contaminant loadings, but are much more expensive (e.g., Aubé & Zinck, 2003; Cravotta, 2010; Skousen et al., 2019).

Understanding and modeling the behavior and evolution of mine water quality over time in flooded workings can provide valuable insight to assist the design and long-term operation, cost, and lifespan of a mine water treatment plant. However, accurate understanding and modeling of mine workings is highly challenging. The nature of underground workings, which are known for their large extent and depth, naturally creates a complex and heterogenous network of intersecting mine tunnels, which have the potential to collapse, further complicating the system(Mack et al., 2010; Wolkersdorfer, 2008). The complicated nature of these systems has often led to them being described as karstic aquifers (Younger, 2000; Elliot & Younger, 2014; Álvarez et al., 2018).

Models for predicting water quality in flooded mine workings can be divided broadly into two categories: (i) numerical models that simulate the hydraulic and geochemical processes (e.g., Hamm et al., 2008), and (ii) field-study based empirical models designed to forecast mine water quality based on curve fitting real-world data (Wolkersdorfer, 2008). Numerical models have been used to simulate mine water behavior (e.g., Vandenberg et al., 2016; Kuchovský et al., 2017; Tomiyama et al., 2020), but they can be oversimplified. For example, workings have been represented by homogeneous pipe networks or ponds (e.g., Banks, 2001; Hamm et al., 2008; González-Quirós & Fernández-Álvarez, 2019), but they are not suitable for larger, complex workings. Numerical models often rely on mine plan drawings that may or may not be available, or no longer represent the true state of the mines (e.g., tunnel collapses or bootleg workings). Incredible efforts are usually needed to develop numerical models that accurately represent these systems.

Empirical models have been developed by observing and analyzing decades of historical mine water quality and trends from minefields worldwide. While they are simpler, in many cases they are equally, or more, representative of mine water behavior than highly complex numerical models while requiring significantly less investment (Younger, 2016). The quality of mine water in mine workings is generally understood to improve over time (Banks et al., 1997; Wood et al., 1999; Demchak et al., 2004; Moore, 2019). When low-quality mine water is extracted from the workings, it is replaced by infiltrating surface water and recharging groundwater, thereby flushing the workings and gradually improving water quality over time. Younger (2000) examined the long-term behavior of mine water in numerous coal mines in the UK and derived what is referred to as the 'first-flush' phenomenon, where contaminant concentrations peak shortly after flooding and

then decrease exponentially, before eventually reaching asymptotic conditions. This phenomenon has described evolving mine water quality in flooded mine workings worldwide, including the USA (Mack et al., 2010; Mountjoy et al., 2018), Poland (Gzyl & Banks, 2007), and South Africa (Huisamen & Wolkersdorfer, 2016).

Empirical models have been developed to represent first-flush mine water behavior. Gzyl and Banks (2007) fitted exponential curves to long-term sulfate measurements from two flooded sections at the Siersza mine in Poland and developed an empirical equation that predicts the time it would take to reach 90% completion of the 'first-flush'. Based on data from five mine pools in West Virginia, USA, Perry and Rauch (2012) proposed a two-phase model with differing decay slopes. The first phase describes a steep, initial decline in concentration, and the second phase describes a long-term, significantly slower decline. Perry and Rauch (2012) did not consider long-term asymptotic water quality suggested by Younger (2000) and Gzyl and Banks (2007). These models have been developed and validated to observed mine water quality data, but they have yet to be used for predicting future mine water quality changes associated with pumping to mine water treatment plants.

The objective of this study is to predict long-term mine water quality and associated operating expenses at an active mine water treatment plant located in the Sydney Coalfield in Nova Scotia, Canada. This study will first assess the suitability and robustness of empirical 'first-flush' models for representing the evolution of mine water quality in flooded mine workings throughout the Sydney Coalfield. The most suitable empirical model will then be applied to predict, both the future quality of mine water influent being pumped into an active treatment plant and the corresponding long-term plant operation costs.

3.2   SITE DESCRIPTION

3.2.1 THE SYDNEY COALFIELD

The Sydney Coalfield in Nova Scotia, Canada, is the oldest mined coalfield in North America, with underground mining occurring from the early 1700s to the early 2000s. Mining of the coalfield, which is composed almost entirely of bituminous coal with a total sulfur content estimated between ~2.5 to 6% (Hacquebard, 1993; Zodrow, 2005), produced over 2.4 billion tonnes of coal from more than 50 underground collieries across 11 coal seams (Shea, 2009). Figure 3-1 shows the location of the Sydney Coalfield in Nova Scotia and outlines the key mining collieries.
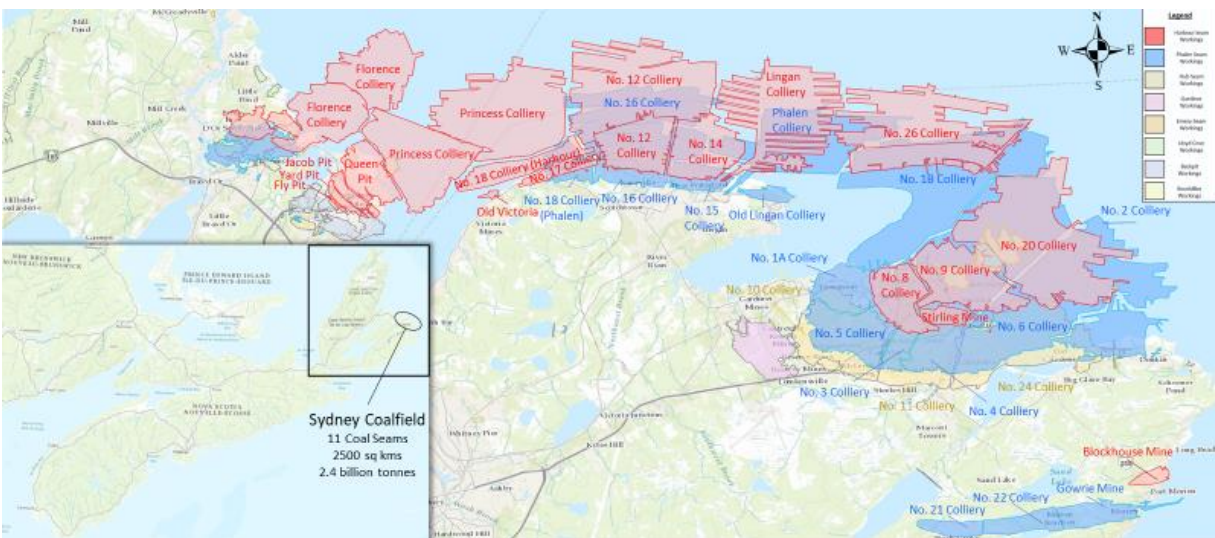
Figure 3-1: Site maps indicating the location of the Sydney Coalfield and outlines of the key collieries

The long history of mining left behind a complex network of underground workings spanning approximately 2500 square kilometers. When the mining activities ceased, the dewatering pumps were turned off and the workings gradually flooded (i.e., mine water rebound) (Gandy & Younger, 2007). Many of these workings are hydraulically interconnected, creating several 'mine pools' that consist of multiple connected collieries. The three largest mine pools – Sydney Mines (SM), New Waterford (NW), and 1B – contain workings that produced 450 million tonnes of extracted coal and left 190 million cubic meters of interconnected void space. Flooding of these workings resulted in AMD-impacted mine water that can be released to the environment when its elevation reaches that of discharge points.

3.2.2 NEW VICTORIA TREATMENT PLANT

In 2001, after mining activities had ceased, a multi-million-dollar mine site closure and reclamation program of the Sydney Coalfield was implemented by Public Services and Procurement Canada (PSPC) (ECBC, 2013). Part of this program was dedicated to the management of mine water and the prevention of AMD release from flooded mine workings. Two treatment plants were constructed: a passive system at Neville Street for the 1B mine pool, and an active system for the SM and NW mine pools.

The active treatment plant was designed and constructed at New Victoria (NV) to manage and treat mine water from both SM and NW mine pools. Figure 3-2(a) presents a site map of the SM and NW mine pools, associated collieries, and the location of the NV plant. The SM mine pool contains the Princess, Florence, and Queen Pit collieries, and was connected to the plant via an underground tunnel. The NW mine pool contains the Dominion No. 12, No. 14, and No.16 collieries, and required various boreholes and interconnections to allow mine water to be pumped from the entire mine pool. Figure 3-2(b) presents a schematic of the various collieries, interconnections, and mine water flow pathways from the mine pools to the treatment plant.

A borehole was drilled into a mine shaft in each of the SM and NW mine pools: the SM borehole (C-165) was drilled into an old airshaft tunnel at 127 feet below sea level (ft bsl), which connects to the SM mine pool at a depth of 1318 ft bsl, while the NW borehole (C-160) was drilled to 385 ft bsl into the No.17 colliery. These boreholes are indicated in the schematic in Figure 3-2(b). A dedicated pump house was constructed, and each borehole was instrumented with a large mechanical pump to extract the water for treatment. The desired elevation ranges for the mine water were determined from expected discharge elevations and recharge rates and were used to control operations at the NV treatment plant.
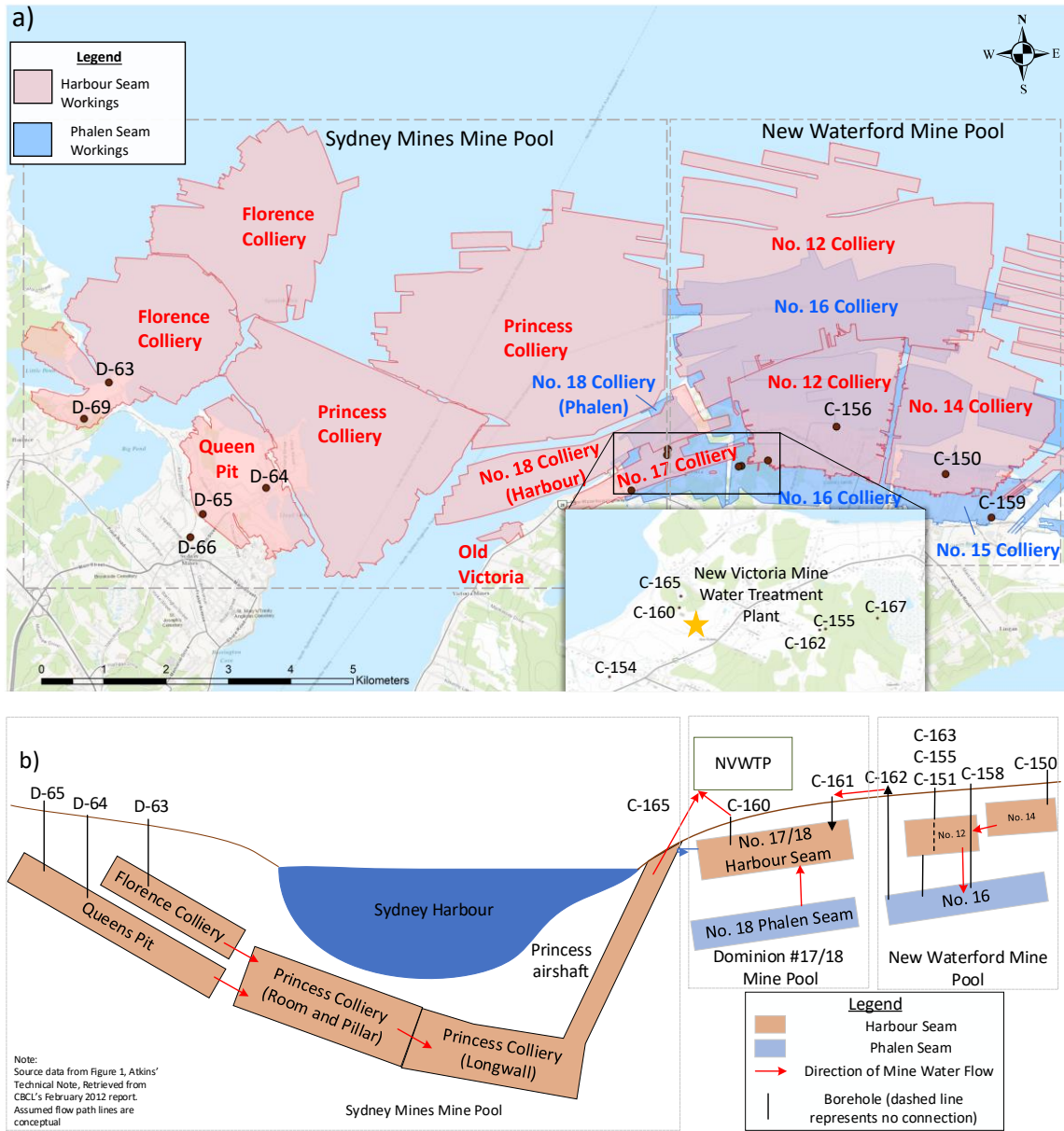
Figure 3-2: (a) site map of the New Waterford (NW) and Sydney Mines (SM) mine pools, indicating the location of the New Victoria treatment plant, and (b) conceptual cross-section showing the complex interconnections within both mine pools

The NV treatment plant includes a high-density sludge (HDS) system utilizing aeration, hydrated lime dosing for alkalinity addition, and a settling pond and reed bed for polishing. Following treatment, the treated water is discharged to the ocean, while the generated sludge is placed in large geotextile sludge bags (geobags) for compression and dewatering and placed in a dedicated landfill adjacent to the plant. An aerial photograph of the treatment plant is shown in Figure 3-3(a). The

treatment plant was designed for a peak pump rate of 500 US gallons per minute (GPM). Monitoring wells in the SM and NW mine pools are instrumented with water level loggers that are powered full-time and connected to the treatment plant to continuously indicate the mine water elevations in real-time. The plant is operated to ensure that the mine water elevations remain below potential discharge elevations.
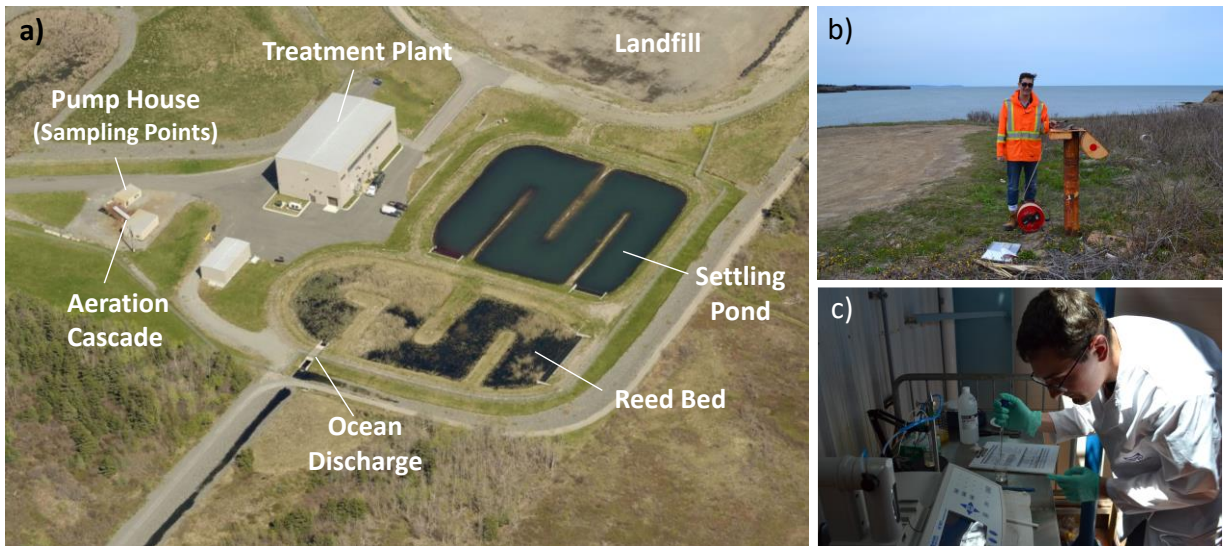
Figure 3-3: (a) aerial view of the New Victoria treatment plant, (b) mine water analysis at the 'in-house' laboratory, and (c) collection of mine water samples from Well D-63 in the SM mine pool

3.3 METHODS

3.3.1 SAMPLE COLLECTION

Over the past 20 years, many monitoring wells have been installed into the various collieries across the coalfield. Mine water levels and water samples (for geochemical analysis) were collected from these monitoring wells at various times and frequencies, with a summary provided in Table 3-1. This sampling data was collected across the Sydney Coalfield by various environmental consultancy firms (e.g., CBCL Limited and EXP) and submitted to PSPC to support their management of mine water across the coalfield. For instance, in 2008, boreholes were drilled into the mine shafts of the various collieries of the SM and NW mine pools and indicated that the mine water would soon reach discharge elevations and AMD would release to environmental receptors and adjacent coastal communities. This led to the design and construction of the NV treatment plant, which was fully operational by 2012.

Table 3-1: Summary of the monitoring wells and sampling throughout the Sydney Coalfield

Mine Pool	Colliery	Year Closed	Year Flooded	Monitoring Wells	Number of Samples	Earliest Sample (yyyy-mm-dd)	Latest Sample (yyyy-mm-dd)
NW	Dom No. 12	1973	2011	4	8	2008-09-04	2019-07-29
NW	Dom No. 14	1973	2011	2	9	2010-03-12	2019-10-30
NW	Dom No. 16	1962	2009	4	66	2008-04-28	2019-08-19
NW	Dom No. 17	1921	1972	3	68	2005-02-21	2017-12-18
NW	Dom No. 18	1921	1972	1	4	2005-02-10	2012-09-08
NW	NV plant	-	-	1	184	2011-01-19	2020-08-19
SM	NV plant	-	-	1	144	2014-03-06	2020-08-19
SM	Queen Pit	1917	2014	2	12	2009-05-05	2017-12-19
SM	Florence Colliery	1961	2014	3	17	2011-08-30	2019-03-15
1B	Dom 10 & 11	1949	1955	1	6	2008-05-22	2017-12-01
1B	Dom No. 1A	Unknown	2003	6	60	2003-11-24	2017-11-30
1B	Dom No. 2	Unknown	2003	1	4	2010-04-14	2016-11-21
1B	Dom No. 24	1953	1981	1	2	2008-09-23	2017-12-04
1B	Dom No. 5	Unknown	2003	7	106	2003-04-08	2017-11-28
-	Dom No. 8	1914	1917	3	6	2007-03-12	2017-12-01
1B	Dom No. 9	Unknown	2003	1	4	2012-12-19	2017-06-12
Neville Street Wellfield (1B)	Dom No. 5	Unknown	2003	9	127	2003-02-21	2018-01-24
-	Four Star	1969	1970	1	3	2009-06-26	2016-11-23
-	Blockhouse	1888	1890	1	10	2009-06-25	2017-12-11
-	Gowire	1897	1901	1	12	2009-06-25	2017-12-07
Dom No. 21/22	Dom No. 21	1925	1926	2	23	2009-06-25	2017-12-08
Dom No. 21/22	Dom No. 22	1930	1931	3	36	2009-05-15	2017-12-08
-	Dom No. 15	1925	1931	1	6	2009-05-05	2017-12-18

Since the start of operations at the NV plant in 2012, bi-weekly samples of the mine water being extracted from the SM and NW mine pools and pumped to the plant have been collected and geochemically analyzed. This high-frequency data can be used to monitor the evolution of mine water quality entering the plant over time. During the summer of 2019, a small mine water analysis laboratory was established at the NV plant to allow real-time monitoring of mine water quality entering the plant. Samples of mine water from each mine pool were collected inside the pump house by opening a valve on each borehole pipe. As part of this study between May and August,a total of 52 samples were collected from each of the boreholes in the SM and NW mine pools. Forty-two samples were also collected from the No.16 colliery through the borehole C-162 drilled 456 ft bsl into the NW mine pool (see Figure 3-2(b)). A summary of the sampling conducted specifically from these boreholes is presented in Table 3-2.

Table 3-2: Summary of sampling of mine water influent to the New Victoria treatment plant

Sampling Period	Mine Pool Influent	Sampling Frequency	No. of Samples	Geochemical Parameters
2012 - Present	New Waterford	Bi-weekly	184	RCAp-MS (e.g., pH, standard acidity, modified acidity, alkalinity, all metals, electrical conductivity (EC))
	Sydney Mines		44	
2019 (May to August)	New Waterford	Daily	52 (No.17), 42 (No.16)	pH, EC, standard acidity, modified acidity, alkalinity, chloride
	Sydney Mines		52	

3.3.2 SAMPLE ANALYSIS

Most samples that were collected outside of the daily sampling period between May and August 2019 were analyzed by Bureau Veritas (formerly Maxxam Analytics), who are a leading provider of analytical services in North America. All samples underwent a general water chemistry analysis (Rapid Chemical Analysis package plus metals scan, RCAp-MS), determining a range of parameters such as pH, modified acidity, standard acidity, alkalinity, electrical conductivity (EC), sulfate, chloride, and metals (total and dissolved). The geochemical parameters that best characterize AMD-impacted water include modified acidity, alkalinity, pH, sulfate, and the key metals: iron (Fe), aluminum (Al), and manganese (Mn).

For the daily, real-time sampling conducted between May and August 2019, a small laboratory was created at the NV treatment plant to examine modified acidity, standard acidity, alkalinity, pH, EC, and chloride. Modified acidity, standard acidity, alkalinity, and chloride were analyzed by following the Standard Methods 2310.4a, 2310.4d, 2320.4c, and 4500-Cl$^-$, respectively (APHA, 1999). An HI-901C1 automatic titrator (Hanna Instruments, Canada) performed all necessary titration calculations for modified acidity, standard acidity, and alkalinity, while a YSI Professional Plus multiparameter meter was used to determine pH, EC, salinity, dissolved oxygen (DO), and oxygen reduction potential (ORP). To confirm the accuracy of the new laboratory, duplicate samples were analyzed by Bureau Veritas and compared with the in-house calculations. The results of this comparison are presented in Appendix A and Appendix B, while a detailed overview of the analysis methodology is presented in Appendix E.

Modified acidity is one of the key parameters used to characterize the mine water in this study. Since many historical samples were not examined for modified acidity, an estimate of this acidity can be obtained from pH and the sum of the milliequivalents of the dissolved metals as follows (Park et al., 2015):

$$Net\ Acidity\ = 50 * \left(2 * \frac{[Fe]}{55.85} + 3 * \frac{[Al]}{27} + 2 * \frac{[Mn]}{54.94} + 10^{(3-pH)} \right) - alkalinity\ ,\quad (3\text{-}1)$$

Where 50 is the equivalent weight of CaCO$_3$, which converts the acidity in milliequivalents per litre into milligrams per litre of CaCO$_3$ equivalent. As shown in Appendix D, the modified acidity values that were available from historical samples were compared to the corresponding calculated acidity values from Equation (3-1). Based on the strong correlation, it was evident that calculated acidity can reliably fill in for any missing modified acidity values.

3.3.3 MINE WATER QUALITY

3.3.3.1 FIRST-FLUSH IN THE SYDNEY COALFIELD

The sampling data summarized in Table 3-1 was assembled and compiled into a comprehensive historical database for detailed analysis and interpretation. As shown in Table 3-1, mine water samples were collected from various mine collieries that have flooded at significantly different

times; for example, the Gowrie mine colliery flooded in 1901 while the SM mine pool (containing the Queen Pit, Florence, and Princess collieries) flooded in 2014. The historical data were then used to examine mine water quality and its relationship to flooding time, and confirm whether mine water quality in the Sydney Coalfield workings was behaving according to Younger's 'first-flush' phenomenon, which is illustrated in Figure 3-4.
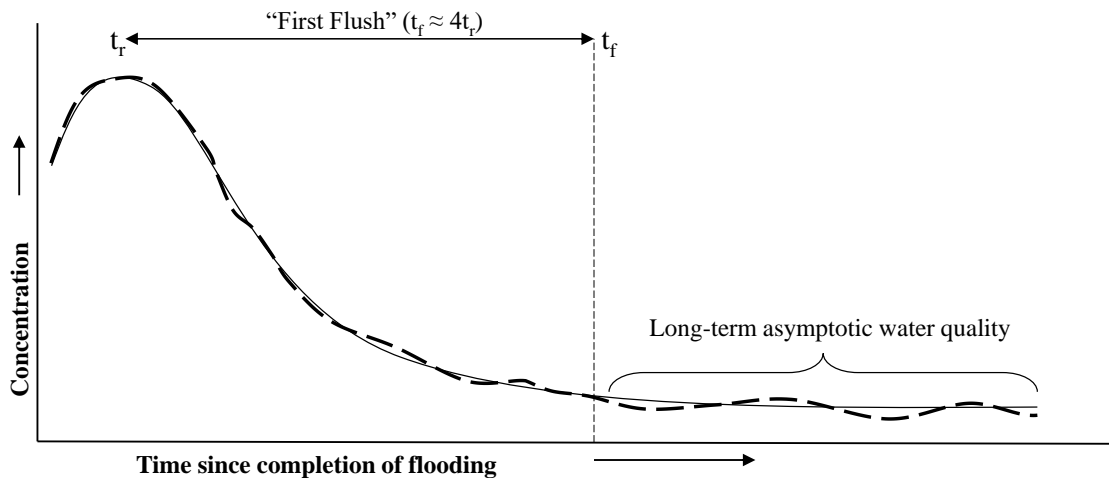
Figure 3-4: Conceptual model of the 'first-flush' that shows a peak in contaminant concentration followed by a rapid improvement leading to an eventual steady-state, asymptotic concentration. Note that t_r represents the initial time for the workings to flood, and t_f represents the duration of the first flush.

3.3.3.2 LONG-TERM PREDICTIONS

Three empirical 'first-flush' models were employed to predict the long-term mine water quality being pumped from the SM and NW mine pools. The following 'single-phase model by Gzyl and Banks (2007) is based on the exponential decay of mine water quality to a long-term asymptotic concentration:

$$C = C_v * \exp(m * t) + C_b, \tag{3-2}$$

where C_v is the peak, or in this case, the initial, concentration at $t=0$, m is the slope of the curve, t is the time, and C_b is the background (asymptotic) concentration, which is estimated as 90% of C_v. It should be noted that this equation starts at the peak concentration of the 'First Flush' curve and only models the subsequent decay over time.

Using historical data from five mine pools in West Virginia, USA, Perry and Rauch (2012) developed a similar model to Gzyl and Banks (2007) but suggested that mine water quality will continue to improve beyond asymptotic concentrations:

$$C = C_v * \exp(m * t) \tag{3-3}$$

Perry and Rauch (2012) also proposed a 'two-phase' model with differing decay constants, as shown in Equation (3-4). The first phase describes an initial rapid decline in concentration, with the second phase describing a long-term gradual decline.

$$C = C_{v,1} * \exp(m_1 * t) \; when \; t < t_{transition} \tag{3-4a}$$
$$C = C_{v,2} * \exp(m_2 * t) \; when \; t \geq t_{transition} \tag{3-4b}$$

Where $C_{v,1}$ is the initial (peak) concentration, m_1 is the initial steep slope, t is time, $C_{v,2}$ is the concentration at the transition between the first and second decay slopes, m_2 is the long-term shallow slope, and $t_{ransition}$ is the time where the model changes from the first to the second decay slope.

The application of these models to predict the long-term quality of mine water influent to the NV treatment plant first required an understanding and estimate of the peak concentrations and decay slopes. As the SM and NW mine pools had flooded at different times, thereby being at different stages along the first flush curve, sampling data from each borehole in these mine pools was combined into a composite curve. Sampling data from the NV plant was not included in this plot. Each of three empirical models (Equations 3-2 to 3-4) were then calibrated to the observed SM and NW data to determine the optimal initial (peak) concentration, decay slope values, initial year, and transition year. Sensitivity Toolbox (University of Dartmouth, New Hampshire, USA) was employed to adjust each parameter until the global root mean square (RMS) error between observed and modeled data was minimized.

3.3.3.3   MINE WATER STRATIFICATION

The existence of mine water stratification in the SM and NW mine pools was investigated by assessing the mine water quality at different depths. In the Florence colliery of the SM mine pool, two monitoring wells were screened at different depths along the same mineshaft: Well D-69 at a depth of 55.7 ft bsl and Well D-63 at a depth of 268.0 ft bsl. Similarly, in Dominion No. 12 of the NW mine pool, Well C-167 was screened at a depth of 48.5 ft bsl, and Well C-156 at a depth of 492.5 ft bsl.

3.3.3.4   TREATMENT PLANT PUMPING STRATEGY

The mine water influent samples collected daily at the NV plant were examined along with the corresponding pumping flow rates and mine water elevations. Operational controls at the plant were adjusted to generate various pumping flow rates and the corresponding mine water quality was assessed to better understand the relationship between pumping flow rate and mine water quality.

3.3.4 COSTING

Knowledge of the long-term mine water quality can be used to forecast the operational expenses that will be incurred by the NV treatment plant over time. In this study, the focus was on expenses associated with lime usage, as it is directly influenced by the quality of the mine water influent to the plant. Using data that has been collected throughout the operational period of the NV plant, a correlation can be made between lime consumption (kg) and acidity loading (kg) to the plant, which is based on the mine water acidity (mg/L) and the pumping flow rate (L/s) to the plant. The following equation was then used to estimate the cost associated with lime usage:

$$Cost\ of\ Lime\ Usage = [(Q_{SM} \times C_{SM}) + (Q_{NW} \times C_{NW})] \times \frac{M_{lime}}{M_{acidity}} \times Cost_{lime}\ , \quad (3\text{-}5)$$

where Q_{SM} and Q_{NW} are the flow rates from the SM and NW mine pools, respectively, C_{SM} and C_{NW} are the acidity concentrations in the mine water from SM and NW, respectively, $M_{lime}/M_{acidity}$ is the correlation between the mass of lime needed for the mass of acidity, and $Cost_{lime}$ is the estimated cost of lime per kg. The flow rates for SM and NW are estimated as 44% and 56% of the total flow rate going into the plant, which is assumed to be 400 USGPM (based on the average

historical flow rate), while the cost of lime is taken as $500/kg (estimate provided by historical costs of lime at the plant). Equation (3-6) was applied to the predicted mine water acidity concentrations to provide projected lime usage costs over the long term.

3.4 RESULTS AND DISCUSSION

3.4.1 FIRST-FLUSH BEHAVIOR

3.4.1.1 THE SYDNEY COALFIELD

Mine water samples collected from the various collieries in the Sydney Coalfield in 2017 were analyzed for key AMD parameters. The modified acidity, iron, and sulfate concentrations for each colliery sample were plotted against the number of years that the corresponding colliery has been flooded, as shown in Figure 3-5. A black polyline is superimposed on each plot to indicate the approximate evolution of mine water quality. It is evident from all three parameters that mine water behavior in the Sydney Coalfield can be reliably described by the 'first flush' phenomenon (Younger, 2000).
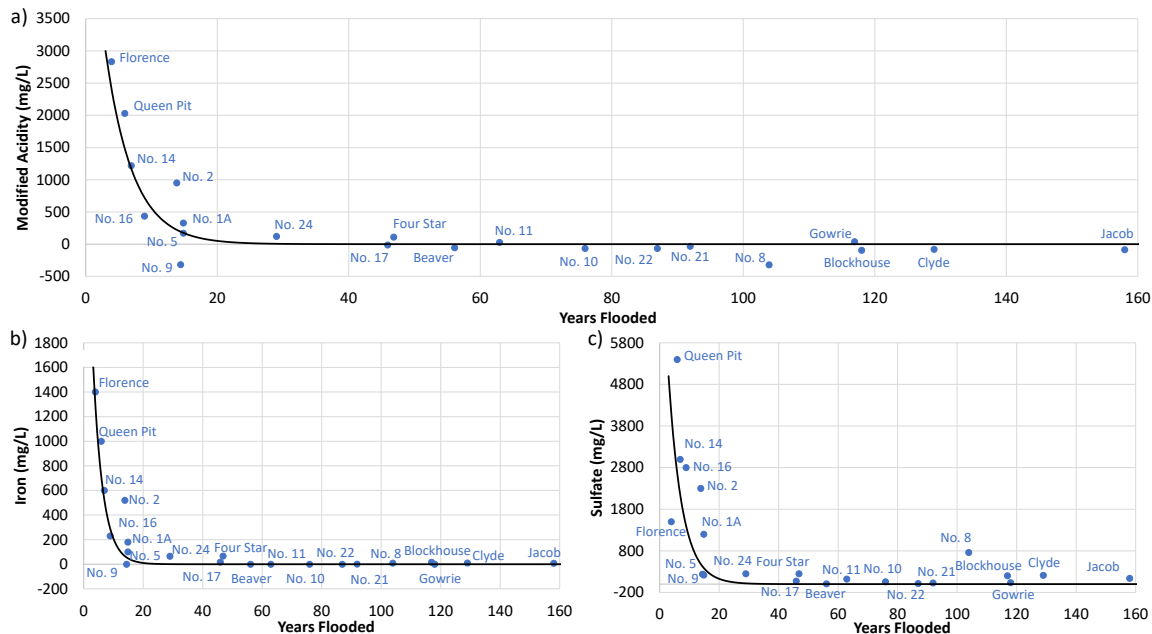
Figure 3-5: Mine water quality of each colliery sample versus the number of years that the colliery has been flooded for (a) modified acidity, (b) iron, and (c) sulfate. The black polyline denotes the approximate evolution of each water quality parameter.

The first flush phenomenon occurring in the Sydney Coalfield was further examined to determine if it could also be used to describe mine water behavior at different depths, particularly as mine water can become stratified over time. Historical samples within the coalfield were categorized by the depth at which they were collected. Two depth range categories were generated: (i) 100 ft above sea level (asl) to 100 ft bsl (hereafter referred to as the 'shallow model'), and (ii) 101ft bsl to 300 ft bsl (hereafter referred to as the 'deep model').

Figures 3-6 and 3-7 present the mine water quality across the coalfield for the shallow model and deep model, respectively. Both models demonstrate clear first flush behavior even though they exhibit different peak concentrations and decay rates. For instance, in the shallow model, the peak modified acidity concentration was ~600 mg/L, while in the deep model it was ~3300 mg/L. The peak concentrations for iron and sulfate also display considerable magnitude differences between the shallow and deep models. These differences also indicate mine water stratification.
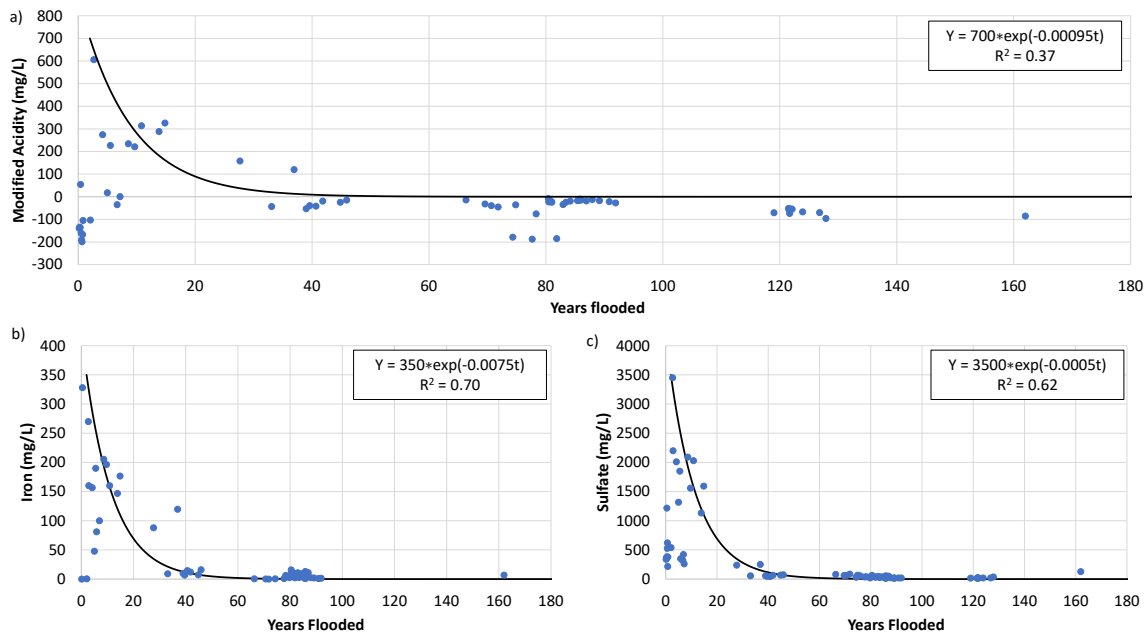
Figure 3-6: Mine water quality versus the number of years flooded for the shallow model (100 ft asl to 100 ft bsl) for (a) modified acidity, (b) iron, and (c) sulfate.

The shallow and deep models also demonstrate differences in decay rates, which confirms the suggestion made by Perry and Rauch (2012). The shallow model takes ~40 years of flooding to decline from peak concentrations to zero, while the deep model takes ~20 years. Therefore, while

the water quality in the shallow model is of better quality, the first flush is slower. This may be due to the upward movement of contaminants from deeper workings through complex advective or convective proccesses. Furthermore, many of the samples presented in Figures 3-6 and 3-7 are from collieries in the SM and NW mine pools that are under the influence of pumping from the NV treatment. Since mine water pumped to the plant is extracted from deeper workings, the first flush in the deeper workings could be accelerated causing the decay slope to become steeper.
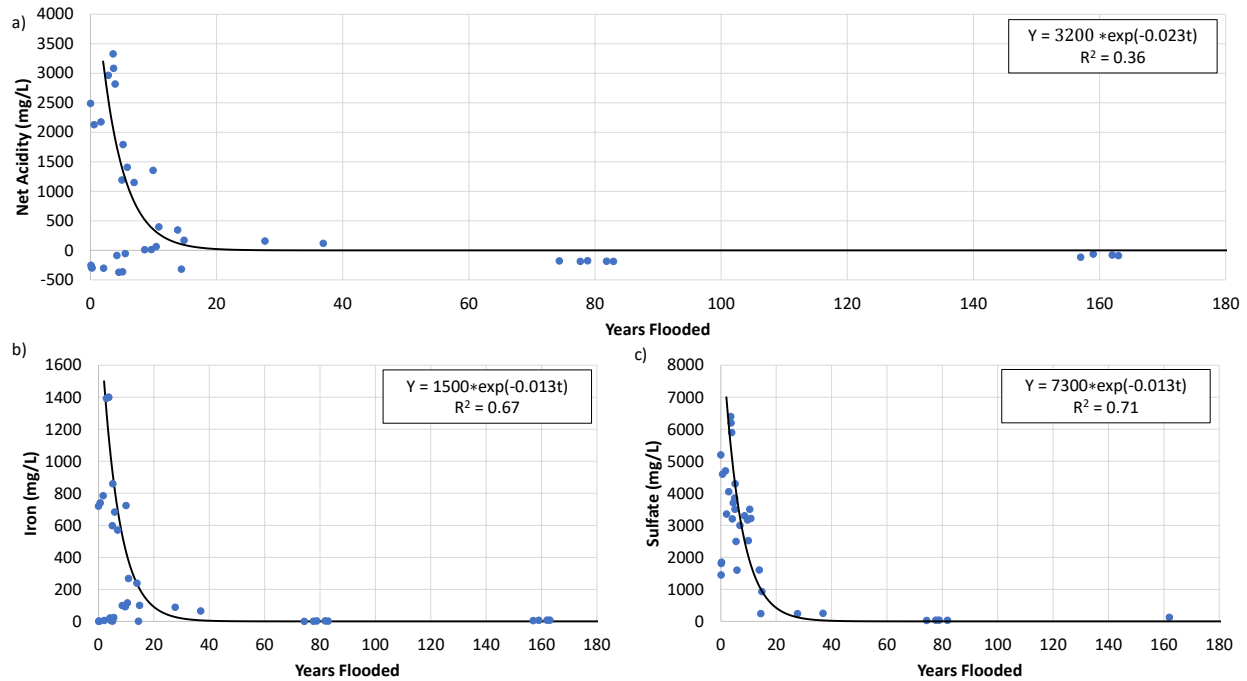
Figure 3-7: Mine water quality versus the number of years flooded for the deep model (100 ft bsl to 300 ft bsl) for (a) modified acidity, (b) iron, and (c) sulfate.

3.4.1.2   SM AND NW MINE POOLS

The modified acidity, iron, and sulfate for all samples available from the NW and SM mine pools are plotted in Figure 3-8. It is evident that the mine water quality versus years flooded in the SM and NW mine pools can also be represented by the 'first-flush' phenomenon. Each of the three empirical models – Gzyl and Banks (2007), single-phase Perry and Rauch (2012), and two-phase Perry and Rauch (2012) – were applied to the plots of modified acidity, iron, and sulfate.
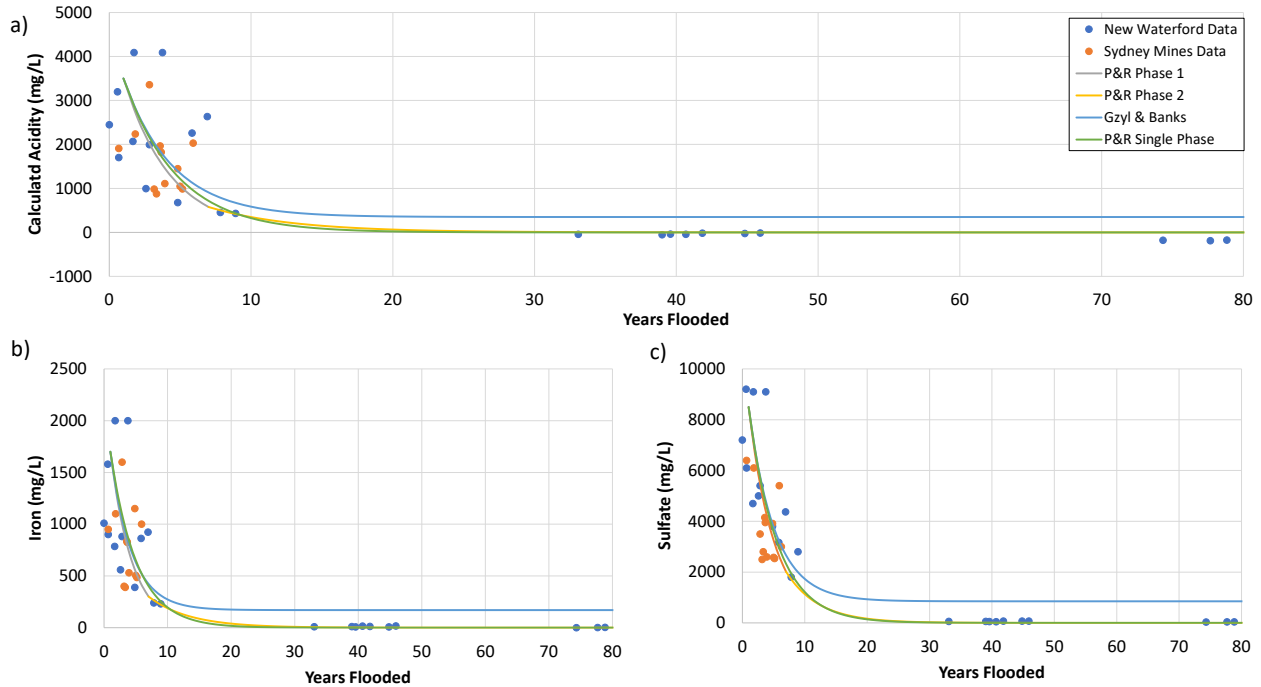
Figure 3-8: Historical mine water quality in the SM and NW mine pools. The calibrated curve for each of the three empirical models for a) modified acidity, b) iron and c) sulfate.

The optimal values of key parameters in each model – peak concentration, decay slope, year of peak concentration, year of decay slope transition – were obtained through comprehensive calibration. Table 3-3 presents a summary of the calibration results for each model, along with the R-squared (R^2) and index of agreement (d) values for the optimally calibrated curves. The calibrated curve of each model is shown for each parameter in Figure 3-8.

Detailed qualitative and quantitative analysis of each empirical model curve indicated that both Perry and Rauch (2012) models are acceptable for modeling the SM and NW mine water quality. The curves for each model in Figure 3-8 are very similar, along with their respective R^2 and d values. For modified acidity, $R^2 = 0.56$ and $d = 0.82$ for single phase, and $R^2 = 0.54$ and $d = 0.79$ for two-phase. In terms of application, the single-phase model uses a single decay slope from peak to zero concentrations, meaning it can be applied to any stage of the 'first-flush' curve; however, a single decay slope value may not accurately capture the curve shape with an initial, rapid decay followed by a slower, long-term decay. In contrast, the two-phase model assigns separate decay slope values for the early-time rapid decay and late-time slow decay, meaning it may better

represent the decay curve shape. However, since it would require sampling data along, or after, the initial decay slope to determine when the transition to the slower decay slope occurs, the two-phase model is more suitable for longer flooded mines where the initial rapid decay has already occurred.

Table 3-3: Calibration results summary showing the range of C_v and slope values tested for each parameter across each model. C_v values for Sulfate were tested in 500 mg/L increments, while iron and modified acidity were tested in 100 mg/L increments. Slope values for all parameters were tested in 0.001 increments.

Model	Parameter	Cv Range (mg/L)	slope range (/month)	Selected Cv (mg/L)	Selected slope (/month)	R^2	d
Perry & Rauch Single Phase	Modified Acidity	2000-4000	-0.01 to -0.06	3500	-0.022	0.56	0.82
	Iron	1000-2000		1700	-0.020	0.56	0.843
	Sulfate	5500-10000		8500	-0.018	0.66	0.895
Perry & Rauch Dual Decay	Phase 1 Modified Acidity	2000-4000	-0.01 to -0.06	3500	-0.025	0.54	0.77
	Phase 2 Modified Acidity	2000-4000		578	-0.014		
	Phase 1 Iron	1000-2000	-0.01 to -0.06	1700	-0.024	0.53	0.81
	Phase 2 Iron	1000-2000		301	-0.013		
	Phase 1 Sulfate	5500-10000	-0.01 to -0.06	8500	-0.020	0.65	0.89
	Phase 2 Sulfate	5500-10000		2013	-0.016		
Gzyl & Banks	Modified Acidity	2000-4000	-0.01 to -0.06	3500	-0.024	0.59	0.77
	Iron	1000-2000		1700	-0.025	0.60	0.78
	Sulfate	5500-10000		8500	-0.02	0.69	0.86

As shown in Figure 3-8, the Gzyl and Banks (2007) model closely matches the Perry and Rauch (2012) models for the early, rapid decline phase, but differs in the later, slow decline phase. This is because Gzyl and Banks (2007) suggest that mine water quality goes to long-term asymptotic concentrations, while the mine water quality in both the coalfield-wide plot and the combined SM-NW mine pool were observed to decline to zero concentrations, or negative concentrations in the case of modified acidity (i.e., net alkaline).

3.4.2 LONG-TERM PREDICTIONS

3.4.2.1 MINE WATER QUALITY

The quality of the mine water being pumped from the SM mine pool (at 1318 ft bsl) to the NV treatment plant is shown in Figure 3-9. It demonstrates that mine water quality reached peak

concentrations in late-2018 and has just started to decay. considerable scatter is evident in the modified acidity values that exceed 5000 mg/L, making it difficult to ascertain the exact start date of the decline.

Figure 3-9: Long-term predictions of (a) modified acidity, (b) iron, and (c) sulfate for mine water influent from the SM mine pool. The black line is the predicted water quality, while the upper and lower limits are represented by the grey band.

Since the mine water quality from the SM mine pool has just reached peak contaminant concentrations, the single-phase Perry and Rauch (2012) model was employed to predict the future mine water quality. The decay slope values used for each AMD parameter (i.e., modified acidity, iron, and sulfate) were determined from the earlier calibration process (Section 3.4.1.2) and are presented in Table 3-4.

Table 3-4: Model parameters for the empirical models used for New Waterford (NW) and Sydney Mines (SM). Note that NW uses the slope values for the second-phase model from Table 3-2.

Parameter	Mine Pool	Sydney Mines	New Waterford
Modified Acidity	Cv	7300	1200
	Slope	-0.0220	-0.0140
	Start Date	2019-09-01	2012-11-01
Iron	Cv	3900	650
	Slope	-0.020	-0.0130
	Start Date	2019-09-01	2012-11-01
Sulfate	Cv	15500	4800
	Slope	-0.0180	-0.0160
	Start Date	2019-09-01	2012-11-01

The start date and peak concentration (C_V) for the model were selected from the observed data where the decay in concentration commenced, though it is acknowledged that this was challenging due to the scattering at these high concentrations. To provide some indication of how the models are capturing the decay, the predicted values are compared to available observed values along the decay. Table 3-5 presents the field observed values and the predicted model values, and the resulting R^2 value, which is also indicated in Figure 3-9.

Table 3-5: Sample and model results used to calculate R2 values for early SM model predictions

Parameter	Date	Real Value (mg/L)	Modeled Value (mg/L)	R Squared
Modified Acidity	2019-09-20	7300	7199	
	2020-02-20	6400	6435	
	2020-03-13	7000	6332	0.75
	2020-07-17	6200	5773	
	2020-08-19	5300	5635	
Iron	2020-03-13	3800	3427	
	2020-06-04	3800	3242	0.50
	2020-07-17	3700	3151	
	2020-08-19	3000	3082	
Sulfate	2020-02-20	12000	13980	
	2020-03-13	13000	13797	0.39
	2020-06-04	14000	13127	
	2020-07-17	13000	12792	

As shown in Figure 3-9, the modified acidity of the influent mine water from the SM mine pool is predicted to decrease to ~2300 mg/L by the year 2025, and then to ~100 mg/L by 2038. Similar trends are predicted for iron and sulfate concentrations, with iron declining to below 10 mg/L by 2045, and sulfate declining to below 100 mg/L by 2044. Figure 3-9 also shows upper concentration limits (UCL) and lower concentration limits (LCL) due to positive and negative changes of 0.005 in the slope value. For instance, the slope value for modified acidity was 0.022, so the UCL and LCL were based on slope values of 0.027 and 0.017, respectively. This 0.005 value was used as it was found during calibration that the slope values that gave suitable model results were largely within this range across modified acidity, iron, and sulfate.

The quality of the mine water being pumped from the NW mine pool (at 385 ft bsl) to the NV plant is shown in Figure 3-10. It is evident that this mine water quality is much further along the 'first-flush' decay curve, with peak concentrations and the initial rapid decay already achieved. Since it is known that the NW mine pool has only been flooded 5-6 years longer than the SM mine pool, it was assumed that the NW mine water quality has just transitioned to the long-term, slower decay slope (whereas SM is 'behind' NW by approximately 5 years in flooding time and is only starting the initial, rapid decay slope).

The second phase of the two-phase Perry and Rauch (2012) model was employed to predict the future mine water quality being pumped from the NW mine pool. Since it was assumed that the NW mine water quality has just started on the long-term, slower decay slope, the decay slope values for modified acidity, iron, and sulfate were equal to the second phase decay slope values determined from the calibration process. Furthermore, the start date and initial (peak) concentration (C_V) were equal to the first observed data point in Figure 3-10 (i.e., the start of the second decay slope). The various model parameter values for NW are presented in Table 3-4.
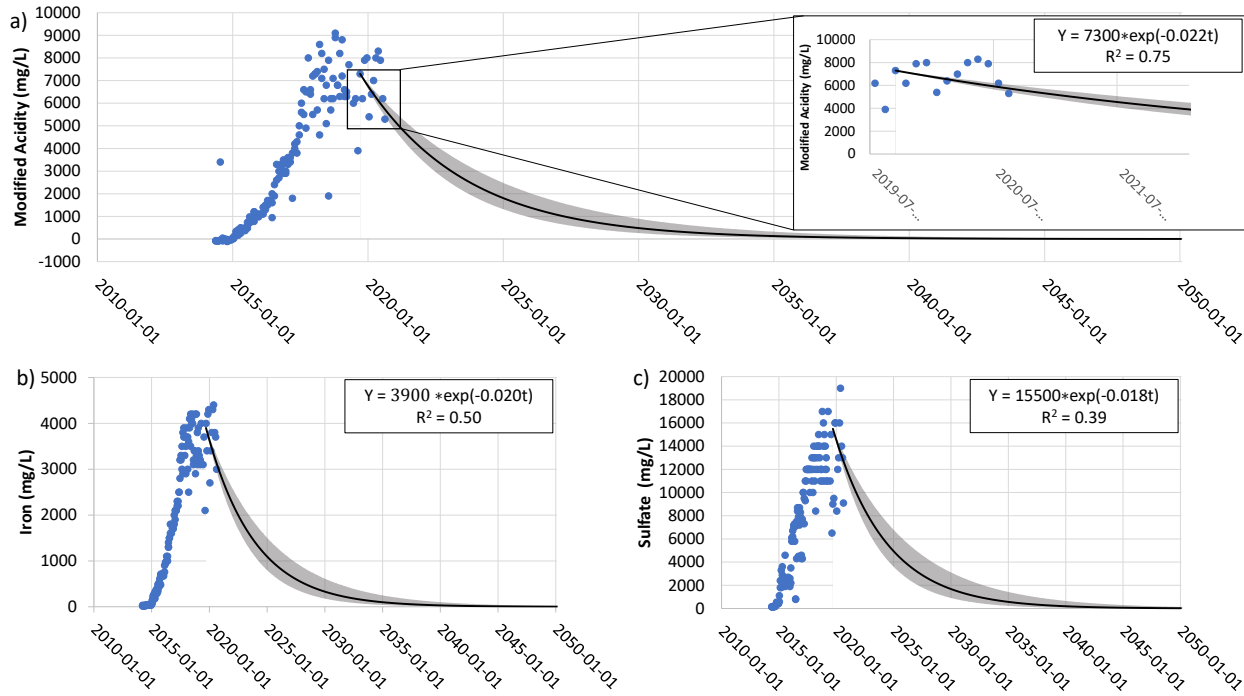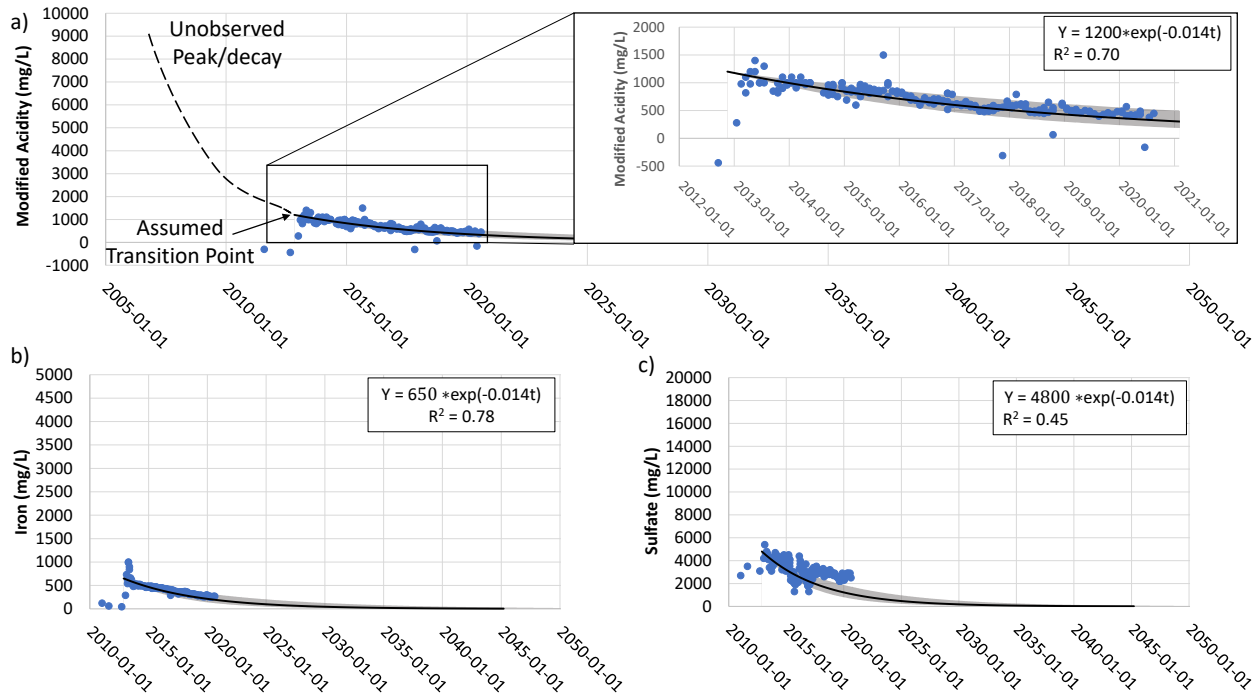
Figure 3-10: Long-term predictions of (a) modified acidity, (b) iron, and (c) sulfate for mine water influent from the NW mine pool. The black line is the predicted water quality, while the upper and lower limits are represented by the grey band.

As shown in Figure 3-10, the modified acidity of the influent mine water from the NW mine pool is predicted to decrease to ~100 mg/L by the year 2025, and then to below ~10 mg/L by 2038. Similar trends are predicted for iron and sulfate concentrations, with iron declining to below 10 mg/L by 2040, and sulfate declining to below 100 mg/L by 2033. The UCL and LCL were again determined from positive and negative changes of 0.005 in the decay slope value. For instance, the slope value for modified acidity was 0.014, so the UCL and LCL were based on slope values of 0.019 and 0.009, respectively.

The total acidity loading at the NV plant (combined SM and NW influent) is expected to decrease to 49,123 kg/year by 2037, which places it below the daily average of 150 kg suggested by Trumm (2010). This indicates that the combined NW-SM service area treated by the NV plant will approach a point where a transition to passive treatment is possible, which would considerably reduce overall plant operational costs.

3.4.2.2 LIME COSTING

Figure 3-11 plots the historical lime usage versus the corresponding acidity loading, which was provided by the environmental consultancy firm, CBCL Limited. From this, we can see that 0.98 kg of lime is required to neutralize 1 kg of modified acidity.
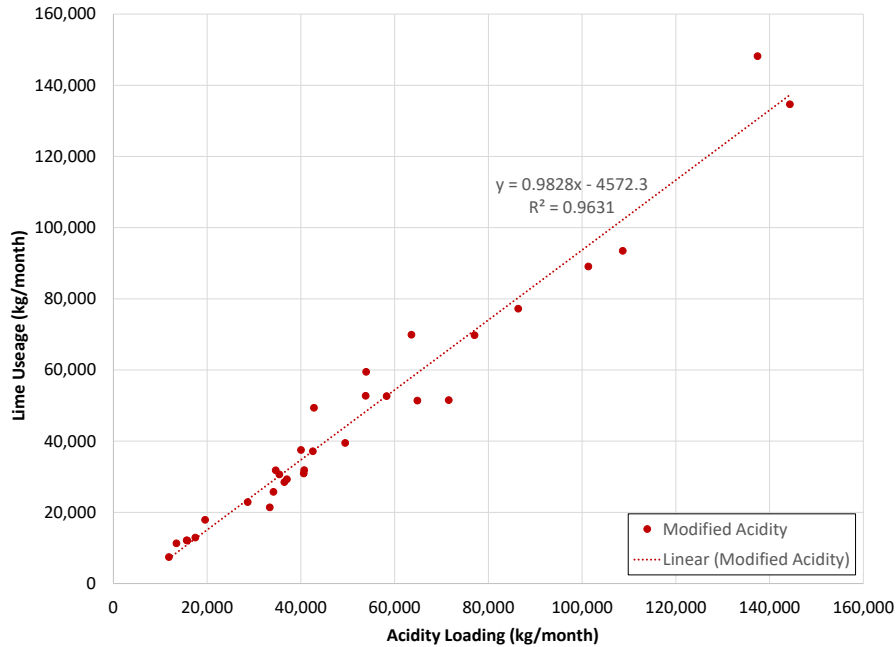
Figure 3-11: Historical lime usage versus corresponding acidity loading at the NV treatment plant. The correlation between the two indicates that 0.98 kg of lime is needed to neutralize 1 kg of acidity.

Using Equation (3-6), the cost associated with lime usage over the long-term was determined. This does not include inflation, changes in utility costs, or any other related operational and maintenance expenses. Figure 3-12 shows the projected cost for lime usage at the NV plant over time, along with upper and lower confidence intervals that were based on the UCL and LCL concentrations of modified acidity in Figures 3-9 and 3-10.

It is predicted that lime expenditure will decrease by 50% between 2025 and 2029. By 2036, the upper confidence limit for lime costs will be less than $100,000 per year. This corresponds to acidity values well below 100 mg/L, or an average daily loading of under 150 kg/day, indicating that a transition to a passive treatment system in 2037 could make financial sense, according to Trumm (2010). These decreases are based entirely on the natural decrease in acidity forecasted by empirical models.
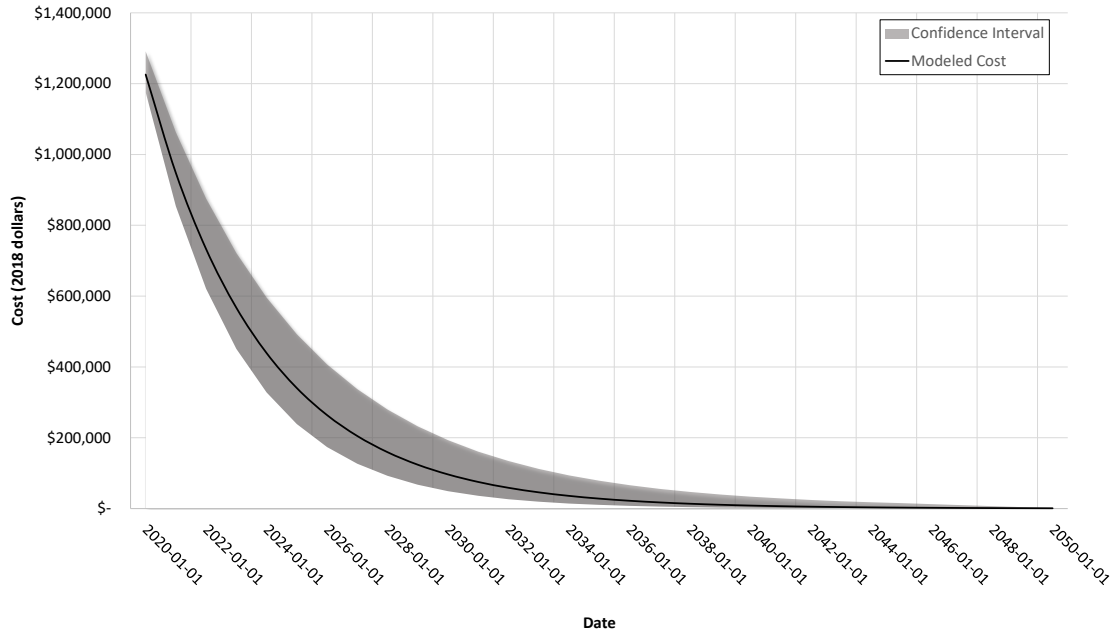
Figure 3-12: Long-term predictions of costs associated with lime usage at the NV plant

3.4.3 TREATMENT PLANT OPTIMIZATION

3.4.3.1   PUMPING STRATEGY

Figure 3-13 plots the daily modified acidity and pH versus the number of days since the pumps were turned back on. For example, each weekday, the plant would continuously pump water to lower mine water elevations to the lower threshold, then on the weekends, the pumps were turned off and the mine water elevations were allowed to increase again.
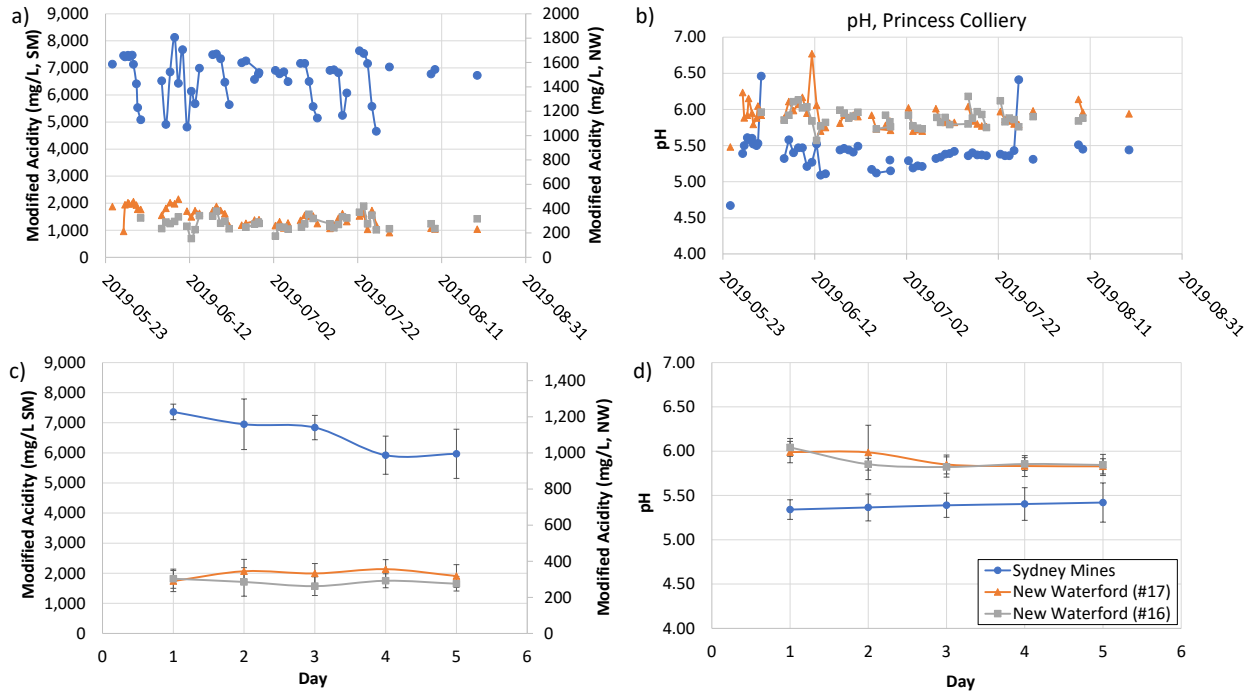
Figure 3-13: Daily measurements of (a) modified acidity, and (b) pH at the NV treatment plant. The mean of these daily measurements was also plotted against consecutive days of pumping for (c) modified acidity, and (d) pH. Each data point represents the mean modified acidity and pH collected on that day of each pumping series, with standard deviation error bars.

Figures 3-13(a) and 3-13(c) demonstrate that the SM mine pool shows a considerable change in modified acidity throughout the typical 5-day pumping period, with acidity vales dropping from ~7300 mg/L to ~6000 mg/L. Figures 3-13(b) and 3-13(d) demonstrate that pH appears to increase a little. The two NW mine pool sampling points show little variation, typically maintaining a modified acidity between 200-400 mg/L, and a pH between 5.5 and 6.5. The stark contrast in behavior between the two mine pools is likely due to two factors. The magnitude difference is due to the different lengths that each mine pool has been flooded, with the NW mine pool having lower magnitudes as it has been flooded (and flushed) longer. The greater variation in the SM mine pool over each 5-day period is likely due to the more direct flow path from SM to the NV plant and that all SM collieries flooded at the same time. In contrast, the flow path through the NW mine pool is much more complex as it traverses multiple collieries (i.e., from Dominion No. 12, 14, and 16 collieries through the significantly more mature Dominion No. 17 and 18 collieries.

3.4.3.2   MINE WATER STRATIFICATION

Table 3-6 presents the modified acidity, iron, and sulfate of mine water sampled from Well D-69 and Well D-63 from Florence Colliery over time. It is evident that the shallower well (D-69) consistently maintains lower concentrations values, while the deeper well (D-63) consistently maintains lower concentrations values. It is evident that the concentration in each well is declining over time, but they are doing it at the same rate. These observations demonstrate reliable mine water stratification that is not changing much over time.

Table 3-6: Samples from Florence Colliery showing stratification

Date	D-69 (55.7 fbsl)			D-63 (268 fbsl)		
	Modified Acidity (mg/L)	Iron (mg/L)	Sulfate (mg/L)	Modified Acidity (mg/L)	Iron (mg/L)	Sulfate (mg/L)
August 2017	550	300	1900	3400	1500	6400
September 2017	540	260	1700	3600	1500	6200
December 2017	470	250	1500	3600	1400	5900
January 2019	290	130	860	2300	900	4300
March 2019	250	110	770	2300	900	4300

Table 3-7 presents the modified acidity, iron, and sulfate of mine water sampled from Well D-167 and Well D-156 in Dominion No. 12 over time. It is evident that the shallower well (D-167) consistently maintains lower concentrations values, while the deeper well (D-156) consistently maintains lower concentrations values. It is evident that the concentration in each well is declining over time, but they are doing it at a similar rate.

Table 3-7: Samples from Dominion No. 12 Showing Stratification

Date	C-167 (48.5 fbsl)			C-156 (492.5 fbsl)		
	Modified Acidity (mg/L)	Iron (mg/L)	Sulfate (mg/L)	Modified Acidity (mg/L)	Iron (mg/L)	Sulfate (mg/L)
November 2013	450	160	2200	3800	1900	9400
November 2016	160	86	350	4100	2100	9100
November 2017	200	110	420	3800	2200	9700

3.5   CONCLUSION

This study assessed the robustness of empirical 'first-flush' models for representing mine water behavior in flooded underground workings in the Sydney Coalfield in Nova Scotia, Canada, and then employed, for the first time, these models to predict the evolution of mine water quality being pumped to an active mine water treatment plant. While numerical models are commonplace across a range of hydrogeological and geoenvironmental investigations, the complexity, heterogeneity, and unknowns in underground mine workings provide challenges for numerical modeling, making them more suitable for when a deep hydrogeologic understanding of the system is necessary. Instead of trying to model the physical, hydraulic, and geochemical processes that may be causing changes in mine water quality, empirical models focus on the resulting mine water quality and the behavior and trends that have been established from decades of data from coalfields worldwide. Therefore, despite its simplicity and ease of use, empirical models can be more suitable when a low cost approach is needed.

The historical AMD-impacted mine water quality samples taken from each colliery across the Sydney Coalfield were analyzed and correlated to the years that each corresponding colliery was flooded, which ranged from 5 years to 100+ years. Concentrations of modified acidity, iron, and sulfate, which are commonly used parameters to characterize AMD, were plotted against years flooded and confirmed that mine water quality in the coalfield follows 'first-flush' behavior.

With the knowledge that the mine water quality in the coalfield has historically followed 'first-flush' phenomenon, empirical models based on the 'first-flush' were then employed for predicting the quality of mine water being pumped to the active treatment plant in New Victoria, which is being used to manage the mine water in the Sydney Mines (SM) and New Waterford (NW) mine pools. The empirical models were first calibrated against historical mine water quality in the SM and NW mine pools to determine the optimal model parameters before the most suitable model was used for long-term predictions. Based on predictions of modified acidity, iron, and sulfate for both the SM and NW mine water, it was shown that mine water quality being pumped to the plant will collectively reach concentrations by the year 2040 that would be acceptable for active treatment to cease and a transition to either passive treatment or direct marine discharge. The predicted acidity concentrations and loadings were then used to determine the associated long-term dosages and costs of lime used in the active treatment process.

This study demonstrated that the 'first-flush' phenomenon accurately represents evolving mine water behavior across the historical Sydney Coalfield. Empirical models that are based on the 'first-flush' are easy-to-use but highly appropriate for predicting the quality of mine water over the long-term, either naturally within the mine pools, or when the mine water is being pumped to treatment plants. Predictions of mine water contaminant loadings, either discharging to the environment, or being pumped to treatment plants are highly beneficial to various stakeholders of abandoned coalfields, including site owners, regulators, and treatment plant designers, and operators. Future work will focus on the stability of observed mine water stratification and the feasibility of pumping and treating mine water from shallower workings.

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4 SUMMARY AND CONCLUSIONS

4.1 SUMMARY

Modeling the evolution of mine water quality within flooded underground mine workings can provide valuable insight into the longevity of associated contamination hazards, namely acid mine drainage (AMD). This information is essential for the designers and regulators of mine water treatment plants that are commonly constructed to prevent and/or control the release of AMD to the environment. It is also valuable for ongoing plant operations and maintenance of these plants and the associated long-term costs. Numerical models have been developed to simulate the hydrodynamics and geochemistry of water within underground workings, but are can be cost prohibitive and effort intensive, often taking years to develop (e.g., Croxford et al., 2004; Winters & Capo, 2004; Rapantova et al., 2007; Betrie et al., 2014). Empirical models of mine water behavior are simpler but still representative of actual conditions. While numerical models are highly dependent on a deep understanding of the physical extenet and characteristcs, which can be difficult to achieve in deep and highly variable workings, empirical models rely on mine water quality and its expected behavior (e.g., first flush principle) that has been ascertained through decades of historical mine water quality trends that have been observed at mine fields worldwide.

The goal of this thesis was to assess the robustness of empirical 'first flush' models for representing the evolution of mine water quality in underground coal mines, and how these models could be applied to predict the quality of mine water being pumped and treated at mine water treatment plants. This thesis focused on the historic Sydney Coalfield in Nova Scotia, Canada, where extensive data have been collected over several decades to allow the evaluation of long-term mine water quality trends. Furthermore, an active mine water treatment plant is currently in operation in the Sydney Coalfield to manage mine water from two of the largest mine pools in the coalfield.

As part of the research goal, three specific objectives were addressed. The *first* objective was to assess whether first-flush based models could accurately represent the evolution of mine water quality in the Sydney Coalfield. Mine water quality was represented by modified acidity, iron, and sulfate, which are key parameters that are commonly used to characterize AMD. The mine water quality that was measured at all monitoring wells in each colliery within the coalfield in 2017 was plotted against the years that each corresponding colliery was flooded, which ranged from 5 years

to 100+ years. The behavior of mine water, which followed the same trend for each of modified acidity, iron, and sulfate, confirmed that mine water quality in the coalfield was following the first flush phenomenon. Mine water quality sampled across the coalfield was then categorized into different depth ranges–based on the depth the mine water was sampled from. The mine water quality also followed first flush behavior for both these depth categories, confirming that first flush behavior also occurs within different, stratified layers of mine water quality.

The *second* objective was to predict the long-term mine water quality being pumped from the Sydney Mines (SM) and New Waterford (NW) mine pools to New Victoria (NV) treatment plant. The mine water quality (represented by modified acidity, iron, and sulfate) sampled at every monitoring well in the NW and SM mine pools over time was plotted versus the flooding time associated with each sample. Three empirical first-flush models (Gzyl & Banks (2007) and Perry & Rauch (2012)) were then applied and calibrated to the combined SM and NW first flush curve to determine the optimal parameters of the first flush model (e.g., decay slope, peak concentration). The quality of the mine water influent to the NV plant from the SM and NW mine pools had been measured bi-weekly since the plant opened in 2012, and the optimal empirical first-flush model was applied to this existing data to provide long-term predictions of mine water quality. Mine water influent from the SM mine pool started to decay from its peak contaminant concentrations in 2018, with modified acidity declining to less than 100 mg/L by 2038, and iron and sulfate declining to less than 10mg/L and 100mg/L by 2040, respectively. Mine water influent from the NW mine pool was already in the long-term decay phase of the first-flush, with modified acidity predicted to fall below 10 mg/L by 2039, with iron and sulfate to fall below 10mg/L and 100 mg/L by 2040 and 2033, respectively. A correlation was then made between evolving mine water quality and lime consumption, allowing a cost estimate for long-term lime usage to be made.

The *third* objective was to assess the initial feasibility of two ideas for optimizing plant operations and expenses. First, the influence of treatment plant controls, specifically influent pumping rates, was evaluated by performing real-time monitoring of mine water quality changes during daily plant operations. These preliminary results show that plant controls can alter the mine water quality being pumped from the SM mine pool. Secondly, the presence of mine water stratification in the SM and NW mine pools was investigated. Samples taken over several years from a shallow and deep monitoring well in each mine pool confirmed that mine water quality in shallower workings

was consistently much higher than the deeper workings. Since the goal of a treatment plant is to keep mine water elevations below expected discharge elevations, then the feasibility of pumping water from shallower regions of the mine pool, which will be much higher quality, should be investigated.

4.2 RECOMMENDATIONS

Chapter 3 evaluated the applicability of First-Flush based models to the Sydney Coalfield and their use in predicting long-term mine water quality and associated treatment plant expenses. The following recommendations are suggested for improving the application of these models and for optimizing treatment plant approaches:

- Samples from the NV treatment plant were evaluated from the start of operations in 2012 to late 2020. Since the SM mine water quality had just started to decline in 2018, additional mine water quality values would allow a more accurate estimation of the model decay slope values and provide greater accuracy to the model predictions.

- Model results indicate that the water quality in the SM and NW mine pools is rapidly improving. However, instead of continuing active treatment until the concentration of mine water quality parameters approaches zero, the treatment plant could transition from an active system to a passive system before that. The feasibility of this transition and the costs and implications associated with it should be investigated.

- This study successfully identified the presence of stratification in the SM and NW mine pools. However, the resiliency of this stratification in these slope-mined systems is still uncertain. This should be further investigated to determine the suitability of a new treatment approach that pumps water from the shallower workings, which would result in significant cost savings due to the higher quality water entering the plant for treatment. Future investigations could include pumping tests at several monitoring well locations within the SM and NW mine pool to assess the quality of the pumped water over time, and if the stratified layering can remain intact during possibly disruptive pumping.

- Recent studies have examined the possibility of recovering and selling rare earth metals from AMD treatment systems (Vass et al., 2019; Ziemkiewicz, 2019; Lefticariu et al.,

2020; León et al., 2021) to offset some of the plant operating expenses. An investigation could be conducted that assesses the technical and economic feasibility for the NV treatment plant to begin recovering these metals as the influent water is pumped to the plant.

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Vass, C. R., Noble, A., & Ziemkiewicz, P. F. (2019). The occurrence and concentration of rare earth elements in acid mine drainage and treatment byproducts: Part 1 - Initial survey of the northern Appalachian Coal Basin. *Mining Engineering*, *71*(11), 49–50. https://doi.org/10.1007/s42461-019-0097-z

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APPENDIX A: VERIFICATION OF THE 'IN-HOUSE' LAB ANALYSIS

OVERVIEW

Following the establishment of the new mine water quality laboratory at the New Victoria treatment plant, it was essential to confirm the accuracy and reliability of the new -in-house' laboratory analysis results. To achieve this validation, a batch of the mine water samples taken from the Sydney Mines (SM) and New Waterford (NW) mine pools were analyzed for standard acidity and modified acidity at both the new laboratory and duplicate samples by the commercial laboratory of Maxxam/Bureau Veritas. The mine water results were then compared for each sample. This comparison was completed immediately following the establishment of the new laboratory and repeated several times throughout the sampling period in the summer of 2019.

PROCEDURE

Standard acidity and modified acidity were analyzed with the Standard Methods of the Examination of Water and Wastewater method 2310 and method 2310B.4a (APHA et al., 2017), respectively. Maxxam/Bureau Veritas were consulted to ensure the same analysis methods were being used. The modified acidity analysis involved taking a mine water sample, adding a small amount of hydrogen peroxide, and boiling the sample for several minutes. The sample was then cooled back to room temperature and titrated with 0.02N NaOH.

RESULTS

Table A-1 presents the analysis results for mine water samples conducted by both the 'in-house' laboratory and Maxxam/Bureau Veritas. It is evident that the modified acidity results are very similar between both laboratories. The standard acidity was not as strongly correlated for the initial samples, but after consultation with Maxxam/Bureau Veritas, it was discovered that they used a dilution factor of 10x. After then using that dilution factor at the 'in-house' laboratory, the discrepancy with Maxxam/Bureau Veritas was considerably reduced. This is evident from sample comparison at later times. Investigation of the dilution factor for mine water samples is discussed in Appendix B.

Table A-1: Comparison between Maxxam and lab results. Samples from NW and SM were collected from the sampling ports at the NV plant.

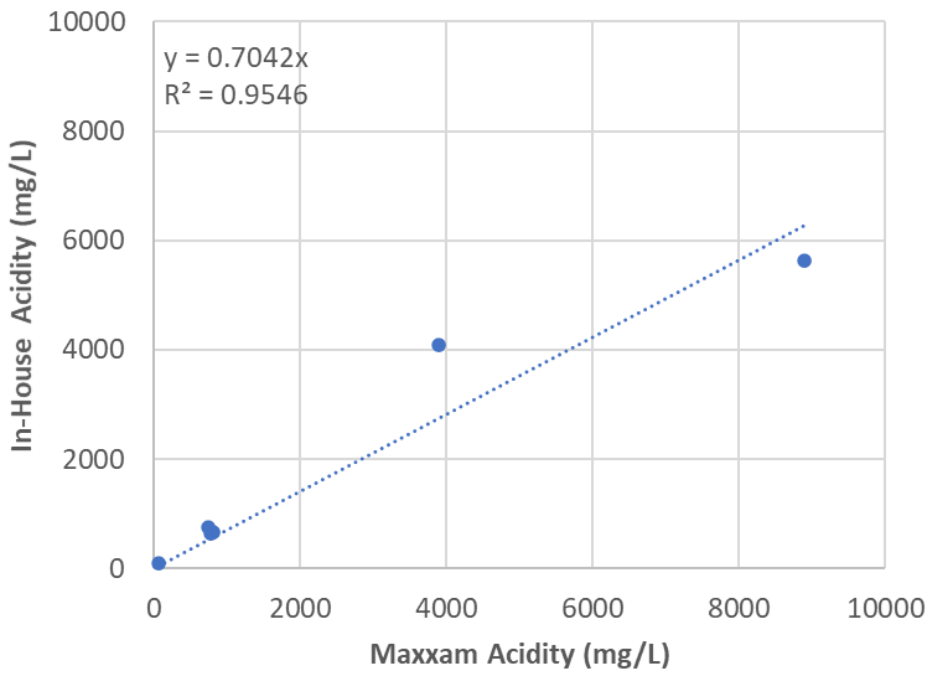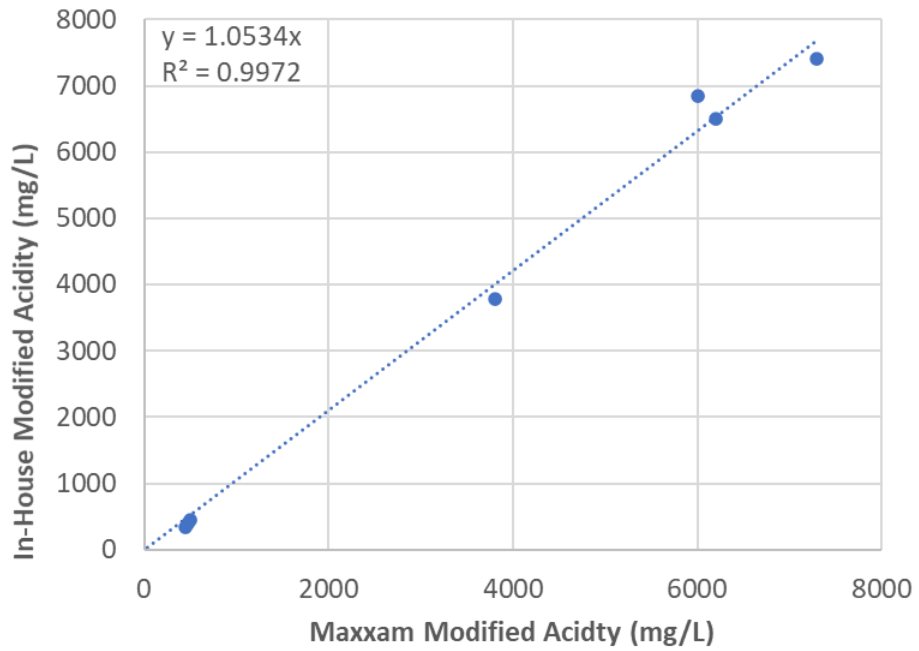| Date	Modified Acidity		Standard Acidity		Source
	Maxxam	**In-House**	**Maxxam**	**In-House**	
2019-05-28	500	440	810	670	NW
2019-05-28	7300	7414.60	8900	5642.10	SM
2019-06-06	470	402.3	770	633.76	NW
2019-06-06	6000	6849.90	-[1]	-[1]	SM
2019-06-28	-28	-62.88	63	96.23	No. 12 (C-167)
2019-06-28	3800	3784.80	3900	4087.40	No. 12 (C-156)
2019-07-10	440	336.4	740	767.93	NW
2019-07-10	6200	6498.80	-[1]	-[1]	SM

[1]Sample not collected

Figure A-1: comparison of results between the 'in-house' laboratory and Maxxam/Bureau
Veritas for modified acidity (top) and standard acidity (bottom)

CONCLUSION

The standard acidity and modified acidity results were found to be highly comparable between the new 'in-house' laboratory at the New Victoria treatment plant and the Maxxam/Bureau Veritas commercial laboratory. This investigation confirms that the analysis results from the 'in-house' laboratory were accurate and reliable.

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APPENDIX B: DILUTION ANALYSIS

B.1 ACIDITY MEASUREMENTS

OVERVIEW

Following the development of the mine water laboratory inside the New Victoria treatment plant, initial measurements of 'in-house' standard acidity were shown to substantially deviate from standard acidity measurements that were done by the commercial laboratory Maxxam/Bureau Veritas. After consultation with Maxxam/Bureau Veritas, it was discovered that they used a dilution factor of 10 when analyzing standard acidity and modified (net) acidity. A dilution test was subsequently conducted at the in-house laboratory at New Victoria to determine the impact of dilution on the sample results.

PROCEDURE

Samples from the Sydney Mines (SM) mine pool were analyzed for both standard acidity and modified acidity. Three samples were created with different dilution factors: (i) an undiluted sample, (ii) a sample with a 5x dilution (i.e., 10mL sample in 40mL deionized (DI) water), and (iii) a sample with a 10x dilution (5mL sample in 45mL of DI water). Analysis of each sample was carried out using the methodology found in the 'Mine Water Laboratory Manual' in Appendix E, which followed the Standard Methods of the Examination of Water and Wastewater method 2310 for standard acidity, and 2310B.4a for modified acidity (APHA et al., 2017). Analysis of the undiluted and 5x diluted samples was performed using 0.1N NaOH, while the 10x dilution sample was analyzed with 0.02N NaOH due to concerns with the titration volume being too low for accurate results.

RESULTS

The sampling results are presented in Table B-0-1 and plotted in Figure B-1. It was found that a substantial increase in standard acidity occurs when the samples were diluted, while the modified acidity seems to be unaffected by dilution.

Table B-0-1: Alkalinity dilution test results for samples from the NW and SM mine pools

Dilution Factor	Standard Acidity	Modified Acidity
0	3794.40	6382.5
5	4607.15	- [1]
10	7503.4	6136.8

[1]modified acidity sample was fouled during analysis and discarded
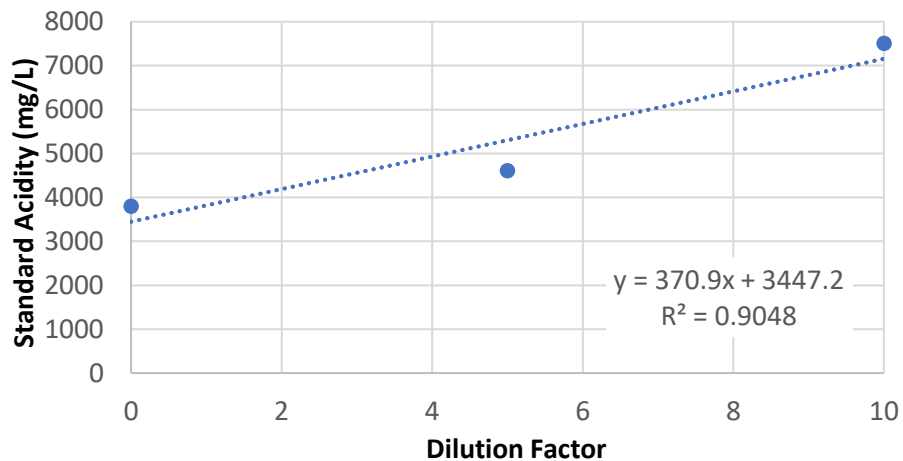

Figure B-1: Standard acidity vs dilution factor showing a linear increase in acidity as the sample is diluted further.

CONCLUSION

It is evident that a linear increase in acidity occurs with an increase in the dilution factor to 10x. Further increases in dilution of the samples would require lower volumes of NaOH which may affect the accuracy of the titration results. In any case, it was found that the 10x dilution factor ensured the 'in-house' standard acidity measurements matched that of Maxxam/Bureau Veritas. An extensive database of mine water quality data exists for mine pools throughout the Sydney Coalfield, with many of this data analyzed by Maxxam/Bureau Veritas. Therefore, it was imperative that the 'in-house' methodology and analysis results matched them.

B.2 ALKALINITY MEASUREMENTS

OVERVIEW

Following the findings of the 'Acidity Dilution' tests, the effects of diluting samples for alkalinity measurements were investigated.

PROCEDURE

Samples from the SM and New Waterford (NW) mine pools were collected and analyzed for alkalinity. Again, three samples were created with different dilution factors: (i) an undiluted sample, (ii) a sample with a 5x dilution (i.e., 10mL sample in 40mL deionized (DI) water), and (iii) a sample with a 10x dilution (5mL sample in 45mL of DI water). Analysis of each sample was carried out using the methodology found in the 'Mine Water Laboratory Manual' in Appendix E, which followed the Standard Methods of the Examination of Water and Wastewater method 2320B for alkalinity (APHA et al., 2017). Analysis of the samples was performed using 0.1N HCl. It should be noted that the low titration volumes in the 5x and 10x dilutions may introduce some errors.

RESULTS

The sampling results are presented in

Table *B-2* and plotted in Figure B-2. It is evident that alkalinity does not change considerably due to dilution in both the SM and NW samples, except for the 5x dilution sample from NW appears to be lower than the undiluted and 10x dilution NW samples. This may have been caused by the low titration volumes used at this dilution.

Table B-2: Alkalinity dilution test results for samples from the NW and SM mine pools

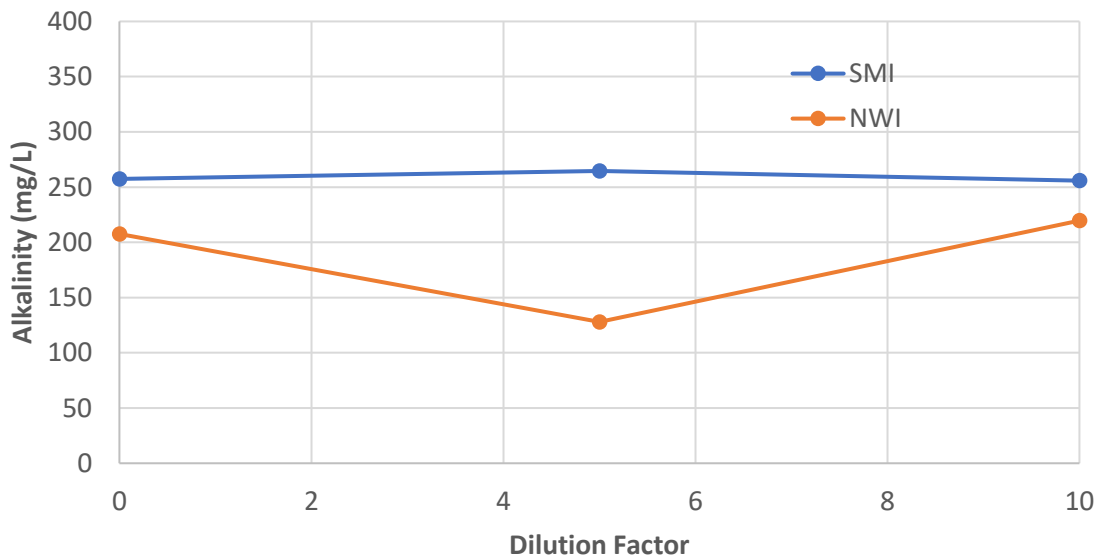| SM				
Dilution	**Start pH**	**End pH (4.50)**	**Vol HCl Added (mL)**	**Alkalinity**
0	6.02	4.49	12.852	257.28
5	5.82	4.47	2.644	264.6
10	5.89	4.47	1.278	255.85
NW				
Dilution	**Start pH**	**End pH (4.50)**	**Vol HCl Added (mL)**	**Alkalinity**
0	6.02	4.49	10.375	207.68
5	5.89	4.47	1.278	127.97
10	6.23	4.48	1.097	219.67

Figure B-2: Alkalinity vs dilution factor showing that alkalinity stayed approximately equal across all dilution factors.

CONCLUSION

These tests demonstrated that alkalinity measurements do not change with varying sample dilution levels. Since excessive dilution should be avoided due to the low volumes of HCl used, which may end up affecting the accuracy of the titration results, it was decided to analyze alkalinity samples with no dilution. This would allow for easier lab analysis and possibly more reliable and consistent results.

REFERENCES

American Public Health Association (APHA), American Water Works Association (AWWA), & Water Environment Federation (WEF). (2017). *Standard methods for the examination of water and wastewater* (R. B. Baird, A. D. Eaton, & E. W. Rice (Eds.); 23rd ed.). American Public Health Association (APHA).

APPENDIX C: VERIFICATION OF NAOH CONCENTRATION

OVERVIEW

During the summer of 2019, a laboratory was created at the New Victoria treatment plant to measure mine water quality in real-time. Mine water samples were analyzed for standard acidity and modified acidity on a daily basis following the Standard Methods of the Examination of Water and Wastewater, method 2310 for standard acidity, and 2310B.4a for modified acidity (APHA et al., 2017). For both methods, titrations were completed with sodium hydroxide (NaOH). Due to the volume and cost of the titrant being used, 0.1N NaOH was purchased and diluted it to 0.02N for the titrations. While 0.02N was the objective, some inaccuracies may occur during dilution. As a result, the real concentration of the diluted solution was determined to ensure accurate titration results for the acidity measurements. Two tests were conducted during the summer of 2019 to verify the actual concentration of the NaOH after dilution.

PROCEDURE

The tests followed a methodology adapted from the HANNA HI0001EN method, which was based on the AOAC Official Methods of Analysis 936.16 (AOAC, 2005). A description of this methodology is presented in the laboratory manual in Appendix E. The tests involved a titration of potassium hydrogen phthalate (KHP) in distilled water to determine the real concentration of NaOH.

A small mass of KHP (approximately 3g) was measured into a beaker, covered with aluminum foil and left on a hot plate set to 140 °C for ~1-2 hours to dry. It should be noted that this drying process would be done in an oven at a lower temperature, but an oven was not available at the time. The KHP was then removed from the hot plate and a small volume (between 0.05 – 0.2g) was measured into a different beaker, then filled with 50mL of deionized (DI) water. The solution was then titrated to the first equivalence point, and results expressed in normality (eq/L) of NaOH. The test was repeated a minimum of three times and the average was taken as the real concentration.

RESULTS

The NaOH concentration was verified twice during the sampling program with good results, as presented in Table C-1.

Table C-1: NaOH concentration Analysis Results

Date	Run	Mass KHP (g)	Vol of NaOH used (mL)	Result (N, eq/L)	Avg N (eq/L) (target: 0.02N)	Std. Dev.
July 2 2019	1	0.07	17.188	0.01994	0.0237	0.409%
	2	0.07	13.857	0.02473		
	3	0.08	17.938	0.03		
	4	0.1	24.183	0.02025		
12-Aug-19	1	0.2	50.995	0.0192	0.0208	0.110%
	2	0.12	27.133	0.02166		
	3	0.18	41.184	0.0214		

CONCLUSION

The tests demonstrated that the dilution of 0.1N NaOH to 0.02N NaOH was accurate and consistent during sampling in the summer of 2019, with only very small deviations from the desired 0.02N NaOH.

REFERENCES

American Public Health Association (APHA), American Water Works Association (AWWA), & Water Environment Federation (WEF). (2017). *Standard methods for the examination of water and wastewater* (R. B. Baird, A. D. Eaton, & E. W. Rice (Eds.); 23rd ed.). American Public Health Association (APHA).

Association of Official Analytical Chemists (AOAC). (2005). *Official Methods of Analysis* (W. Horwitz & G. W. Latimer (Eds.); 18th ed.). Association of Official Analytical Chemists.

APPENDIX D: CALCULATED VERSUS ANALYZED NET ACIDITY

OVERVIEW

The extensive historical database of mine water quality data collected across the Sydney Coalfield contains sample measurements between 2002 and 2021. Many of these samples were not analyzed for modified (hot peroxide) acidity, which is a key parameter of interest in this study. However, almost all these samples were analyzed for many other parameters, including pH and metal concentrations. Previous studies have developed an equation that can be used to obtain 'calculated net acidity' from pH, iron, aluminum, and manganese concentrations, which was shown to correlate strongly to actual 'modified acidity' measurements (Park et al., 2015). As a result, this equation could be used to generate calculated net acidity for all available samples in the historical database, and most importantly, be used to 'fill in' any missing modified acidity measurements. To ensure the reliability of applying this equation to the Sydney Coalfield, a wide range of samples taken from the Sydney Mines (SM) and New Waterford (NW) mine pools were used to compare calculated net acidity to modified acidity.

PROCEDURE

The net acidity equation is shown in Eq. E-1. Park et al. (2015) suggest several variations of the calculated acidity equation depending on water quality. Method E2 from Park et al. (2015) was determined to be best match for the chemistry of the historical samples, as it is best suited for samples with an SO_4^{2-} concentration greater than 400 mg/L and a pH >4.0, which all historical samples had, with the exception of a few very early samples from the SM mine pool.

The net acidity can be calculated using the following equation:

$$Net\ Acidity\ (mg/L\ CaCO3)\ =\ calculated\ acidity - alkalinity \qquad \text{(E-1)}$$

Substituting method E2 from Park et al. (2015) yields:

$$Net\ Acidity\ =\ 50 * \left(2 * \frac{[Fe]}{55.85} + 3 * \frac{[Al]}{27} + 2 * \frac{[Mn]}{54.94} + 10^{(3-pH)}\right) - alkalinity \qquad \text{(E-2)}$$

The data from the SM and NW samples were compiled and the actual modified acidity was plotted against the calculated net acidity for each sample. Park et al. (2015) suggested using dissolved concentrations of metals for the calculated net acidity, but in this appendix, the results for using both dissolved and total concentrations of metals were presented to compare the difference.

RESULTS

Figure D-1 plots the modified acidity against the calculated net acidity (using dissolved metals) for both the SM and NW mine water samples. It is evident that very good agreement exists for all samples. The strong correlation does diminish for acidity values >5000 mg/L.
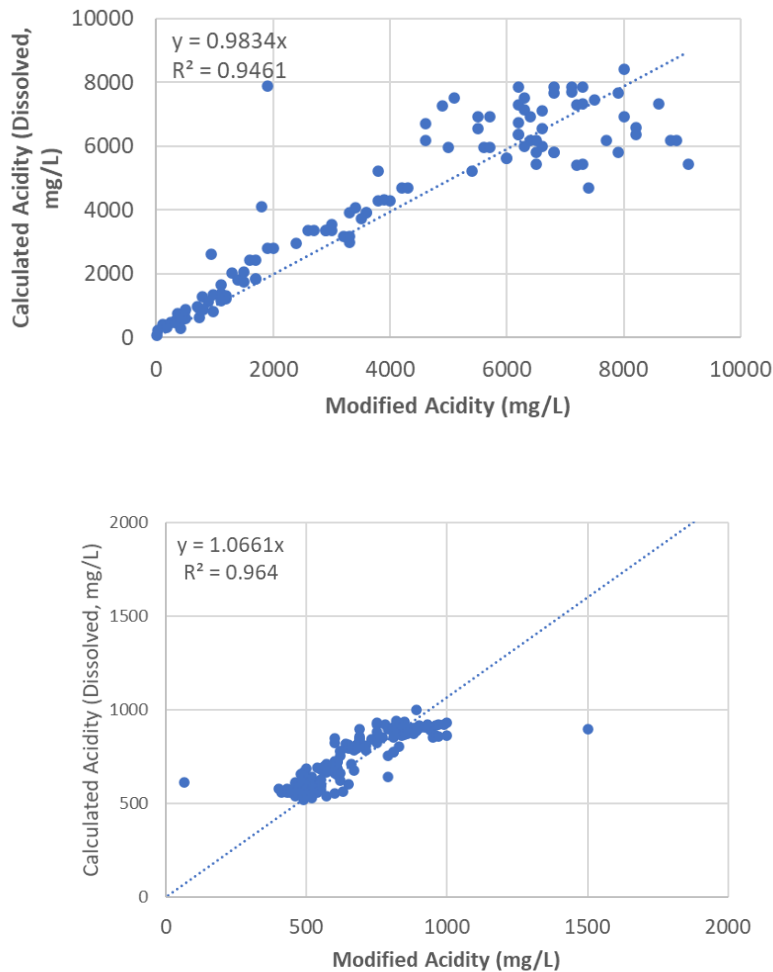

Figure D-1: Calculated acidity using filtered parameters vs modified acidity vs for top) Sydney Mines (SM) and bottom) New Waterford (NW)

Figure D-2 plots the calculated net acidity with dissolved metals against the calculated net acidity with total metals. It is evident that very strong correlations exist, indicating that the calculated net acidity equation by Park et al. (2015) may perform effectively if only total metal concentrations exist.
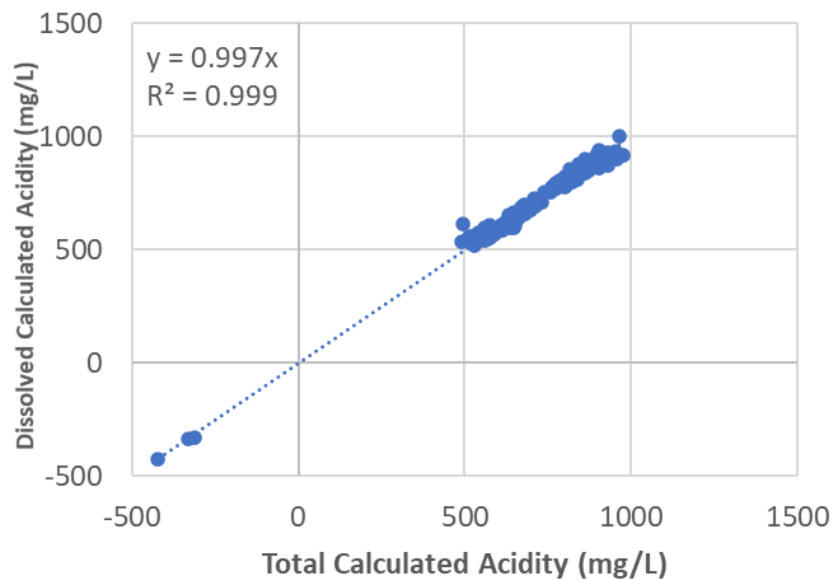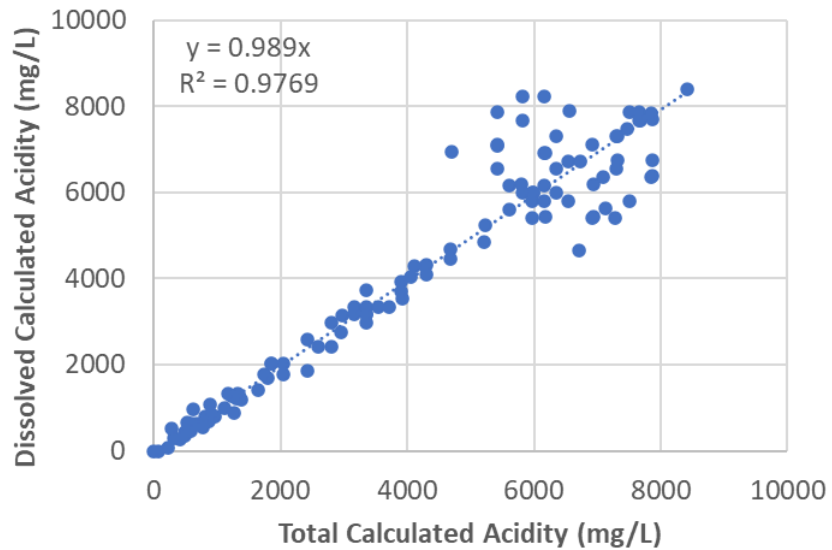

Figure D-2: Calculated acidity using filtered parameters vs modified acidity vs for top) Sydney Mines (SM) and bottom) New Waterford (NW)

CONCLUSION

This investigation demonstrated that calculated net acidity values from the equation generated by Park et al. (2015) can provide a strong correlation to actual modified acidity results. It also indicated that this correlation is strong whether you use dissolved or total concentrations of metals in the equation. However, given that the original equation was generated using dissolved metal concentrations, total metal concentrations should only be used for samples that did not have dissolved metal concentration measurements. Overall, this investigation confirms that for historical samples that do not have actual modified acidity measurements, calculated net acidity values can be reliably used instead.

REFERENCES

Park, D., Park, B., Mendinsky, J. J., Paksuchon, B., Suhataikul, R., Dempsey, B. A., & Cho, Y. (2015). Evaluation of acidity estimation methods for mine drainage, Pennsylvania, USA. *Environmental Monitoring and Assessment*, *187*(1). https://doi.org/10.1007/s10661-014-4095-9

APPENDIX E: LAB MANUAL

The following is a copy of the lab manual provided to PSPC summer 2019.

Mine Water Geochemical Analysis

New Victoria Treatment Plant Laboratory

Operation and Maintenance Manual

For Public Services and Procurement Canada (PSPC):

Produced by: Patrick Merritt

Reviewed by: Chris Power

August 23, 2019

Table of Contents

1. Sample Collection

1.1   Cleaning Bottles

Bottles should be cleaned prior to new sampling:

- Clean with warm water and dishwashing fluid in a plastic tote/bucket.
- Make sure to rinse out the suds/bubbles with clean tap water. Leave to dry.

1.2   Rinsing Bottles

During the collection of the mine water sample, <u>the sampling bottle should first be rinsed with the mine water 3 times</u>:

- To rinse a bottle, fill the bottle to approx 1/3 full with the sample water.
- Cap the bottle. Shake for 5 sec. Empty the bottle away from the collection area or into a waste bin.
- Repeat this process 3 times before keeping/collecting the final sample.

1.3   Bottle Headspace

- When collecting samples, <u>fill the bottles to leave as little air as possible trapped in the bottle</u>. This will reduce the exposure of the sample to oxygen and prevent oxidation, which can affect results.

1.4   Sampling of Princess

- The sampling point for Princess is located within the pump house at the New Victoria plant. The tap is located to the right-hand side of the entrance door and points vertically down.
- Since Princess is a tap directly off the pipe into the plant, almost no purging time is required.
- Turn the tap on. <u>Wait for the flow to turn from frothy-white to clear</u>.
- Rinse the bottle 3 times before collecting the final sample.

Princess Sampling Point
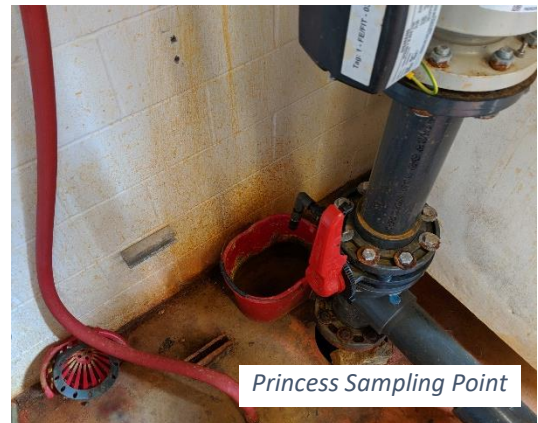
1.5   Sampling of #17

- The sampling point for #17 is located within the pump house at the New Victoria plant. The tap is located on the piping closest to the far left-hand corner from the entrance door and is horizontal.
- #17 is also a tap directly off the pipe into the plant so does not require purging time.
- When collecting the sample do not open the tap wide, as particulates (black specks/debris) from the tap nozzle will enter the sample bottle. Instead, <u>open the tap very slightly to produce a slower flow to avoid this issue</u>.

#17 Sampling Point

1.6   Sampling of #16

- The #16 sampling point is located at Cameron Lane, inside the manhole closest to the building on site.
- The sampling port is tied to the top rung of the ladder and does not require entry into the manhole.
- Since there is a hose between the pipe carrying the sample water and the tap, <u>it should be flushed for approximately 3-5 minutes to ensure fresh sample water is collected</u>.

#16 Sampling Point

1.7   Collecting Maxxam/Bureau Veritas Samples:

- Samples for Maxxam/Bureau Veritas should be collected in bottles obtained directly from Maxxam/Bureau Veritas.
- These bottles should not be rinsed before collecting a sample, as the containers may have acid or another storage agent in the bottle.
- Bottles should be filled to the fill line indicated on the bottle or per the instructions on the bottle label.

1.8   Sampling of Monitoring Wells

Determining Pumping Time

To calculate the approximate time a well should be pumped before sampling, calculate the volume of water from the top of the well to the mine workings. To do this you need:

- Borehole log indicating the depth of the mine workings
- Diameter of the borehole shaft/casing

To calculate the volume of the well use the volume equation:

$$Volume \ (ft^3) = \frac{\pi * diameter^2}{4} * Depth \ to \ mine \ workings$$

Note: all units should be in feet

To convert cubic feet to gallons multiply by 7.480:

$$Volume \ (gal) = Volume \ (ft^3) * 7.480$$

To determine the time to pump one well volume, divide the volume in gallons by the pumping rate. The well should be flushed approximately 3 times before sampling:

$$Total \ Pumping \ Time = \frac{3 * Volume \ (gal)}{Pumping \ Rate \ (gpm)}$$

Pumping Times for Common Wells

Below is a list of common pumping times, assuming a typical pumping rate of 20 GPM. <u>Note that these times are approximate and that the YSI should be used to determine the exact sampling time</u>. Real sampling times are frequently shorter than estimated.

Well	Time
C-150	20 minutes
C-167	30 minutes
C-166	30 minutes
C-158	30 minutes

Using YSI Multiparameter Meter

- To assist in determining when water is being pulled directly from the mine workings, the YSI should ideally be used in a flow cell. A flow cell keeps the sample water isolated from air while you measure.
- If a flow cell is not available, place the YSI in the protective field cap and place it in a bucket. Direct the water from the outlet of the sampling pump into the bucket.
- When the readings have stabilized (meaning we are getting constant readings with time) and total pumping time is approaching the estimated time (shown above), it is safe to assume the water is directly from the mine pool.
- <u>Record readings from the YSI every few minutes</u> to verify the stability of the readings.
- <u>The YSI should be calibrated within 24 hours of use</u> and calibration buffers should be kept in the case with the probe in case of emergency.

YSI With Protective Field Cap

YSI and Sampling Hose in Bucket

2. Lab Methodology

2.1   Modified Acidity of Water

Reference

Standard Methods for the Examination of Water and Wastewater 21st edition, Method 2310.

Glassware & Materials

- Distilled Water Squirt Bottle
- 50 mL graduated cylinder
- 250 mL Beaker
- 200 mL beaker
- 50 mL Beaker
- Kim Wipes
- Magnetic stir bar and retriever
- Two 5 mL pipettes and dropper for Hydrogen Peroxide
- Tin Foil (for boiling cap)
- Datasheet
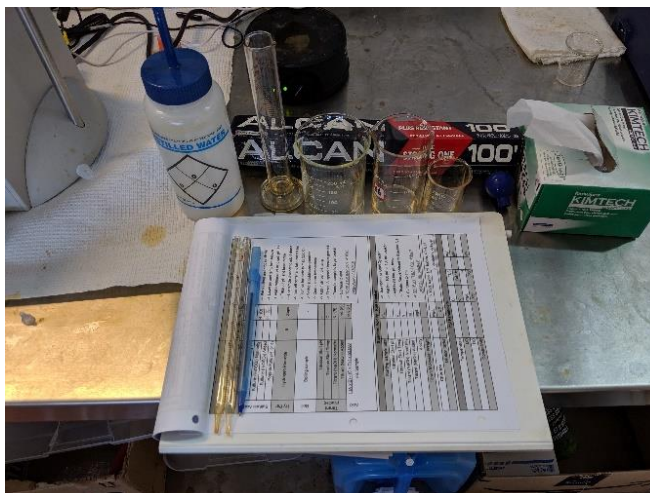
Reagents

- 0.02N Sodium Hydroxide (NaOH)
- Distilled Water (DI water)
- 0.02N Sulfuric Acid (H_2SO_4)
- 30% Hydrogen Peroxide

Procedure

Titration

1. Ensure pH and temperature probes are connected.
2. If the pH probe has not been calibrated within the last day, recalibrate it (see Section 3 on page 12).
3. Press 'Select Method' from the main screen and select "0.02N Acidity of Water".
4. Half-fill the '250 mL beaker' with distilled (DI) water.
5. Get the 200 mL beaker. This beaker will be your sample beaker throughout the test.
6. Using the 250 mL beaker with DI water, add 45 mL of DI water to the 50 mL graduated cylinder.
7. Place this 45 mL of DI water into the 200 mL beaker.
8. Use one of the 5 mL pipettes to extract 5 mL of my water sample from the sample bottle.
9. Add this 5 mL of mine water sample to the 200 mL beaker which already contains the 45 mL DI water. Swirl gently to mix.
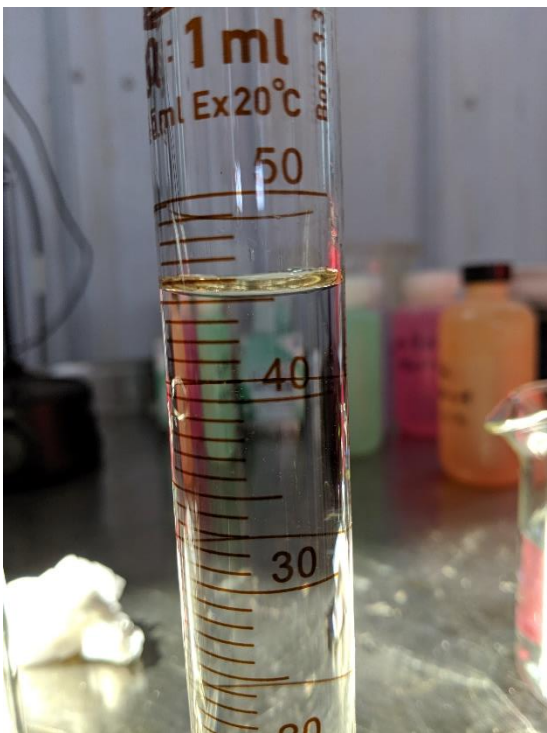
50mL Graduated Cylinder with 45mL DI Water   *5mL Pipette with Sample*

10. Rinse the stir bar with DI water. Dry with Kimwipes. Drop it into the sample (200 mL beaker).
11. Rinse the pH probe and temperature probe with DI water and dry with Kimwipe.
12. Place the 200 ml beaker (which contains the sample) onto the magnetic stir plate.
13. Lower the pH and temperature probes into the sample. Make sure the junction at the bottom of the pH probe is submerged in the sample (the tiny white ceramic spot just above the bulb should be submerged).
14. Turn the magnetic stirrer speed dial on. Make sure the stir bar spinning at the bottom of the 200 mL beaker is not hitting the pH and temperature probes or the sidewalls of the beaker.
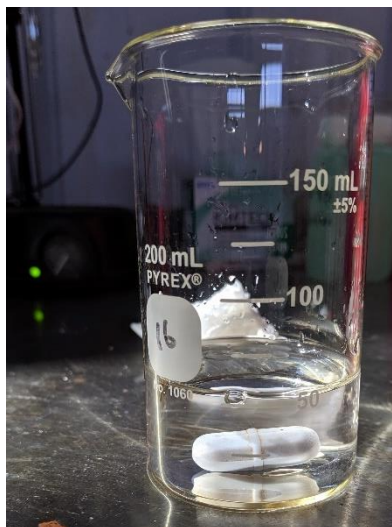
| Stir Bar in Sample | Sample with Stir Bar and Probes | Sample with stir bar and probes |

15. Position the 'titrant dispensing tube' so that it is aimed directly into the center of the sample/beaker and not at the sidewalls of the beaker or the probe.

16. Read the pH reading from the titrator screen. Record this starting pH on the datasheet under the 'Modified Acidity' section.

17. Add approximately 10 - 20 mL of 0.02N Sulfuric Acid to the 50 mL beaker.

18. Use the second, clean pipette to extract 5mL of 0.02N Sulfuric Acid from this 50 mL beaker and add to the sample (which is still constantly stirring).

19. Wait several seconds until the pH reading stabilizes. If the pH does not lower to less than 4.0, then add 5 mL of 0.02N Sulfuric Acid. Check pH reading. Repeat until 'pH is less than 4.0', adding 5 mL increments of Sulfuric Acid each time.

20. Record the amount of Sulfuric Acid added on the datasheet.

21. *Note*: if you are doing multiple samples per day, you can just store the 5 mL pipette used for sulfuric acid on the table, as it can be used for the next analysis needing sulfuric acid. However, the 5 mL pipette used earlier for the mine water sample should be put away and cleaned for each analysis, as each mine water sample is completely different (we do not want cross-contamination).

22. Use the soft plastic dropper/pipette to extract a small volume of 30% Hydrogen Peroxide.

23. Carefully add 5 drops of this hydrogen peroxide from the dropper into the still stirring sample. The sample may occasionally change colour to a dark red/brown colour.

Dropper Extracting Hydrogen Peroxide

24. Raise the pH and temperature probes out of the sample.
25. Use the magnetic retriever stick to raise and remove the magnetic stir bar from the sample.
26. Note that the retriever should not be placed directly into the sample. Use it against the bottom of the sidewall until you see the stir bar become attached, then slide the retriever bar up the sidewall, before the stir bar comes out the top.
27. Cover the top of the sample beaker with tin foil. This speeds up the boiling process and prevents the sample from evaporating. We do not want to evaporate too much sample as this will badly affect our volumes and acidity results.
28. Activate the hot plate and set it to 280 degrees Celsius.
29. Place the sample onto the hot plate. Heat the sample until it has boiled for 2-3 minutes. If doing 2-3 samples at once, the total boiling time is approximately 12-15 minutes. However, this is just a guide and it is best to check the samples periodically and start timing once they have begun boiling.
30. Remove the sample from the hot plate and remove the tin foil. Turn the hot plate off.
31. Allow the sample to cool to at least 25 degrees. You can drop the temperature probe into the sample to check its temperature. This usually takes approximately 30 minutes.
32. Note: if needed, the cooling process could be sped up by placing the beaker containing the partially cooled (<40 degrees) sample into a bowl containing cooler tap water. The cooler water in the bowl will cool down the outside walls of the sample beaker, thereby speeding up the cooling.

Sample on hot plate

Sample cooling post boil

33. Rinse the stir bar, pH probe, and temperature probe with DI water (they were last used when adding hydrogen peroxide in Step 22). Dry with Kimwipe.
34. Once the sample is cool, drop the stir bar into the now cooled-down sample. Place the sample onto the magnetic stir plate.
35. Lower the pH and temperature probes into the sample. Turn the stir assembly on and ensure the stir bar is not hitting the probe or the sidewalls of the beaker when it spins.
36. Like before, ensure the titrant dispensing tube is aimed directly into the sample and not at the sides of the beaker or the probe.
37. Record the pH and temperature on the datasheet under the 'Modified Acidity' Section.
38. Press 'Start/Stop' on the titrator machine to begin the titration.
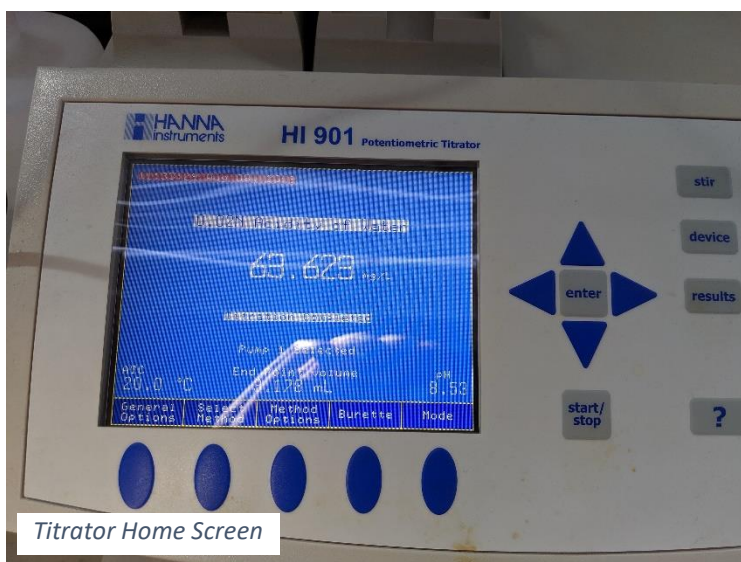
Titrator Home Screen

39. The titrator will continuously add titrant to the sample while measuring the pH. The titration will continue until the pH reaches approximately 8.3. It will then finish.

40. Record the 'titrant volume added' on the datasheet.
41. Make sure all boxes on the datasheet are filled in. Otherwise, you may have missed something critical.
42. Use the equation to calculate the final modified acidity value.

Sample:		Date:	Time:	Analysis Date	Time:
C-173		Aug 20/19	9:45	Aug 22/19	10:20

Hot Acidity - Run Number: T. 14

Sulfuric Acid	Starting Sample Size	50	mL	-> Use Pipette or Grad Cylinder
	Starting pH	6.62	-	-> Put into 100 mL or 150 mL beaker
	Sulfuric (H₂OSO₄) Normality	0.02	N (D)	-> Put on stirrer and drop in stir bar
	Sulfuric (H₂OSO₄) Added	15	mL (C)	-> Lower pH and temp into sample
	Post-Sulfuric pH (< 4)	3.05	-	-> Add increments of acid until pH < 4
Hy Per	Hydrogen Peroxide	5	drops	-> Take out pH and temp probe; -> Use simple dropper to add 5 drops; -> Turn off stirrer and take out stir bar
Boil	Boiling sample	-	-	-> Turn on hot plate to max (280 C); -> Boiling at bubbles/evaporation; -> Cool to room temperature
Titrant (NaOH)	Titration Start pH	2.92 25.9	-	-> Add in stir bar, pH, temp
	Titration Start Temp	25.9	C	-> Titrate. Suspend if beaker gets full
	Titrant (NaOH) Normality	0.02	N (B)	-> Transfer sample to larger beaker
	Titrant (NaOH) Added	4.432	mL (A)	-> Continue to end.
Acid	[(A x B) - (C x D)] x 50,000 / mL Sample	8.33	end pH	-> TAKE STIR BAR OUT WHEN DISPOSING SAMPLE

- 429.36 mg/L

$$\frac{((4.432 \times 0.02) - (25.9 \times 0.02)) \times 5}{50}$$

Standard Acidity - Run Number:

Starting Sample Size		mL	-> Use Pipette or Grad Cylinder
Titration Start pH		-	-> Put into 100 mL or 150 mL beaker
Titration Start Temp		C	-> Add in stir bar, pH, temp
Titrant (NaOH) Normality		N	-> Titrate. Suspend/transfer if beaker full
Titrant (NaOH) Added		mL	-> Continue to end.
Acidity		mg/L	-> TAKE STIR BAR OUT WHEN DISPOSING SAMPLE
Titrant Molecular Weight			

Chloride			mg/L	-> 10mL samp, 1mL hadide, 40mL DI
Dilution factor	1:4	x 5		in graduated cylinder

YSI Parameters

Temperature	15.6	C	TDS	786.5	mg/L
DO	37.2	%	Salinity	0.60	ppt
DO	3.63	mg/L	pH	6.66	-
Conductivity	988	uS/cm	ORP	-78.1	mV

Completed Data Sheet. Note: Standard acidity was not run for this sample and is crossed out

Record Digital Version of Results

- Once finished, press the results button and select 'Review Last Analysis Report'
- Select 'View Graph' then 'Save as Bitmap'
- Select 'Review Report' and fill out the datasheet.

2.2   YSI Multi-meter Parameters

Glassware & Materials

- Datasheet
- 250 mL beaker
- Squirt bottle for DI water
- YSI Calibration/Storage Cup

Procedure

- Fill the 250mL Beaker with DI water
- Unscrew the calibration/storage cup from the YSI probe and remove the sponge
- Fill the storage cup approx ¼ full of DI water.
- Thread the storage cup back onto the probe and shake vigorously for 5-10 seconds
- Discard the Distilled water.
- <u>Initial rinse of the probe heads with sample water</u>: fill the storage cup approx ¼ full of sample, thread the probe into the cup and shake vigorously for 5-10 seconds. Empty the cup.
- Refill the storage cup to approximately ¾ full, and thread probe into the cup.
- Wait until readings stable and record all readings on the display screen onto the datasheet.

Calibration/storage cup

2.3   Standard Acidity of Water

The standard acidity test is the same as the Modified Acidity test, except we skip the 'Add Sulfuric Acid', 'Add Hydrogen Peroxide', and 'Boiling/Cooling' steps. We just take the 50 mL sample (45 mL DI water + 5 mL mine water sample) and put it straight into titration mode.

Reference
Standard Methods for the Examination of Water and Wastewater 21st edition, Method 2310

Glassware & Materials
- Datasheet
- 200 mL beaker
- Squirt bottle with DI water
- 5 mL pipette
- 50 ml graduated cylinder

Reagents
- 0.02N Sodium Hydroxide
- Distilled Water (DI water)

Procedure
Titration

- Ensure pH and temperature probes are connected
- If the pH probe has not been calibrated within the last day, recalibrate.
- Press Select Method from the main screen and select "0.02N Acidity of Water"
- Fill the 50 mL graduated cylinder up to the 45 mL line with DI water.
- Transfer this measured 45mL of DI water to the 200mL beaker.
- Use the pipette to add 5mL of sample to the beaker and swirl to mix.
- Rinse the stir bar with DI water and dry, then add it to the sample.
- Rinse the pH and temperature probes with DI water and dry with Kim wipe.
- Place the sample on the stir plate and insert the probes. Turn the stir assembly on and ensure the stir bar is not hitting the probe or the sides of the beaker when it spins.
- Ensure the titrant dispensing tube is aimed directly into the sample and not at the sides of the beaker or the probe.
- Record the temperature on the datasheet under the 'Standard Acidity' section.
- Press 'start/stop' and wait for the titration to complete. Write results into a data sheet.

Record Digital Results

- Once finished, press the results button and select 'Review Last Analysis Report'
- Select 'View Graph' then 'Save as Bitmap'
- Select 'Review Report' and fill out the datasheet.

2.4   NaOH Titrant Concentration Test

Knowing the concentration of the Sodium Hydroxide (NaOH) titrant is critical for the calculation of acidity values. As such we must know for certain what the actual concentration of the titrant is. Note that this test should be repeated three times and the results averaged. This method uses a titration of Potassium Hydrogen Phthalate (KHP) in distilled water to determine the concentration of sodium hydroxide. For this titration, the KHP is required to be dried before use. The titration endpoint is 8.6.

Required Materials

- 50mL beaker
- Stir Bar
- Spoon/Scoop
- 200mL beaker
- Scale
- Distilled water
- Potassium Hydrogen Phthalate (KHP)

Method

- Ensure the titrator is connected and filled with Sodium Hydroxide (typically 0.02N). If the titrator is not, purge the titrator as outline in the 'Titrator Maintenance' Section.
- Place approx. 3 grams of KHP into the 50mL beaker. Crush any large pieces of KHP. Set the hot plate to 140 degrees and place the beaker on the hot plate. Let heat for approximately 1-2 hours to remove moisture. Crush any large pieces of KHP.
- Place the 200mL beaker on the scale and zero it by pressing the Power/TARE button. Add between 0.1 and 0.2 grams of KHP to the beaker. Record the final weight.
- Fill the beaker with 50mL of Distilled Water.
- Place the stir bar in the beaker and place it on the stirring platform. Set the stir bar to a speed sufficient to suspend the KHP particles.
- Change the titrator mode to "0.02N NaOH Conc."
- Place the temperature and pH probes into the beaker. The pH should approximately 4.0
- Start the titration and wait until complete.

Record Results

Once the titration has finished:

- Press the results button and select 'Review Last Analysis Report'
- Select 'View Graph' then 'Save as Bitmap'
- Select 'Review Report' and record the following information on the datasheet
  - Start pH
  - End pH
  - Volume Used
  - Result
  - Run Number

3. Titrator Operation & Maintenance

3.1   Preparing Titrant

The lab stocks Sodium Hydroxide in concentrations of 0.1N. The concentration of all titrants used during testing is 0.02N. Lowering the concentration of the titrant increases the volume of titrant required, ensuring that enough is used to provide an accurate reading. This also lowers the volume of titrants being consumed, lowering operational costs.

To create 0.02N titrant from 0.1N titrant: add 200mL of 0.1N titrant to 800mL of distilled water and mix.

Materials

- 1 L Bottle
- 600 mL beaker
- 800 mL Distilled water
- 200 mL 0.1N Titrant (Sodium Hydroxide)

Procedure

- Fill the 600mL beaker to the 500mL line with Distilled water and add to the 1L bottle.
- Fill the 600mL beaker to the 300mL line with Distilled water, and add to the 1L bottle.
- Add 200mL of 0.1N titrant to the 600 mL beaker and then add to the 1L bottle.
- Cap the bottle and invert several times to mix. Ensure the bottle is labeled with the titrant name and new diluted concentration. Store until needed.

Note: when creating the diluted titrant, it should not be directly added to the container used by the titrator, as the entire volume will not fit in an already partially full container. Instead, pour the solution into a spare 1L bottle and label it with the titrant name and concentration.

Note: This same process also applies to diluting any other titrants. While sodium hydroxide is the only titrant that is used in Modified or Standard Acidity, sometimes you may do an Alkalinity test that uses Hydrochloric Acid as the titrant. If hydrochloric acid also comes in 0.1N bottles, it can be diluted to 0.02N using the above procedure (0.02N = 200 mL of 0.1N + 800 mL DI water).

3.2   Changing Methods

*Note: **If you are only doing Modified Acidity (or Standard Acidity), then you will always just use the '0.02N Acidity of Water' method**. However, the option is there to change to other methods if needed (e.g., Alkalinity).*

To change the analysis method, select the 'Select Method' option from the Titration Home Screen. Use the up and down arrows to the right of the screen to navigate to the desired method and press 'Select'.

3.3   Titrator Backup and Memory Clear

To download and backup results store in the system, the data can be downloaded to a USB through the USB port on the side of the titrator. From the Home screen, select the 'General Options', then 'Save to USB'. From there, files can be saved individually or as a batch. Note that the titrator can only store 100 results, so data should be backed up and the titrator memory cleared regularly. To Backup and clear the Titrator use the following procedure:

- Plug a USB into the USB port on the titrator
- Navigate to the 'Save to USB' menu as described above
- Select the 'Copy All' option and wait for it to finish
- Return to the Home screen using the 'Escape' button and wait for the USB activity light to turn off.
- Remove the USB drive and connect it to the computer that will store the downloaded data
- Navigate to the 'HI901' → 'Reports' Folder. This is where the data files are stored.
- Cut and paste the files to a folder on the computer and name the folder with the date of the download
- Once the files are successfully backed up on another computer, press the 'Delete All' option and wait for it to complete
- The titrator memory is now empty and new samples will begin indexing from 1

3.4   Switching Titrants

*Note: **If you are only doing Modified Acidity (or Standard Acidity), then you will always just use the '0.02N Sodium Hydroxide NaOH' and you won't need to switch titrants.** However, this section describes if you want to switch from Sodium Hydroxide and use another titrant (e.g., hydrochloric acid for Alkalinity test).*

When switching titrants, the burette must be thoroughly rinsed before use to prevent cross-contamination. To switch titrants:

- Disconnect the tubing from the initial titrant container
- The plastic connections can be very tight and may require a clean pair of pliers to unscrew. The connections are very fragile so care should be used when handling.
- Screw the tubing connector onto the distilled water container

- From the Home screen, select the 'Burette' option
- Select the 'Prime Burette' option and press '3' on the number pad to rinse the burette 3 times.
- Press 'Accept' and wait until the process has finished.
- Next, Disconnect the tubing from the distilled water container and attach it to the new titrant container.

- Repeat the 'Prime Burette' process with the new titrant connected
- The titrator is now ready for use

4. pH Probe Operation & Maintenance

4.1   Using the pH Probe

When using the pH probe, it is important to remove the fill cap and keep the glass frit at the bottom of the probe clean. Removing the cap creates a pressure differential that allows the fluid inside the probe to leak through the frit and mix with the sample, improving reading stability. The titrator temperature probe should always be used with the pH probe, as pH is influenced by temperature and the titrator will calculate corrections based on the temperature of the sample.

4.2   Storing pH Probe

When the pH probe is not going to be used for several hours, the probe should be placed in storage solution and the fill cap should be put back on. The green cap on the storage solution container can be loosened so that the probe slides easily into the storage solution container. It can then be tightened slightly to ensure the probe stays connected to the storage solution container. When the probe is to be used ensure the screw cap is removed and that the probe is rinsed with distilled water before use.
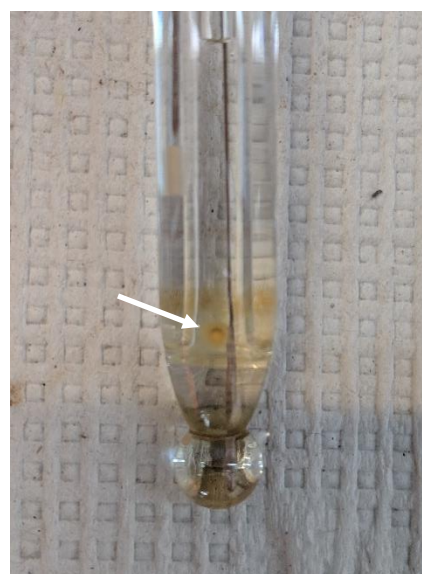
4.3   Cleaning pH Probe

During regular use, the pH probe will become stained. To maintain the probe's accuracy and response time, the probe should be cleaned using Hanna's HI7074L Inorganic Cleaning solution. To use, pour roughly 10mL of solution into a 50mL graduated cylinder. Place the probe into the cylinder, ensuring the stained area is fully submerged. Let stand for approximately 15 minutes. Do not leave the probe submerged for longer than 15 minutes as the solution will damage the probe with prolonged exposure. When finished, rinse the probe with DI water. Finally, wipe the probe dry and store it. After cleaning, the probe should be recalibrated before use.

pH probe ready for use   *pH probe ready for storage*   *Ceramic frit with staining*
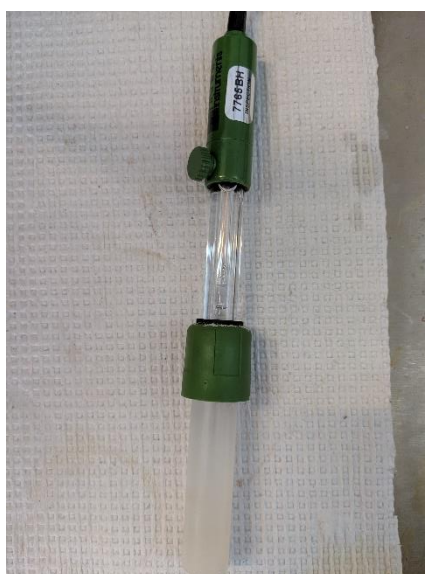
4.4   Calibrating pH Probe

When being used daily, the pH probe should be calibrated at least every other day. If not being used frequently, the probe should be calibrated before every use. The probe is calibrated with a 3-point curve using pH buffers of 4.01, 7.01, and 10.01. The probe should be calibrated in ascending order, starting with the pH 4 buffer.

To calibrate the pH probe, you will need:
- pH 4.01 buffer
- pH 7.01 buffer
- pH 10.01 buffer
- 50mL beaker
- Distilled water

Steps to calibrate:
- From the home screen, select 'Mode', then 'pH'
- From the pH menu, select 'pH Calib.'

- Press the 'Previous Buffer' button until the 4.01 buffer is selected.
- Rinse the pH probe, temperature probe, and beaker with distilled water.
- Fill the 50mL beaker with 20mL of pH 4.01 buffer.
- Swirl the 4.01 buffer around the beaker to rinse it with buffer.
- Then pour this buffer over the probes to rinse them too.
- Now refill the 50mL beaker with 40mL of 4.01 buffer.
- Insert the temperature and pH probe into the solution, ensuring the glass frit on the probe is submerged.
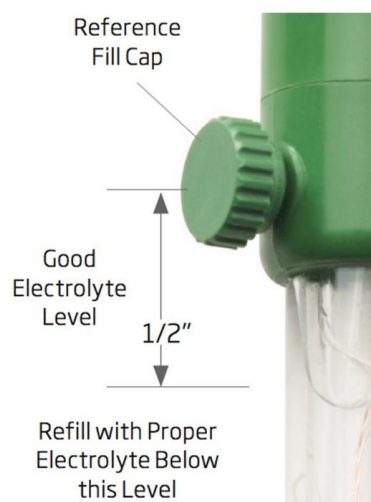- Wait for the reading to stabilize and select 'Accept'.
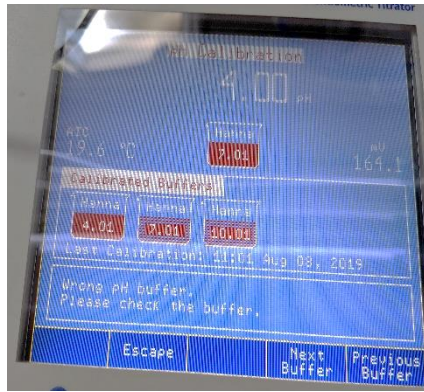
- When the probe is ready for the next buffer, the screen will display the 'Wrong pH buffer' as shown below.
- Return the buffer to its container and rinse the probes and beaker with Distilled water.
- Repeat the process with the pH 7.01 and pH 10.01 buffers.

When finished, press 'escape' to return to the pH home screen

4.5   Refilling pH Probe

The Hanna HI1131 pH probe used on the titrator is a refillable probe, filled with a 3.5M Potassium Chloride (KCl) reference electrode solution. During use, this solution flows through the glass frit near the bottom of the probe into the sample solution. This helps with stabilizing the reading from the probe. <u>Occasionally the probe must be refilled to maintain the level of solution in the probe</u>.

The probe should be refilled when the level of solution in the probe falls below half an inch of the center of the fill cap as shown:


Reference Fill Cap

Good Electrolyte Level

1/2"

Refill with Proper Electrolyte Below this Level

pH electrodes that are refillable need to have their electrolyte (salt) level checked. The probe should be filled when the level falls below ½" from the fill hole opening. Having enough fill solution ensures that the reference wire is in solution for a single junction electrode and continuity with the inner junction for a double junction electrode. A proper level also allows for adequate head pressure to force electrolyte through the junction.

Source: https://hannainst.com/ph-electrode-maintenance-calibration-guide

To refill the probe, you need the following materials:

- HI 7082S 3.5M KCl Reference Electrolyte Fill Solution
- Dropper
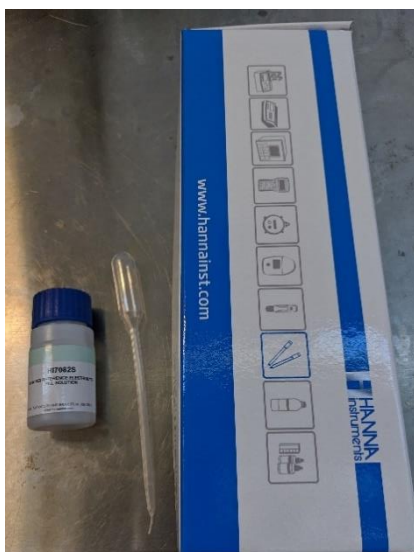
Both items are stored in the pH electrode box. To refill the probe:

- Open the Fill Solution Container
- Squeeze the bulb of the dropper and insert into the solution.
- Release the bulb and all allow the dropper to fill
- Unscrew the fill cap and insert the tip of the dropper into the cap
- Gently squeeze the bulb until the probe is full.
- Replace the fill cap
- Return any remaining solution in the dropper back to its container
- Replace the cap on the Fill Solution Container and store.
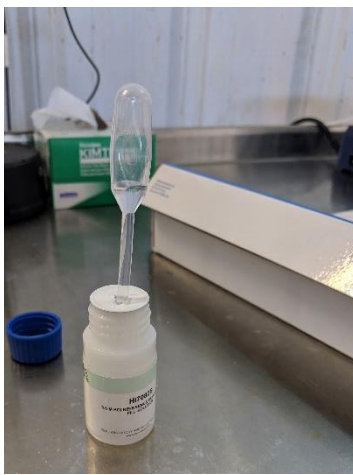
5. YSI Calibration & Storage

5.1 Calibrating pH

Like the probe on the titrator machine at the plant, the YSI uses a 3-point calibration curve using pH 4.01, 7.01, and 10.01 buffer.

Rinsing the Probe

The probe should be rinsed before and after each buffer solution:

- To rinse the probe, fill the calibration cup approximately ¼ full of distilled water.
- Thread the cup onto the probe and shake vigorously for 5-10 seconds.
- Following the rinse with distilled water, the probe should be rinsed again with the next calibration solution.

Calibration

1. From the main screen, press the 'CAL' button on the YSI to open the calibration menu.
2. Select 'ISE1 (pH)'. This will open the pH calibration menu.
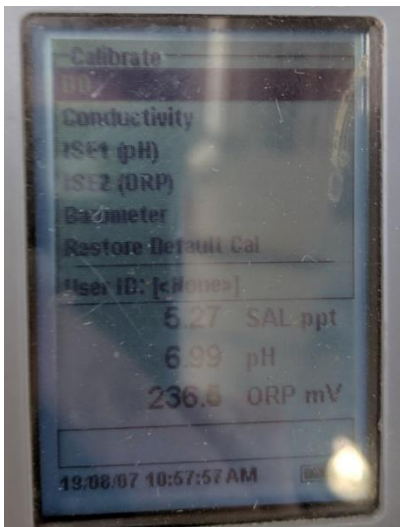
YSI Calibration Menu

Calibration Cup Fill Level

3. If not done already, rinse the probe with distilled water, and then with the first buffer solution (pH 4.01).
4. Fill the calibration cup 2/3 full with buffer and thread the cap onto the probe.
5. Ensure the 'Calibration Value' matches the concentration of the buffer. If it doesn't match, select the 'Calibration Value' option. This will open a number pad that you can use to enter the concentration of the standard. Select the 'Enter' option when finished.
6. Wait for the reading to stabilize and press 'Accept Calibration'.
7. Return the buffer to the storage container. Update the storage container with fresh buffer every 2 weeks.
8. Rinse the probe as described above and repeat the process with the pH 7.01 and pH 10.01 buffers.
9. After calibrating with all three buffers, press the 'Cal' button to finish and accept the calibration.

5.2   Calibrating Conductivity

Selecting Calibration Standard

- The conductivity probe utilizes a 1-point calibration. The standard used to calibrate the probe should reflect the values you expect to measure.
- Conductivity measured in the collected mine water samples typically ranges from 4000-5000 uS/cm in the #12,14,16,17 collieries to above 40,000 uS/cm in Princess.
- As a result, the 12880 uS/cm was thought to be a suitable middle ground for this application.
- If analyzing samples that may fall outside this range, it could be beneficial to use a different calibration standard.

Rinsing the Probe

The probe should be rinsed before and after calibration:

- To rinse the probe, fill the calibration cup approximately ¼ full of DI water.
- Thread the cup onto the probe and shake vigorously for 5-10 seconds.
- Following the rinse with DI water, the probe should be rinsed again with the calibration solution.
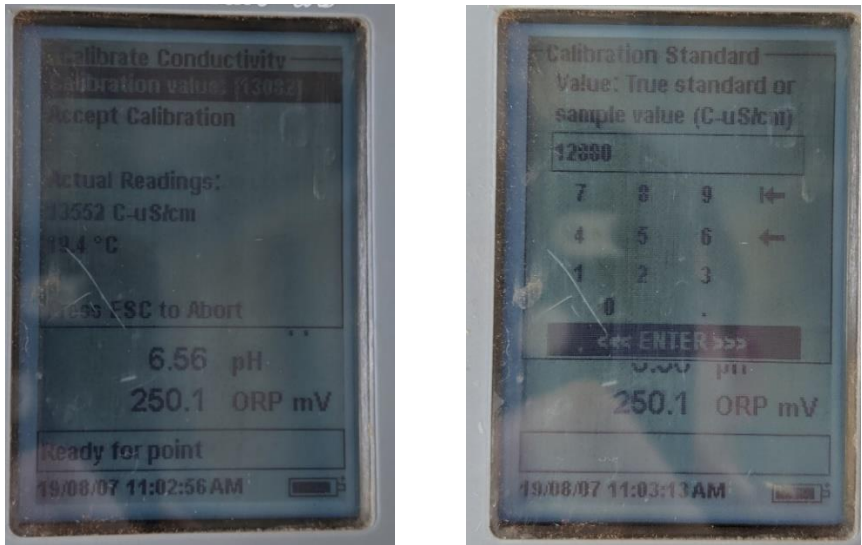
Calibration

The following steps outline the calibration process:

1. From the main screen, press the 'CAL' button on the YSI to open the calibration menu.
2. Use the arrow keys to select the 'Conductivity' option from the parameter selection screen.
3. Once again, use the arrow keys to select 'Conductivity'
4. Select the micro-Siemens per centimeter (uS/cm) option. This will bring you into the calibration screen for conductivity.
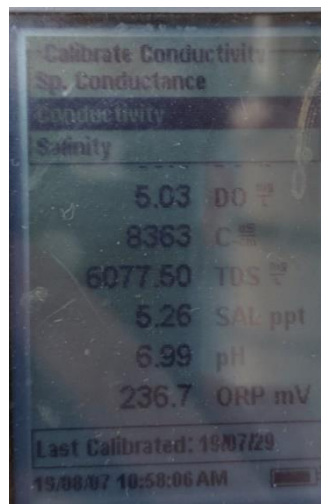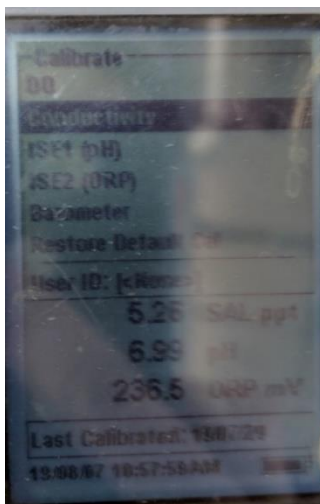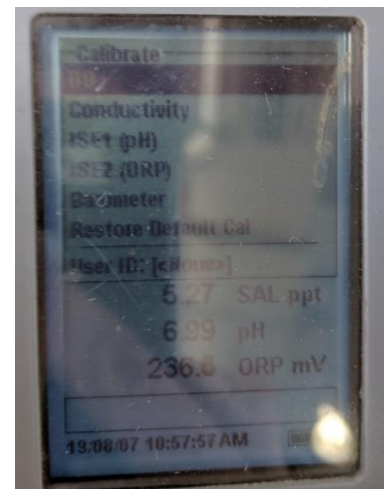

Navigating the YSI Calibration for Conductivity (Steps 2-4)

5. Change the calibration value to the desired value by selecting the 'Calibration Value' option. This will open a number pad that you can use to enter the concentration of the standard. Select the 'Enter' option when finished

Conductivity Calibration Screen (Step 5)

6. Once the value has stabilized press the 'Accept Calibration' option. The probe will calibrate and return to the main screen.
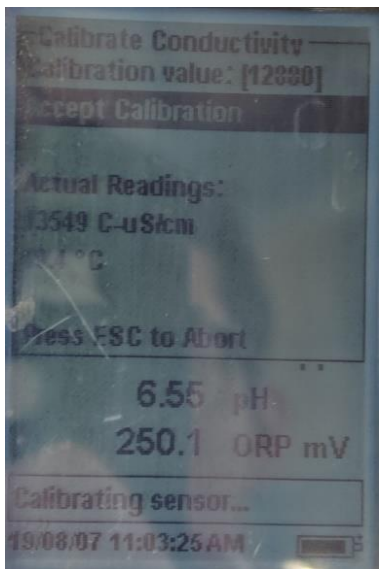
Accept Conductivity Calibration Screen (Step 6)

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