Dewatering Strategies and End Use Examination of Paper Mill Residuals

by

Brittany A. MacDonald

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Abstract

Thesis study objectives included a definition of dewatering technologies and methods which can be actively applied to the Port Hawkesbury Paper (PHP) in their secondary treatment regime. Literature review and contact with paper mills within the country led to a focus on acid injection to dewater PHP sludge followed by additional methods such as sonication. PHP desired an economic analysis of the acidification process to provide proof of concept, as well as present an estimated return on investment period which would ultimately adhere to company standards.

Dewatering is an interminable concern in the pulp and paper industry due to the copious amounts of residuals produced by the paper making process, better known as 'sludge.' This sludge residual product is composed of bio solids, wood fibers, and clay (MacDonald *et al*., 2017). In the case of PHP, this sludge leaves to be burned for power generation and/or to become part of a limited timeframe landfill topping project. PHP desires to move away from the landfilling option and also increase the value of their sludge for burning by improving its typical 25-38% dryness (depending upon the season). Increasing dryness would relieve the mill of moisture penalties for low value sludge and would also open the door to explore further end use opportunities of this waste product, such as pelletizing which is briefly explored in this study.

Acidification proved economically viable through a series of bench scale and *in-situ* trials which comparatively investigated ferric sulfate versus 93% sulfuric acid. A payback period of less than two years was estimated, and trial success led to laboratory scale investigation and visitation to a paper mill in Alberta (Alberta Newsprint Company), who demonstrated interest in the results of this study at PHP. Initial trials also took place to define pelletizing potential of sludge in its non-acidified state, further highlighting the need for increased dryness of PHP's sludge, leading to additional examinations into sonication. Sonication however, has shown little improvement in sludge dryness via separation of solid and liquid portions and is not currently economical for PHP, but has shown the ability to change the consistency of sludge samples creating a slurry which may prove useful in other treatment facilities.

List of Abbreviations and Symbols Used

AD	Anaerobic Digestion
ANC	Alberta Newsprint Company
CHP	Combined Heat and Power
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
FPI	Forest Products (FP) Innovations
GHG	Greenhouse Gas
IRAP	Industrial Research Assistance Program
IWS	International Wastewater Systems
MLSS	Mixed Liquor Suspended Solids
NAFTA	North American Free Trade Agreement
NSERC	Natural Sciences and Engineering Research Council
PCDD/Fs	Polychlorinated dibenzo- p-dioxins and Dibenzofurans
PHP	Port Hawkesbury Paper LP
RCF	Relative Centrifugal Force
SE	Standard Error
WAS	Waste Activated Sludge
WERF	Water Environment & Reuse Foundation
WTO	World Trade Organization
WWF	World Wide Fund for Nature
α	Significance Level
u	Uncertainty

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Sludge samples were initially tested in late early 2015 by consultant, Robert Anderson of Robert Anderson Consulting. Anderson has been worked closely with PHP to initially provide data on the components of the sludge produced at the mill and whether or not all criteria by law are met. Dale Scott and the staff at SF Rendering, Centerville, Nova Scotia were also very gracious in allowing us to tour their facility and perform a pelleting trial with PHP sludge.

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Chapter 1: Introduction

1.1 The Industry

1.1.1 Pulp and Paper

Beginning in the 1800's the pulp and paper industry flourished in Canada the rudimentary nature of paper making technology; however, over the years this has changed, creating a technology-dependent industry that due to declining market patterns, is now fighting for survival. From the early 1900s, Canada's areas, abundant in woodlands allowed it to become the prominent newspaper producer, holding the largest share of the industry in North America until the ~1920s (Kuhlberg, 2015). Over expansion of the industry soon after became an issue. Regardless, through wars and decades the newsprint industry stayed strong. Particularly, the government began playing a part in the success of certain industrial settings:

> [i]n the late 1950s, for instance, the Nova Scotia government convinced a leading Swedish pulp and paper maker, Stora Kopparberg (now Stora Enso), to construct a major sulphite pulp mill in Port Hawkesbury by offering it access to the local supply of pulpwood (Kuhlberg, 2015).

However, in recent years, Canada has faced a slew of mill closures, among other reasons, reduced consumer demand, increased international competition, woodlot depletion, the disruption of technological innovations as well as tariffs between producing and consuming jurisdictions (Kuhlberg, 2015).

Nova Scotia is now home to only two pulp and paper operation, Northern Pulp (Pictou, Nova Scotia) and Port Hawkesbury Paper (Port Hawkesbury, Nova Scotia) following multiple mill closures a few years ago (Woodbridge, 2015), (Hoffman *et al*., 2015). These remaining mills have come under new ownership since a series of other mill closures and

> "both businessmen have brought fresh new ideas, new attitudes and innovation. As a result, Nova Scotia's pulp and paper sector—which almost disappeared three years ago – is now

> emerging as a more profitable and sustainable long term contributor to the province's economy. Many existing jobs were saved, and new ones created" (Woodbridge, 2015).

Northern Pulp has undergone much scrutiny in recent years, not unlikely in the paper industry, but in Pictou, Clean Pictou Air, a group formed to advocate against pulp mill pollution has become involved in the tourism sector affected by the Northern Pulp mill (Hoffman *et al*., 2015; The New Glasgow News, 2014) . It is expected that any emission producing process would undergo similar concern; emissions include "acetaldehyde, formaldehyde, lead, manganese, and chlorinated hydrocarbon byproducts" (McCarthy, *et al.*, 2009). Regulations have changed over a number of years regarding acceptable emissions, however now focusing more heavily on fine particular, more likely to enter into the human body.

> "The sources and formation pathways of ground-level particulate below 2.5-micron diameter (<$PM_{2.5}$) are very different from those for larger particulate matter. Thus, $PM_{2.5}$ composition generally changes between the stack exit and point of deposition. The control of ground-level $PM_{2.5}$, therefore, has to focus not only on particulate leaving the stack, but also on both stack and atmospheric sources of SO_x, NO_x and VOC, since their chemical reactivity with the suspended material makes them fine particulate precursors" (Bruce, & van der Vooren, 2003)

Comparatively, Port Hawkesbury Paper has undergone not only numerous ownership changes but also the presence of tariffs; all paper producers face variable issues, however; effluent is a common concern in the paper industry. Effluent is commonly a concern for the fish populations in the nearby area and following studies conducted on bodies of water connected to outfall, even in the cases of assumed non-lethal effluent (Mower *et al*., 2010; Munkittrick *et al*., 2013; Chiang *et al.*, 2011; Dahmer *et al.,* 2015), notably, with the implementation of a secondary treatment processes this concern is mitigated but not removed. Chlorine was a halogen of high concern, prompting 'adsorbable organic halide' regulations, to the point of no tolerance; this was thought to be linked to reproductive issues (Munkittrick *et al.,* 2013); however this effort did not succeed nor was it proven; however, chlorite, a derivative is known to be very hazardous in toxicity testing at concentrations at and above 0.01ppm (Ken Mitchell, Port Hawkesbury Paper LP, Environmental Compliance Officer, February 2017, *pers comm.*) Concise identification of specifically harmful chemicals is immensely difficult, with the best solution being to monitor points upstream as well as downstream of outfall (Mower *et al.,* 2010). A 2011 Chile study proved that the endocrine system can be affected by pulp mill effluent and that long term reproductive affects are possible such as increased gonad size in close proximity to outfall (Chiang *et al.*), furthermore, study in the Canadian Jackfish Bay, Lake Superior showed following brief closures and ownership changes slight recovery in the aquatic ecosystem. However, long-term remnants persisted, the focus of this study being Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) typically linked to bleaching processes and ingested by the fish (Dahmer et al., 2015). The issue of PCDD/Fs has since been mitigated through regulatory measures.

1.1.2 Target Industry

Overall, in Canada, forestry related products are responsible for 3% of the gross domestic product but also consumes close to 25% of the available energy; energy is a key component in the production process (Benchmarking Energy Use in Canadian Pulp and Paper Mills, 2015). In recent years, three Nova Scotian pulp and paper mills were shut down within a short period of time; Minas Basic Pulp and Power Company Ltd., NewPage Paper and the Bowater Paper mill. The NewPage facility was purchased in 2012 and re-opened as PHP; in this case it was able to rebound and secure a spot in the dwindling industry (CTV News Atlantic, 2017). However, this situation is not without the constant pressure to remain competitive and economically viable.

Port Hawkesbury Paper (PHP) is one of approximately 30 paper mills in Canada surviving, down from 50 operations in 2000. The facility produces a variety of super calendared paper products, in order of decreasing brightness, Artisan (magazine or catalogue), Prominence Plus (magazine or catalogue), Prominence (magazine or flyers), and Maritime (inserts or flyers). The mill itself has gone through numerous owners and changes as outlined in the chronology below:

- Built in 1960 – Stora
    - Newsprint Producer
- 2006 Lockout for 10 months
- 2007/2008 Stora sells to New Page
    - Newsprint and Magazine Paper Producer
- 2011 NewPage closes indefinitely
- 2012 Vancouver company purchase
- 2012 Port Hawkesbury Paper opens
    - Super Calendar Paper and Newsprint
- 2013 Paper Machine 1 (PM1) shutdown indefinitely
- 2015 PM1 demolition commences

Perhaps most notably, PHP has had a trade tariff placed upon them by the United States government of an additional 20%; however, they are in the midst of an appeal under the North American Free Trade Agreement (NAFTA) with the World Trade Organization (WTO); nonetheless they are always looking to increase cost efficiency and production to better the mill's competitive structure (Irish, 2015).

1.2 The Process

The paper-making process as described by Smith (2015) begins with harvesting of forest materials (trees) from which the bark will be removed, and the debarked trees processed into smaller chips. Pulp is made from these chips through a pressure cooking process along with the addition of various chemicals. The pulp then goes through a unique process which can include bleaching, dye addition, further crushing, etc., to then go through a screen where water is removed and taken away for reuse or treatment. The screened pulp is then transferred to system of rollers to further drain water and formulate the initial paper product. This product can then go through further processing to achieve the desired final products, (*i.e.* calendar, newsprint, etc.) (Smith, 2015).

As with all large industrial operations, this process creates a large quantity of waste; in the case of PHP over 6 tonnes per hour of sludge residual is released from the plant. Part of this sludge is burned in a biomass boiler located near the site, but the remaining is spread around the grounds of the mill and form a landfill; so much so that part of the landfill has already been capped. The capped land allows for vegetation growth, but the area needed to accommodate all the sludge is considerable and at some point will reach capacity. Landfilling is accompanied with environmental concern such as leachate (Mukherjee *et al*., 2014); however, with the composition of PHP sludge being that of wood fibres, clay, and secondary treatment bio solids, this sludge does not pose a great concern. Maintaining safe landfilling practices is also possible through monitoring of leachate plumes and components of typically high COD and BOD values (Mukherjee et al., 2014). In the past, a portion of this sludge was used as a soil replacement (gardens, etc.) with promising results (Port Hawkesbury Paper, Engineering Department, 2015, *pers comm*.). However, the presence of coliform, whilst insignificant, is undesirable and rendered this option unappealing to the average consumer; this soil replacement option quickly came to a standstill.

1.3 Research Questions/ Study Significance

The first and greatest roadblock, which must be overcome to find additional uses for sludge is moisture content. Currently, PHP averages a solids content of slightly greater than 30% which fluctuates depending on additions to the sludge mix, seasonal conditions, and primary to secondary sludge ratios. The mill has studied various potential options for reuse, with common choices being burning, as is the case at PHP, and anaerobic digestion (Port Hawkesbury Paper, Engineering Department, 2015, *pers comm.*).

Pelletizing the sludge is another option as there are two very useful types of pellets which can be made from sludge residual: wood pellets for residential/ commercial burning and agricultural pellets which are used as a soil replacement/ augmentation. Wood pellets would be of a great advantage for the Cape Breton economy, its inhabitants, and also other areas of the world. Domestic demand for wood pellets both in Cape Breton and mainland Nova Scotia has dramatically increased in recent years. Consumer demand so exceeds local supply that line-ups for wood pellets at retail outlets are commonplace (CBC News, 2015).

1.4 Objectives

As previously mentioned, energy is a major expense in the production of forestry products such as paper; at PHP the opportunities to either produce energy internally or to generate additional value by exploiting all available waste streams is being investigated. For example, for the initial duration of this project pelletizing was the primary focus. However, it became apparent during preliminary investigations that there are many challenges to overcome during the initial preparation of sludge if it is to be used in the pelleting process. Focusing then on the current PHP sludge waste destination, burning, through discussion with industry experts as well as literature review acidification became a likely solution for a moisture-rich (low calorific value) product. This involves injection of acid to affect mobility via pH alteration with the intent of microorganism eruption of increase water removal. Two acids, ferric sulfate (10% sulfuric acid) and concentrated 93% sulfuric acid were to be compared; these acids were chosen based upon a 2015 study done by FP Innovations which suggested sulfuric could act as a dewatering agent and reduce requirement for thickening chemicals (coagulant and polymer). Ferric sulfate was also tested briefly at PHP and has the potential for increased safety compared to sulfuric acid as well as iron recirculation, odor reduction and thickening chemical reduction (Brad MacLean, Kemira, Technical Sales Rep. September 2015, *pers comm*.). Sonication was also investigated as a follow up method of dewatering due to the potential for sample disruption through the use of ultrasonic waves.

The overall objectives of this study were: a) to determine the most cost-effective drying method for PHP's sludge; and then b) investigate the potential for pelleting the dried sludge. Within each of these objectives, there were a number of sub-objectives that needed to be addressed such as whether a physical or chemical treatment is most effective and if a chemical treatment is effective, determining the optimal acidifying agent (sulfuric acid or ferric sulfate) to reduce the moisture content. In this instance, this includes analyses of pH changes in the sludge following acid addition, moisture release, and effects on polymer and coagulant use. The latter is important as acidification may decrease the need for these additions in the current dewatering process and therefore result in cost savings. In addition, such analysis would be valuable when published in the primary literature as a defined pH for control of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) has yet to be properly documented.

Improvement upon sludge dryness and in turn decreasing volumes of sludge produced will not only affect PHP and the environment positively both physically and economically, but this will also improve public perception surrounding pulp and paper operations which has been examined by Hoffman *et al*. (2015) in the areas of concern regarding employment (competitive nature of industry improved with sustainable practices), transparency, and community involvement .

1.4.1 Research Questions

1) Can a dryness increase at PHP be best obtained through technology or chemical addition?

    a. Acidification (chemical)
    b. Sonication (physical)

2) If using acidification, which acid is the most economical, ferric sulfate or 93% sulfuric acid?
3) Can an overall relationship be drawn between PHP's experimental results and those of other paper mills/ waste producers?

1.5 Introduction to Following Chapters

Chapter 2 provides an overview of sludge dewatering methods as well their relative success potential. Comparisons between methods include economics, end goals, and process requirements. This chapter along with discussion with industry professionals in the pulp and paper field led to a choice in methodology best suited for the case study mill, PHP, in the case of this project being acidification.

Chapter 3 explains methodology used in each stage of my project, beginning with acidification, followed by a brief examination of the potential for PHP's sludge be pelletized in it's initial state, and finally an additional method of dewatering, sonication. This chapter also provides notable construction aspects which will allow readers to replicate the process with minimal error.

Chapter 4 presents the bulk of the results of an acidification trial at PHP on both a laboratory scale as well as *in situ* trial structure; this chapter has been presented in publication form.

Chapter 5 includes supplemental information and data relating to Chapter 4, that which has not been included in the publication. This chapter also includes results of the first month of operation of a permanent acidification process put into place at PHP following *in situ* trial success.

Chapter 6 briefly discusses results of an off-site investigation into acidification potential which took place at the Alberta Newsprint Company; this is then further supplemented in Appendix F.

Chapter 7 contains a comparative analysis of acidification and sonication with the goal of investigating the potential of each alone as well as in combination to produce a product of increased dryness. Results have been performed on a laboratory basis and is intended to indicate if sonication should be further investigated in relation to PHP. This chapter has also been presented in the form of a publication.

Chapter 8 comprises pelleting data from trials conducted early within the project in Centerville, Nova Scotia, along with information collected during tours of waste treatment and usage facilities in the Halifax, Nova Scotia area. The data seen here has been used to show the need for increasing sludge dryness prior to end use designation outside of the current strategies used at PHP.

Chapter 9 finally presents conclusions regarding best dewatering choices at PHP as well as recommendations for moving forward and further exploring the potential for PHP to broaden their product horizons.

Chapter 2: Literature Review

Many methods of sludge dewatering have been documented; however,he most common/successful have been highlighted below.

2.1 Freeze/Thaw

The freeze/thaw method of sludge dewatering usually requires a two-compartment system which allows for freezing and thawing using energy and then again creating further energy. Researchers suggest that this process works best with inorganics if alum is added for conditioning (Electric Power Research Institute, 2002). Crystallization of water within the samples will occur while in the freezing process allowing for a differentiation between water and other sample composite sources due to the binding of crystal structures (Electric Power Research Institute, 2002). Variables to control in this process are solids concentration as well as freezing rate and duration. One particular technology, a "Biofreeze unit" which has a relatively small footprint- that of a flatbed truck, was used to determine dewatering abilities of inorganic and biological samples. Results were positive regarding volume decrease of inorganic samples; however, this is not the case for all samples of varied composition (process dependent, *i.e.*, chemicals, microorganisms, and wood fibers) (Electric Power Research Institute, 2002). Energy required for such processes is also a concern, but this particular technology also had the unique ability to recover batch energy (Electric Power Research Institute, 2002).

The downfall of this technology is its cost: the construction of a unit to complete the freeze/thaw process would be over a million dollars. This is typically not feasible as most mills will already have a water removal system in place; the economic gain from replacing this would not be worthwhile (Reed *et al.,* 1986).

2.2 Anaerobic Digestion

"The anaerobic digestion process generally consists of four stages, hydrolysis, acidogenesis, acetogenesis and methanogenesis" (Kim *et al*., 2003). Anaerobic digestion (AD) allows an activated waste product from the breakdown of organic compounds to be turned into a beneficial energy source such as methane. This energy can then be used as a heat source to further dry a sludge product, but it can also kill dangerous components such as pathogens, improving the ease of end use (Mills *et al.*, 2014). Depending on the composition of the input sludge and the desired output materials, anaerobic digesters, through their reactive breakdown process can provide a dewatered product in comparison to the input sludge. The final drying is accomplished on a drying bed or belt filter press (Streicher, n.d.). Figure 1 shows the flow of an anaerobic digester.

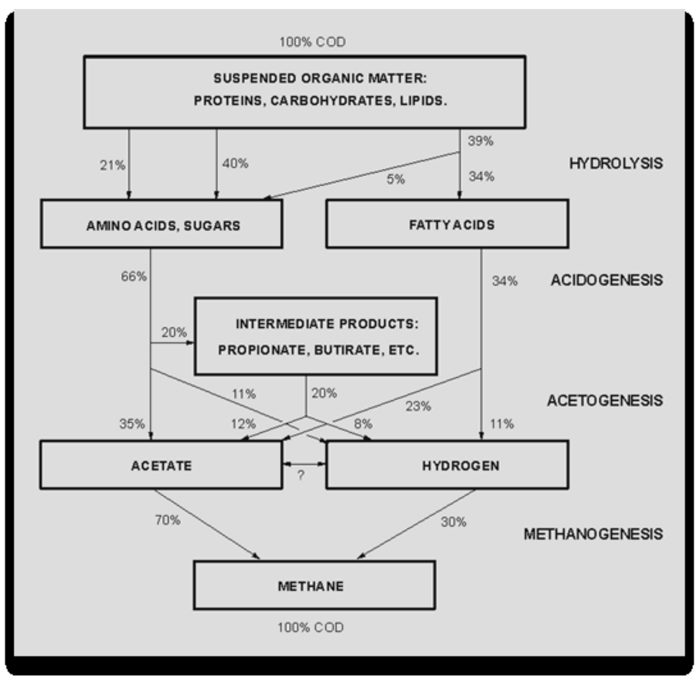

Figure 1 – "Schematic representation of the decomposition pathways of excess activated sludge (and other organic material) by anaerobic digestion" (from Haandel & Lubbe, 2007).

However, anaerobic digestion can be extremely expensive even at a pilot scale, and typically needs additional skill sets not normally associated with the operation of a pulp and paper mill.

2.3 Gravity Drying

Gravity drying is a type of natural drying (Alturkmani, 2012) that is typically the cheapest of all methods. In most cases it simply requires a large tract of land and turnover farm-style equipment. However, this method is tends to be most successful in temperate, dry climates – somewhat different than that which would be found in Nova Scotia, and more specifically Cape Breton. To improve the drying rate in less than ideal environmental conditions, air can be injected into the pile which is especially useful if the end use is as biomass fuel for incineration (Frei *et al*. 2006). However, industry specialists are currently formulating a similar process to that of gravity drying, but developed to service wetter of climate (Conrad Allain, TransAqua, Director of Technical Services, 2015, *pers comm*). Using the idea of a gore-tex covered area with airflow a process is being designed that begins with 30% dryness (equivalent to PHP) and then mixes the sludge with bark to provide a volume for release of moisture and increased porosity to support improved airflow thereby promote drying. At the time of writing this system is slated to be implemented at a facility near Moncton, New Brunswick in the near future.

Frei *et al*. (2006) developed a brief scenario based synopsis for mill has been helpful in determining if implementation on any particular mill site is feasible by using a set group of parameters (most importantly being an initialdryness of 26%) to allow for further extrapolation:

- "Worst Case Scenario: Long residence time requirement in the reactor and only 45% dryness achieved, low sludge and woodwaste energy content, high woodwaste/sludge mixing ratio of 1:1, low internal drying temperature;
- Best Case Scenario: Short residence time in the reactor and 60% dryness out of biodrying, high sludge and woodwaste energy content, low woodwaste/sludge mixing ratio of 1:0.25, high internal drying temperature, short-distance material handling conveyors; and
- Likely Scenario: Similar to base case except that existing material handling facilities at the mill are adequate (i.e., no cost was included for conveyors and mixing equipment), i.e., likely values for residence time, sludge and woodwaste energy content, and mixing

ratio (1:0.5), 55% dryness out of biodrying, low internal drying temperature" (Frei *et al.* , 2006).

An alternative method includes a simple filtration system tested in a small-scale study, which revealed that addition of water to a dry sample for such a process inhibits the ability to release water without an additional drying force or step, as sludge is likely to withhold the moisture (Markovic *et al*., 2014). Comparatively, vacuum filtration is much less time consuming and does produce a greater dryness (over a set time period) (Logsdon & Jeffrey, 1966)., however, likely still requiring additional drying steps which in the initial description of gravity drying is accomplished either due to the location based environmental temperatures, or heating mechanisms.

2.4 Acidification

Acidification involves the addition of a strong acid with the intention of breaking molecular bonds and of eruption of bugs within the secondary sludge compound; acid would breakdown the organisms to release water These chemical and physical transformations improve the dewatering abilities of the sludge. Acidification has proved promising in mills within the country as well as within specialized research groups, such as FP Innovations (FPI). For example, FPI have demonstrated that ferric sulfate can increase product dryness and also decrease coagulant requirement, but with both coagulant and acid present, the dryness had seen a maximum point (FP Innovations, 2015). Such information was documented in a short presentation to PHP and further explained through discussion with FP Innovation's Research Manager, Talat Mahmood (2015, *pers comm*). A bacteria removal aspect is an additional benefit of the acidification process.

Acidification acts not only as a method that decreases moisture retention, but can also potentially improve the release of heavy metals that have been found to bond to sludge particles (Ong *et al*. , 2008). The addition of acid enhances heavy metal removal as concentration increases (Fen, Hu, Mahmood, Long, & Shen, 2008). Heavy metals have known toxic effects on the receiving environment and also on the performance of biological waste treatment processes (Ong *et al*., 2010). Therefore, acidification has an additional value if the goal is to expand the end use of the sludge beyond that of burning, for example to be used as a soil amendment.

2.5 Fournier Rotary Press

Fournier Rotary Presses are specialized to intake reactant into a flocculent tank and combine it with an optimal amount of polymer additive. This piece of equipment is also manufactured for ease of cleaning as the two presses within are non-clogging, less electricity intensive and quieter than most systems. Final cake dryness can be controlled by the operator of the conveyor-like machine which is a huge benefit along with the containment of odor (Rotary-press.com, 2015), (Elliot, n.d.).

This technology has been of ongoing interest to PHP, however, laboratory trials, approximately 1 yr ago took place estimating the effects of implementation of this press into the mill and the results proved unsuccessful (Elliot, 2014) From contact with other waste treatment facilities, this type of press has been useful in the past at facilities such as the Halifax Waste Water Treatment Facility, but are currently being replaced (Halifax Aerotech Wastewater Treatment, 2105, *pers comm*).

2.6 Sonication

Sonication is a process where rapid sound vibrations initiate cell lysing which can allow for ease of water release from cells within sludge (Figure 2). Laboratory scale sonicators run generally from $1000 and up (Sonicators, Homogenizers, 2017) depending on the desired wattage and result, but are also accompanied by the benefit of a user safety aspect. When using this device, the user is in much less danger, requiring for the most part only ear protection from the very high pitched sound ("Sonicator Safety | Lab Manager", n.d.), but this would reduce or erase the need for increased acid contact or spillage.

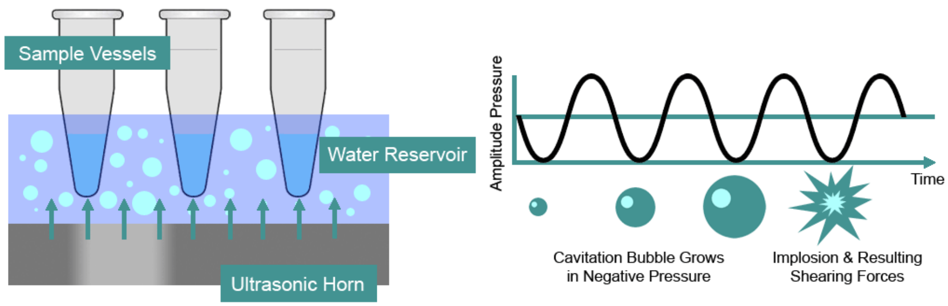

Figure 2 - Simplistic view of sonication process (from Epigentek.com, 2015).

At an industrial scale, this may be an expensive process. Research demonstrates improvement in solids content from 0 to almost 2500 mg/L (on top of the initial solids contents) through a 35 min period at a power intensity of 125.8 W/cm^2 (Zhang *et al.*, 2008); however it is often noted that the medium being sonicated can be a needs for unique changes in operating parameters.

2.7 Cyclone Based Technology

A cyclone based drying in a blower style atmosphere seems to be a simplistic, yet extremely successful technology ("Resource Converting, LLC", 2017). The 'Dryclone™' by Resource Converting, LLC boasts the potential to dewater to less than 15% moisture ("Resource

Converting, LLC", 2017); in the case of moisture rich sludge (70-75% moisture), this would greatly increase the overall energy content of the sludge and increase its value in a context where it is being used as biomass fuel. The technical information available for this technology specifically names ‘paper sludge’ as an acceptable waste type for processing ("Resource Converting, LLC", 2017). The purpose of this technology is to dry all material present to avoid the need for sorting portion according to moisture content. The system utilizes air blowers to create a centrifuge-like operation which allows material to dry (removing moisture in a separate product stream) and presenting an overall dry basis product ("Resource Converting, LLC", 2017).

2.7 Summary

Various technologies of sludge dewatering investigated; literature and anecdotal information has indicated that may have proven successful in various treatment and dewatering plants across the globe. However, a key element in choosing the best option is a better understanding of the unique sludge properties and composition being managed; this will better inform to how the material will react in the case of each method. In addition, a number of facilities using these technologies often have no intention of using the dewatered sludge in a way that adds value, it is simply to reduce the weight of material for the purpose of transportation. In the case of this research, we are seeking to produce a useful product from the material. Moreover, climatic conditions can also impact the viability of certain technologies. For example, as previously noted, the gravity drying process often takes place in warm climates with little humidity or rain allowing for a natural effect without the use of much energy or fuel to heat. In a very cold, damp, and/or rainy climate (or season), efficient natural gravity drying may be next to impossible. Also, often times the addition of a new piece of equipment to replace the current sludge presses is not ideal; economically it may be better to simply supplement current processes with as little expenditure (in money and installation time) as possible.

Chapter 3: Materials and Methods

Prior to an experimentation, sludge was dewatered to the extent possible using Port Hawkesbury's existing equipment and processes. For further information on the existing dewatering process at PHP please see a more detailed description in Chapter 4.

3.1 Pelletization

Pelleting trials took place at SF Rendering, Centerville, Nova Scotia, where PHP sludge was tested for a high enough dryness to stay in pellet form (mechanical integrity in hopper, during auger movements) and also to produce sufficient sample mass for burning trials.

SF Rendering is in the possession of two pelleting machines previously used to manufacture grass pellets (Robert Anderson, Robert Anderson Consulting Ltd., July 2015, *pers comm.);* the owner (Dale Scott) of the plant allowed PHP to run pellet trials in their machines which developed a small pellet product for testing and also provided information regarding their drying processes and the degree of additional dryness one might receive from a pellet machine. A Super Sac of PHP sludge was used and shoveled directly into the pelletizer in one case, and was pre-dewatered through an expeller also found onsite at SF rendering in the second trial. These trials were conducted without measured sample inputs. Following experimentation, samples were returned to PHP for dryness testing using consistency pads. 250-500 mL samples are weighed wet, then again after being put in a speed drier for approximately 20 min at 100^{o}C. Final dryness values are the difference between wet and dry measures.

3.2 Acidification

3.2.1 Experimentation (Laboratory and *in situ* trial scale)

This sub-section acted as a guidance plan for the duration of the project with minimal re-organization/changes throughout.

Initially, pre-dating the choice of acidification, visits occurred to various facilities (N-Viro, Halifax Waste Water Treatment, C&D Tire Recycling) who agreed to provide and/or allow tours. These tours allowed for in-depth questioning regarding process flows, treatment methods, successes, and challenges faced, allowing for comparative discussion with regards to PHP operations. Although these plants have a commercial focus other than paper making, they all struggle with the similar challenge of waste end use and/or dewatering. Further and specific to paper-making, phone consultation to occur via phone with managers of FP Innovations and Tembec Matane who were also open to providing information regarding sludge dewatering practices.

Following discussions with paper mill representatives utilizing acidification, laboratory/bench scale acidification trials in collaboration with FP Innovations to supplement previous work conducted suggesting the potential for success with the addition of acid. Also, trials conducted in-house used 60% ferric sulfate and concentrated 97% sulfuric acid.

Introduction of acidification pilot plant (*in situ* trial) followed the bench scale experiments using sulfuric acid (93%) and ferric sulfate (10% sulfuric acid) as dewatering agents by mixing with primary and secondary sludge. This pilot plant required, in the case of the ferric sulfate, a large tanker truck to be parked within range of the sludge pumping stations to introduce this agent into various locations in the secondary sludge stream prior to where mixing of primary and secondary wastewaters occur. This test took place during colder months given the higher BOD and COD content and the greater amount of secondary sludge. With acidification, microorganisms in secondary sludge rupture to release water contained in their cells, facilitating easier removal in PHP's screw presses (the current method is dewatering to ~30% solids). Sludge entering the mill's mix tanks began at 3% consistency, moves through the rotary drainers increasing consistency to 8% and finally continues through the screw presses to obtain a final dryness of ~30%. The sulfuric acid was stored in totes and pumped into the same area as the ferric sulfate once the ferric trials were complete. A comparative analysis was then performed. Based on the results decision regarding the cost-effectiveness were assessed to determine if such a system should be integrated permanently.

Looking at the process of investigation and data collection, control systems were set up for analog readings to be transmitted from 3 pH probes; one in the initial dewatering pipe (10 min after acid addition) and one in each flocculent mix tank (1 hr after acid addition). Control dynamics used these values to regulate the pump speeds, as well as the values of secondary sludge being input into the mix tanks. Controls were set to run on shutdown and critical conditions.

General variables investigated regarding the acidification process included (data would appear in PI program used at PHP for real-time data management):

- Flow Totals per Day
- Waste Activated Sludge (WAS) amounts
- Metering Screw #1, 2 motor speeds (sawdust)
- Polymer Feed Flows to #1, 2 presses
- Coagulant Flows to #1, 2 presses

- #1, 2 Press Loads
- #1, 2 Press Speeds
- WAS Ratio (secondary/primary)
- Reactor Loads
- Bar screen and Influent Samples
- COD value
- BOD value
- pH
- Secondary Clarifier 1 WAS Values
- Primary Sludge Percent Consistency (Dryness)
- Sludge Gate Position (% going to boiler vs. % to landfill)
- Press Cake Percent Consistency (Dryness)

Changes in pH were assessed approximately 250 m after the acid addition to allow for a high degree of mixing. Investigations were also completed into effects of acid addition on coagulant and polymer use, secondary sludge produced, and impacts on BOD, and COD. Again, most of these readings were not taken by hand in a laboratory, but were available from on-line monitoring in the mill's data analysis system or obtained by operators (Appendix B). This allowed for real-time information on the plant and its processes.

Initial sludge dryness was completed using consistency pads (for WAS or recycled activated sludge (RAS)) or cake (final product) samples. In the case of consistency pads, 250-500 mL samples are weighed wet, then again after being put in a speed drier for approximately 20 min at $100^{o}C$. For cake samples, 500 g of sludge is placed on an 11 in by 13 in pan in an oven at a temperature of $105^{o}C$+/- $5^{o}C$ for 18 h and weighed again following drying.

Manipulation of primary and secondary collective composition (ratio) was controlled by operators along with addition of thickening chemicals which was lowered on a daily basis provided dryness values remained above the desired 30%. Thickening chemical values are lowered assuming acid can replace the need for currently used expensive chemicals.

The overall trial was run in a staggered fashion, running each acid for 1-2 d before switching, however, this ideal method could not be followed as a corrosion issue occurred causing the use of sulfuric acid to be discontinued on a trial scale.

3.2.2 Full-scale Trial

A full-scale trial was completed at the PHP site. Throughout the installation of the necessary equipment, various notable choices were made regarding materials and setup which would be useful to those seeking to emulate such a process.

Storage versus transportation of 93% sulfuric acid was a concern. A review of literature and communications with key experts indicated that 316 Stainless Steel was ideal for transportation and Carbon Steel was recommended for storage (InyoProcess, 2015). Existing infrastructure could be repurposed for acid storage.

Injection strategies were also key; during the initial *in situ* trial stages a leak was experienced causing a spray of concentrated sulfuric acid and in turn a discontinuation of use of this acid for the rest of the trial. This issue was later linked to the point and style of injection; during the *in situ* trial piping was simply connected into the outer portion of the WAS pipe (pipe receiving injection) which created a corrosion friendly zone due to acid sitting near the point of injection along the interior surface of the pipe. Over time there was some corrosion, so to ensure this wasn't an issue during any permanent installation, a quill technology (direct injection into the center of the stream) was implemented which would allow for injection into the center of the sludge flow rather than along the interior surface; sludge would be carried away upon contact removing the corrosion potential.

To further ensure protection, a chemical wrap, Wrap Shield by Drake Specialties, was placed around areas of concern and injection (Figure 3). Litmus paper in this wrap allows for early leak detection due to a color change.

Figure 3 - Chemical leak indicator wrap found on point of acid injection into WAS line.

In a permanent operation, pumps would be sized to match a certain acid and desired flow rate, however, during the *in situ* trial, two acids differing greatly in injection volumes were passed through a common pump skid. The pumps supplied for the *in situ* trial by Kemira were sized for ferric sulfate; however at this point, for the short duration of run time, the minimal use of capacity during sulfuric run times was negligible to the lifespan of the pump.

3.2.3 Site Layout

Permanent operations were implemented in the same area that *in situ* trials took place: however, there were major changes between the two operations. The overall area chosen is seen in Figure 4.

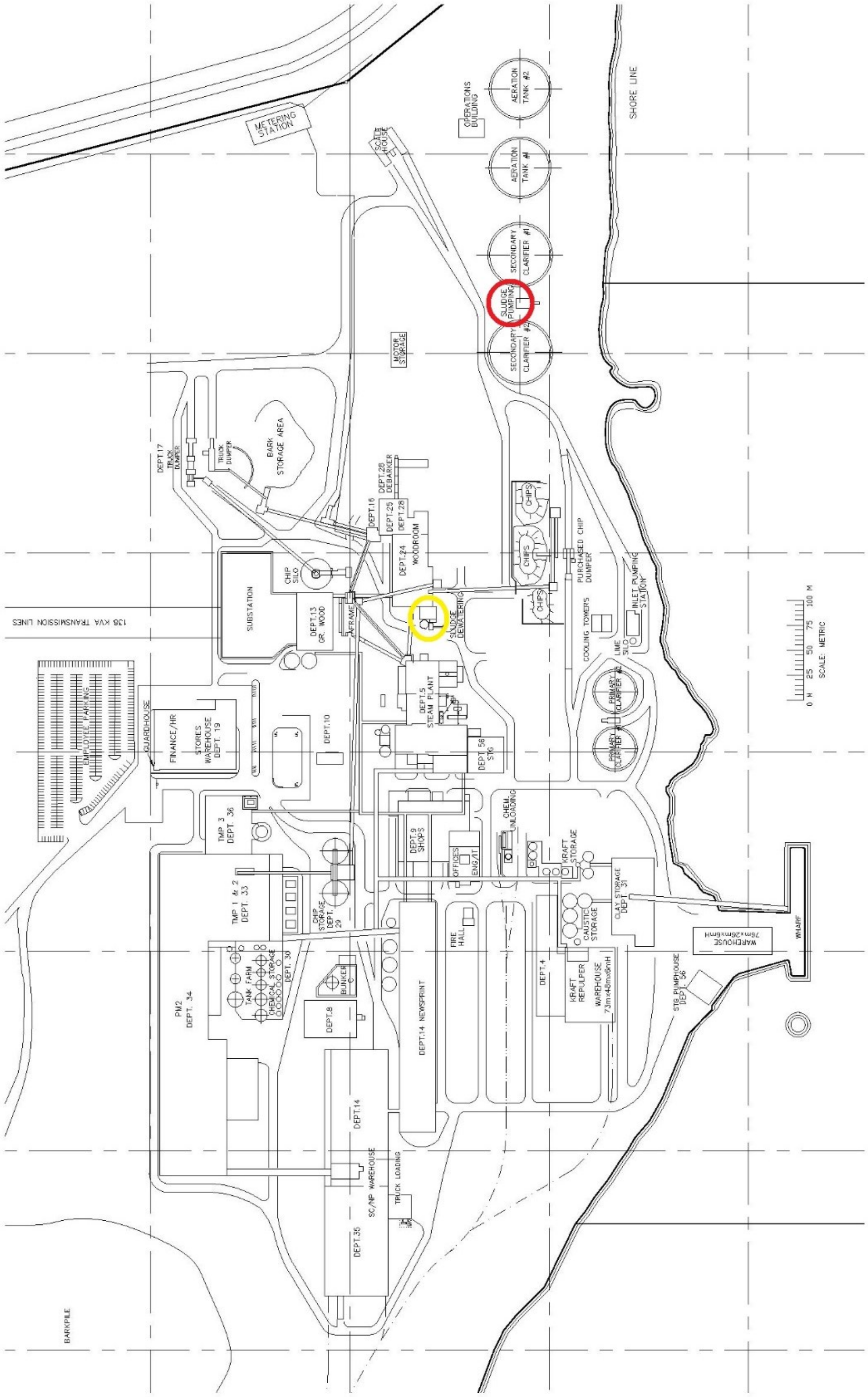

Figure 4 – Labelled site map of Port Hawkesbury Paper LP. Area indicated in red signifies injection/ storage area and yellow signifies pH measurement area.

All other aspects of the site can be found in Appendices A-E.

3.3 Sonication

3.3.1 Determination of Sonication Based Dewatering Abilities

Initial testing evaluated the limits of mechanical removal of water through physical pressure exerted over a progressively thin mixture of sludge relative to impinging surfaces. Various paired products, which exhibited complementary tolerances and angles allowing thin sludge layers for compressive forces to act against, were evaluated in pairs, with a goal of over 50% insertion into one another to allow. The design must further allow reproduce-able application of consistent force, and for extruded water from a sludge sample to be released (*i.e.* mesh screening) for quantification while pressure is retained to avoid resorption. Products evaluated at the laboratory-scale included Tupperware containers, small traffic pylons, red Solo™ cups, and stacking trays; typically the lower positioned of the paired items required drilled holes to allow for water removal with screening to allow for retention of solids. While similarities with all devices were observed, and may facilitate rapid assessment and inexpensive assessment at many workplaces the most consistent and reproducible water-removing device was a cider press, and unless otherwise indicated, was used for results shown. Extruded water was collected in a Pyrex beaker. With sufficient replication to accommodate inter-trial human error regarding ability to exert reproducible force, this protocol would allow for the determination of physical and/or chemical influences on the potential for sludge dewatering on a gross basis.

Samples chosen for sonication were introduced into a SONICS Vibracell VCX750 Ultrasonic Cell Disrupter, using a ½ in titanium alloy probe. Measurements of wet and dry mass, along with volume of water removed were taken prior to sonicating. Typical sonicating time was 10 min at an amplitude of 80% unless otherwise stated. Following sonication, samples were dried in a

Thermo Heratherm oven for 12 h at 85 ^{o}C. Non-sonicated samples were handled in an identical fashion, but did not undergo the sonication process.

3.3.2 Determination of Sonication Parameters

A 4 US gal Macintosh Apple Cider Press with stainless basket (Pleasant Hill Grain) was used for reproducible force for extraction of water. A SONICS Vibracell VCX750 Ultrasonic Cell Disrupter, using a 1/2 in titanium alloy probe was employed for sonication throughout the reported tests.

For each trial, two sludge samples of each mass were weighed out; each sample was placed in the press and a complete; one sample for sonication, other samples should be used as benchmark, non-sonicated samples. With the non-sonicated sample, input into press and turn press handle until all threads have been used/ further immovable for exact pressure replication between trials. Measure amount of water removed and move retentate to oven. Sonication is then performed on 100 mL samples as previously stated for 5 min per sample unless otherwise stated in the results section. Following sonication, the cider press was again used to extract liquid, with retentate dried for 24 h at 95^{o}C in a Thermo Heratherm Oven. A post dry weight is finally obtained. Non-sonicated samples forgo the sonication process and go directly to the oven drying step.

3.3.3 Bench Scale Determination of Acidification Potential

Laboratory scale experiments were performed in beakers to determine potential for water removal upon acid addition; with the addition of a more precise de-watering evaluation by follow-up centrifugation. Mix tank sludge was examined; a mixture of both primary and secondary sludge. Mix tank sludge samples (30 mL) were injected with pre-determined aliquots of sulfuric acid, from 0 mL to 0.2 mL in 0.05 mL increments. Samples were placed into 50 mL Falcon™ Conical Centrifuge Tubes and centrifuged at 3000 xg Relative Centrifugal Force (RCF) for 5 min in a Heraeus Megafuge 40 centrifuge. Water extracted as supernatant was measured following centrifuging.

3.3.4 Acid Effects on Sonication Abilities

40 mL samples of acidified and non-acidified sludge mix tank sludge (mix of primary and secondary sludge, ~3% dryness) are sonicated and/or dryness measures are to occur consistent with section 3.3.2. Finally, centrifugation will occur consistently with the regime described in section 3.3.3.

Chapter 4: Molecular Disruption through Acid Injection into Waste Activated Sludge: A Feasibility Study to Determine the Economics of Sludge Dewatering

This chapter has been prepared as a standalone article and has been submitted for review in the *Journal of Cleaner Production*. For this reason, there may be some repetition from the previous methods section.

4.1 Abstract

Industrial productivity is often judged solely by the primary product's marketability, while opportunities for secondary products derived from process by-products are often overlooked. In paper mills, large volumes of moisture-rich paper mill residuals (cellulose sludge) are produced, for which commercial usage is difficult. Port Hawkesbury Paper LP, Port Hawkesbury, Nova Scotia, produces over 7 t/hr of waste sludge with a seasonally dependent dryness ranging from 25-38%. To enhance end-use value, further dewatering occurred through a comparative *in situ* study contrasting ferric sulfate and sulfuric acid; yielding a ~4% increase in dryness, with commensurate potential for numerous economic and environmental benefits.

4.2 Highlights

- Methods for dewatering waste pulp and paper mill sludge are proposed.
- Acid injection ruptures water containing molecules.
- Use of thickening chemicals reduced due to increased ease of dewatering.
- Local paper mill used for generating industry applicable data.
- 93% sulfuric acid deemed best dewatering agent based on economics and performance.

4.3 Keywords

Acidification; Sludge; Dewatering; Sulfuric Acid; Ferric Sulfate; Wastewater Treatment

4.4 Introduction

Shifting market and environmental paradigms faced by the pulp and paper sector worldwide forces increased innovation not only with paper production, but also with environmental discharges and fate of waste products. In the paper industry, sludge is paper mill residuals which, depending upon the paper product being manufactured, may be variously comprised of wood fibres, clay, and secondary treatment bio solids (micro-organisms). Bio-solids are known to have combustion applications as well as land application (NEBRA, 2017). Like many mills, Port Hawkesbury Paper LP, Mill A, located on Cape Breton Island, Nova Scotia, Canada, has identified the need to focus on alternative strategies to handle their sludge production and end use/disposal. Currently, a portion of the sludge is transported off-site to be burned as a biomass product, with the balance incorporated into a limited timeframe landfill topping project. Both disposal methods have their inherent challenges. As a biomass product for incineration, the sludge, high in moisture content (25-38% dryness, depending upon the season) requires much of its contained energetic potential to evaporate off moisture as water vapour, thereby dramatically reducing its overall heat value. In this specific case, it also means that PHP incurs financial penalties for delivering sludge with dryness values under 30% to a local CHP facility as prescribed under agreement conditions regarding sludge incineration. Alternatively, landfilling options are limited and not considered a best practice option. Acidifying sludge can increase constituent mobility, allowing for the weakening of binding forces leading to the release of chemicals and metals. This behaviour is consistent with the theory of biosorption, as it pertains to paper mill sludge, where sludge often acts as a binding site for heavy metals which can then be released through the addition of acid (Ong *et al.,* 2010). Moisture has the potential to be liberated by adding acid (hydrogen ion rich), which acts similarly to thickening chemicals used in typical treatment processes by "bringing the zeta potential of sludge flocs at or close to the point of zero charge" (Mahmood & Elliot, 2007). Consequently, two acids (93% sulfuric acid and ferric sulfate - 10% sulfuric acid) were compared to define the best dewatering performance that was economically achievable.

4.5 Materials and Methods

4.5.1 Laboratory Scale

Determining the ability of acids to dewater PHP's sludge was first tested on a lab scale through titration-based acid additions using 60% ferric sulfate and 97% sulfuric acid. Differences in concentration from the lab to industrial scale-up were negligible, as the laboratory scale experiments were purely to demonstrate capacity of these additions to dewater sludge. Titrants were diluted by a 1:10 ratio by volume as seen in Table 2. 100 mL samples of waste activated sludge (WAS) were used throughout the titration and pH was measured using an ATI Orion perpHecT LogR Model 310 Benchtop Meter.

4.5.2 Preliminary *in situ* Trial

Prior to the onset of a permanent implementation at Mill A, a preliminary, short-term manipulation of the secondary treatment process was initiated, and parameters to be measured were noted, as shown in Figure 5. Fennofloc XP 136H10 (ferric sulfate) was obtained through Kemira and 93% sulfuric acid was obtained through ChemTrade.

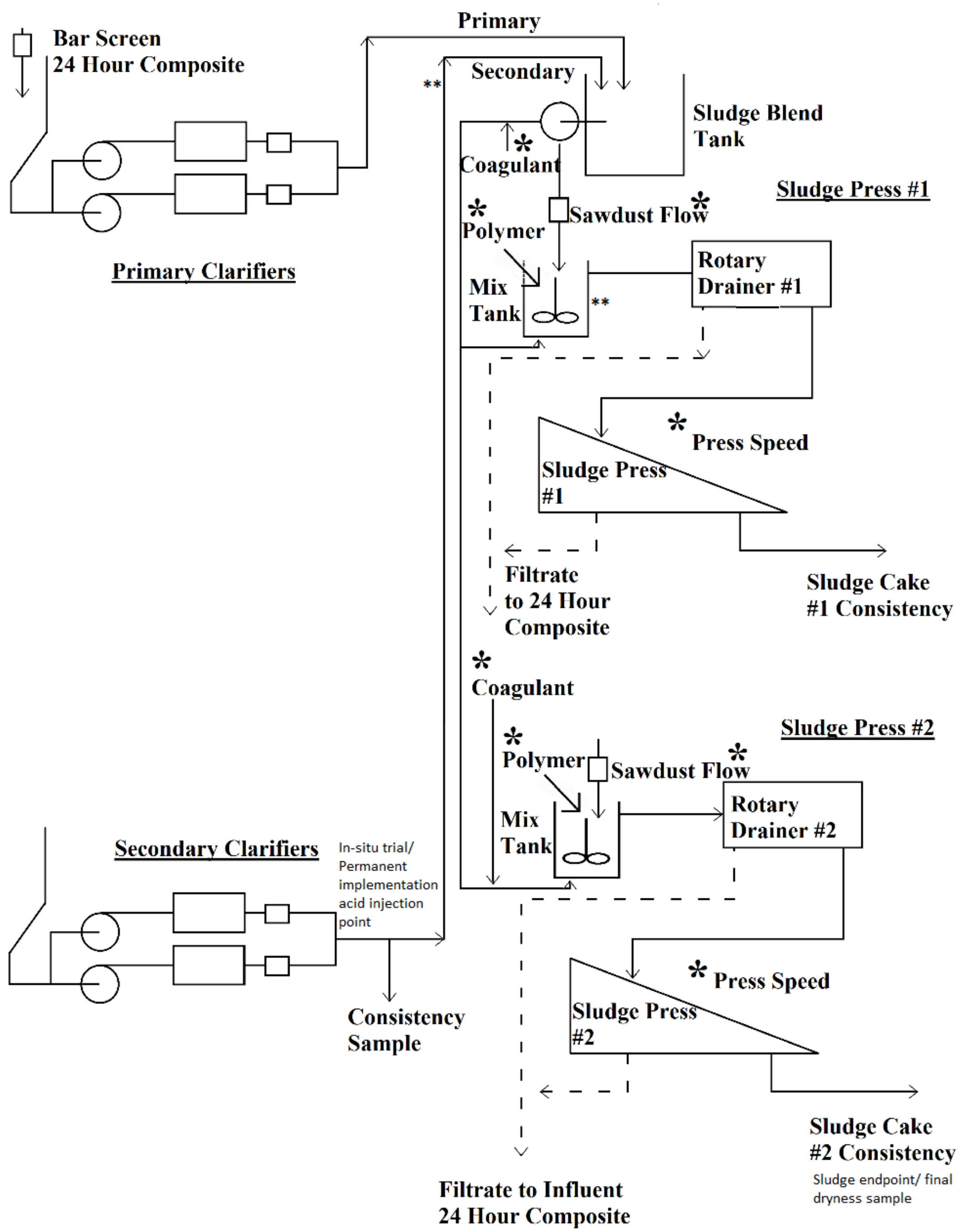

Figure 5 - Flow based schematic of secondary treatment process monitored during acidification trial. Double asterisks (**) represent points of pH measurement and single asterisks (*) represent points of parameter monitoring (Adapted from Mitchell, 2015).

To capture treatment effects over the ever-changing conditions of an operational facility, the addition of the two acids was alternated on a weekly basis to optimize acid concentration and thickening chemical use during subsequent, permanent system modifications. During the preliminary trial, acid was injected into the waste activated sludge (WAS) as seen in Figure 1, a secondary sludge with an initial solids content of 2-3% (in contrast, primary sludge is ~4% solids content). The injection point was prior to mixing with the secondary sludge. The main parameter monitored was pH, which typically within Mill A's WAS is around pH 8; however, in consulting the primary literature review, and through discussion with other paper mills and in deference to laboratory scale trials done with FP Innovations, it was determined the desired pH should be ~3.5. Two acid injection pumps (ProMinent™ Sigma/1 positive displacement) were put in temporary locations within the secondary treatment stream, with only two being utilised at any given time with. pH monitoring took place at two points (Figure 5) using ProMinent™ Dulcometer DMT On-site Measurement Transducers, approximately 10 min (250 m) downstream of the initial injection point and prior to mixing with primary sludge, and then again approximately 1 h post-injection, and following blending.

Parameters inventoried are those noted in Figure 1 by asterisks, also including Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), and Sludge gate positions (% open to boiler vs. % open to landfill). A complete list of parameters measured is found in the attached Supplementary Information.

COD analysis was conducted using the dichromate method; BOD analysis using a 5 day standard test method, CPPA H.2. Dryness values are done using consistency pads (for WAS or recycled activated sludge (RAS)) or cake (final product) samples. In the case of consistency pads, 250-500 mL samples are weighed wet, then again after being put in a speed drier for approximately 20 min at 100^{o}C. For cake samples, 500 g of sludge is placed on an 11" by 13" pan in an oven at a temperature of 105^{o}C+/- 5^{o}C for 18 h and weighed again following drying. Final dryness values in both cases are the difference between wet and dry measures. This preliminary full-scale industrial trial took place during the winter months when sludge de-watering is most problematic, to ensure a minimum 30% dryness can be achieved, while providing a 'worst-case' chemical cost estimate.

4.5.3 Permanent Process Implementation

Sulfuric acid was chosen for permanent implementation based on the outcome of the previous trial. It was pumped into the WAS at the same injection points as with the preliminary full-scale industrial trial. Lutz- Jetsco Memdos DX50 Motor-driven Diaphragm Dosing Pumps were used as the relatively low injection volumes of sulfuric acid (in comparison to ferric sulfate allows these pumps to run at near engineered capacity, reducing mechanical issues. Internal programming meters the amount of acid injected based upon the flow rate and pH of WAS and blend tank sludge pH. The pH probes were retained *in situ* from the preliminary full-scale industrial trial, providing readings approximately 10 min following initial injection and again approximately 1h post-injection and upon mixing in the blend tank. Injection manipulation on this trial is automatic based on the flow rate of the secondary sludge, pH of the blend tanks and WAS; these inputs regulate pump speeds, and in turn, sulfuric acid input flow rates. Initially, a 1:1 ratio of WAS flow in m^3/hr to acid injected in L/hr was implemented with a WAS pH objective of 4, before ultimately lowering to 3.5 once system stabilized.

4.5.4 Notable Issues/ Strategies

As will be noted throughout the preliminary *in situ* trial scale investigation only two days of data for the sulfuric acid trial are available due to a materials compatibility (corrosion) issue. Pre-exiting fittings/ points of injection should be evaluated prior to acid injection. A quill type in injection strategy should also be implemented to avoid further corrosion. Storage and piping materials were chosen to be carbon steel (stationary acid) and 316 stainless steel (flowing acid).

4.6 Theory/Calculation

4.6.1 Purpose

High-moisture waste sludge produced in agricultural, municipal, and industrial contexts are often, as is the case at PHP, simply stored on site due to a lack of alternative uses and/or high energy costs of de-watering. (Resource Converting, LLC, 2017). Consequently, the need for reduction of the amount of waste produced, its moisture content, as well as its' ultimate integration into a circular economy setting where the waste of one process (ex. paper production) becomes a feed for other products is critical. Drying can be part of the solution by creating additional utilization options for waste products. However, typically, the price may not be worthwhile unless such residual products can be the feedstock for another industry. Drying the sludge reduces mass and volume of the product, making it's storage, transport, packaging and retail easier. For lower value waste, it also enables the incineration or co-incineration of sludge (Flaga, 2005).

4.6.2 Dewatering Strategies

Many methods of sludge dewatering have been documented. The most successful are briefly highlighted in the following subsections.

4.6.2.1 *Freeze/Thaw*

This method usually requires a two-compartment system allowing for freezing and thawing, cyclically using energy and then recovering energy. Freeze/thaw works to create an ice complex throughout the sample which allows for ease of water release upon melting. (Diak & Örmeci, 2016). This process works best with inorganics if alum is added for conditioning. Variables to control in this process are solids concentration, freezing rate, and freezing duration. The drawback of this technology is cost. Construction of a unit to complete the freeze/thaw process would be economically unfeasible when a water removal system is already in place. The returns on such an investment would be questionable (Reed *et al.,* 1986), such as the need for consistent operating conditions, even in the presence of a cold climate would be difficult to maintain (Water Research Foundation, 2000).

4.6.2.2 Anaerobic Digestion

The anaerobic digestion process typically consists of four stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Kim *et al.,* 2003). This process produces methane from the breakdown of organic compounds, which could be used as a heat source to further dry a sludge product. Depending on the composition of the input sludge and also the desired outcome, anaerobic digesters, through their reactive breakdown process are guaranteed to provide a dewatered product relative to input sludge. The final drying is accomplished on a drying bed or belt filter press (Chemistry@Elmhurst, 2015). Implementing an anaerobic digestion process, even at the pilot scale level is extremely expensive and not currently a feasible option at the mill, but may be pursued in the future.

4.6.2.3 Gravity Drying

The most inexpensive dewatering strategy, in many cases requiring only an expanse of land, turnover equipment, this near natural drying process does require a warm climate (Alturkmani, 2012). Nova Scotia, and especially Cape Breton, has a colder and wetter climate than optimal for this process, although limited windows may occur to implement this process during summer months (Nordic Waste Water Treatment, 2008).

4.6.2.4 Gravity Thickening

Gravity thickening is a currently employed during PHP's processes in the clarifiers where a mixing motion allows for settling of solids, which are removed by a rake for further processing However, this process leaves much of the moisture still intact (less than 5% solids).

4.6.2.5 Acidification

The addition of a strong acid to breakdown water-filled pockets or molecules and disrupt cell membranes of micro-organisms within the secondary sludge, thereby further releasing water, will also decrease the overall pH of the process waste stream. Earlier FP Innovations trials at other Canadian mills proved promising, demonstrating ferric sulfate can increase product dryness and also decrease a coagulant requirement, up to a point beyond which it is not economically viable (Talat Mahmood, FP Innovations, Research *Manager*, *pers comm*). Removal of bacteria is an interesting aspect of the acidification process, as this can enhance again, the potential for re-use of sludge products.

4.6.2.6 Fournier Rotary Press

Fournier Rotary Presses are engineered to introduce reactant into a flocculent tank and combine with an optimal amount of polymer additive. These presses are also manufactured for ease of cleaning as both internal presses are non-clogging, require minimal electrical inputs, and run quieter than other comparable systems. Final cake dryness can be controlled by the operator of the Fournier Rotary Press, which along with the containment of odor, is a huge benefit (Rotary-press.com, 2015). This technology has been of ongoing interest to PHP; however, recent laboratory trials evaluating the benefits of implementation within the mill proved less successful than acidification.

4.6.2.7 Sonication

Rapid vibrations initiate cell lysing, releasing water from cells within sludge as seen in Figure 2 Laboratory-scale sonicators retail from $3,500-$8,000 depending on wattage, require no continuous acid inputs, a significant human health concern (spillage, burns, corrosion of infrastructure) and ongoing cost. However, when this device is in operation hearing protection is required by all adjacent personnel, potential limiting activities in immediate area.

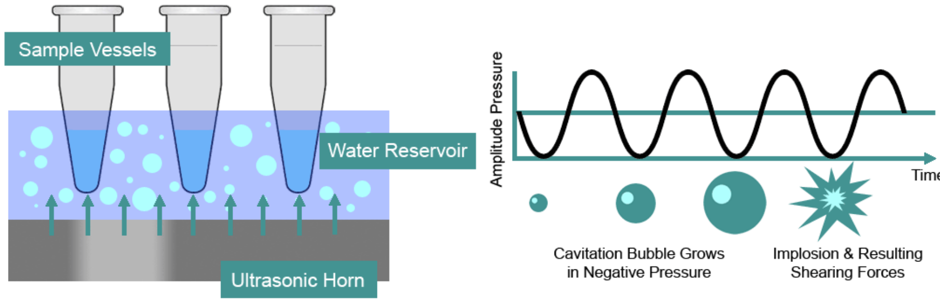

Figure 6 - Simplistic view of sonication process (Epigentek.com, 2015)

Although commercial, full-scale sonicators are available for industry, this would be an expensive process to implement, even augmenting and not replacing the mill's existing technology. Literature suggests sonication can improve solids content from 0 to almost 2500 mg/L over 35 min at a power intensity of 125.8W/cm^2 (Zhang *et al.,* 2008).

4.6.2.8 Cyclone-based Technology

Cyclone-based drying is a simple yet extremely successful technology utilizing air blowers to create a centrifuge-like operation which allows material to dry (removing moisture in a separate product stream) and presenting an overall dry basis product. The 'Dryclone^{TM}' by Resource Converting, LLC boasts the potential to dewater to more than 85% dryness, which in the case of a moisture rich sludge (25-30% dryness), would greatly increase the overall value ("Resource Converting, LLC", 2017). Corporate brochures specifically mention paper sludge as an acceptable waste for processing.

4.6.2.9 Strategy Summary

Various sludge dewatering technologies have proven successful in diverse treatment and dewatering plants globally. However, a key element in choosing the best option for a particular mill is to understand the unique sludge composition and properties to better understand how the product will react under each method. Many plants using these dewatering technologies do not produce any value-added by-products and also the geographical placement of these mills may dictate the processes chosen. For example, the gravity drying often takes place in warm climates with little humidity or rain, facilitating natural effects with little to no energy or heat inputs. The climate for the mill in this study is cold, damp, and rainy, making efficient natural gravity drying next to impossible outside a narrow summer window. Sonication is the newest alternative of interest, as the safety and effectiveness look promising, and lysing would increase water loss.

Table 2 further summarizes mechanisms of dewatering sludge, and the processes currently used at Mill A include the screw press which is accompanied by a low cake solids content, which is again, the reasoning such research must be done to improve upon this process through addition of another step or to implement new technology altogether.

Table 1- "Summary of Mechanisms, Advantages, and Disadvantages of the Dewatering Devices Considered (from Water Environment & Reuse Foundation (WERF) - Innovations in Dewatering Sludges, 2008)".

Dewatering Methods	Mechanism and Advantages	Disadvantages
Belt-Press filter	Pressure and shearing Simple, visual process	Good flocculation vital Often operated with high hydraulic loads or low residence times
Filter press	High pressure without shearing	Semicontinuous (but automated)
Solid-bowl centrifuge	High G forces and high shearing	Often operated with high hydraulic loads or low residence times
Vacuum drum filter	Low pressure without shearing	Low throughput or low cake solids contents
Hyperbaric filters	High pressure without shearing	Low throughput or low cake solids contents
Screw Press	High Pressure without shearing, Low capital costs	Low throughput or low cake solids contents Prefers high solids contents
Tube press	Very high pressure without shearing	Semicontinuous (but automated)
Wring alternating press	High pressure and high shear	Prefers high solids contents. Low throughput or low cake solids contents
Electrodewatering filter press	Electric field promoting electro-osmosis and heating for moisture removal High pressure without shearing	Electrical costs-but offset by high solids Semicontinuous (but automated)

Dewatering Methods	Mechanism and Advantages	Disadvantages
Thermal filter press	Heat and vacuum promoting moisture removal. High pressure without shearing	Electrical costs-but offset by high solids Semicontinuous (but automated)
Centridry centrifuge	Combined thermal drying and dewatering	Energy costs-but offset by high solids Additional flowsheet unit operations vital
V-fold belt-press filter	Tolerates poor flocculation Pressure and shearing Simple, visual process	Low throughput
Electrodewatering belt-press filter	Electric field promoting electro-osmosis and heating for moisture removal Pressure and shearing	Still under development Electrical costs-to be offset by high solids
Impulse dewatering	Combined heat and mechanical pressure promoting moisture removal	Development stalled due to low throughput

4.6.3 Acidification Review

Addition of acid to improve properties of various types of waste products has been previously investigated under a variety of applications. In one case, wastewater treatment plant biosolids were examined and the addition of sulfuric acid, similarly to the trial at Mill A, demonstrated promise in dewatering, however it has been suggested that a threshold exists where volume increases rather than decreases due to gas bubbles (Texier, 2008). Gas bubble formation has not been an issue at PHP, likely due to the volume of acid addition, composition of the sample, or the mechanical drying technologies employed following the acid injection portion of the treatment process. The results of Texier’s 2008 study, while relevant in theory, are not comparable in the absence of an industrial trial scale operation and the presence of digested sludge, which is not part of the waste stream at PHP.

Acidification of textile sludge has also been investigated, with the key difference in this case being the broad range of organic components creating difficulty in obtaining products of high dryness values (Li *et al.,* 2005). A 2008 study also noted an increase in overall volume following acidification, attributing the increase to repulsion of particles (Li *et al.,* 2005).

Perhaps the most relevant literature is that of Mahmood & Elliott (2007) focusing on paper mill sludge, comparing sulfuric, phosphoric, and acetic acid additions being mindful of the cost of thickening chemicals, in particular polymer. Consistency or dryness of the final sludge cake was found to most promising with the use of sulfuric acid. In this 2007 study, "the small gain in solid consistencies at higher contact times [was attributed to] hydrogen ions [diffusing] into the sludge flocs and/or for the conformational changes in sludge constituents taking place" (Mahmood & Elliott, 2007).

4.6.4 Estimated Values

Regarding calorific value, in the absence of bomb calorimetry data, it can be simply stated the drier the material, the greater the ease, efficiency, and net energy released during burning, especially in wood based products such as the sludge produced by PHP. The Dulong and Vandralek equations (Equations 1 and 2) have been previously compared for higher calorific value (HCV) determination of waste products (Nhizou *et al.,* 2014), allowing a plausible comparison of PHP's sludge. These simplistic formulas demonstrate the multiplicative value in elemental component increase seen in a sample which may, in weight be equivalent; however, in a dry sense are vastly un-relatable. In the case of PHP, with dryness values less than 40%, a great loss is seen in burning.

$$HCV = 4.18 * (78.4 * C + 241.3 * H + 22.1 * S) \tag{1}$$

$$HCV = 4.18 * (85 * C + 270 * H + 26 * (S - O)) \tag{2}$$

Where HCV is in kJ/kg, 4.18 represents the specific heat of water in J/g^{o}C, 78.4 and C, H, O, and S represent elemental percentages found in samples (Nhizou *et al.,* 2014).

Using wet wood as a benchmark substance (due to the ever-changing composition of pulp mill sludge), Equation 3 provides a comparative result based solely upon dryness to provide a lower calorific value (LCV).

$$LCV = 19.2 - (0.2164 * MC) \tag{3}$$

Where MC is the moisture content in percent of total weight (COFORD, 2006) and LCV is in GJ/tonne, and 19.2 represents a typical wood calorific value.

4.7 Results and Discussion

With project scope in mind, proof of concept has been concluded and results will be limited to the preliminary *in situ* trial operation due to the need for further configuration and optimization of the permanent, recently introduced process.

4.7.1 Laboratory Scale

Through acid addition into Mill A's WAS with an initial pH of approximately 6.37, Table 2 displays results of a 1:10 dilution ratio of the titrants by volume acid injection measures. It is shown in this table that a lesser amount of 97% sulfuric acid is required to trigger a large decrease in sludge pH. However, it must be noted that ferric sulfate has the capacity to create the same change pH change, but requires a larger volumes of acid. It was estimated that the addition of each acid is related by a 1/5 ratio, meaning that to create a common result, 5 times as much ferric sulfate as sulfuric acid would be required to compensate for the concentration of hydrogen ions present (with sulfuric acid being most concentrated).

Table 2 - Initial titration based acid addition trial results comparing ferric sulfate (10% sulfuric acid) and concentrated 97% sulfuric acid in 100 mL volumes of Waste Activated Sludge (WAS).

Sulfuric Acid Added (mL)	WAS pH	Ferric Sulfate Added (mL)	WAS pH
0	6.37	0	6.37
0.1	6.06	0.1	6.31
0.2	5.72	0.2	6.25
0.3	5.29	0.3	6.20
0.4	4.82	0.4	6.15
0.5	4.32	0.5	6.10
0.6	3.87	0.6	6.04
0.7	3.39	0.7	5.97
0.8	2.99	0.8	5.90
		0.9	5.82
		1.0	5.75
		1.5	5.25
		2	4.75
		2.5	4.35
		3	3.89
		3.5	3.49
		4.0	3.10
		4.1	3.07
		4.2	3.04
		4.3	3.20
		4.4	3.00

Sulfuric acid t-based p-value ($\alpha = 0.05$), t-critical value = -1.86 and $p < 0.05$

Ferric sulfate t-based p-value ($\alpha = 0.05$), t-critical value = -1.72 and $p < 0.05$

One would expect to observe a clear differentiation between supernatant and sludge volumes after acid addition if cell lysis/sludge densification and commensurate water liberation was a significant outcome of acidification (Figure 7). The rightmost sample from left, with 0.52 mL sulfuric acid addition, clearly yields the greatest water liberation. Even in the case of the pure sludge sample, a water layer is formed due to gravity settling. Overall, in each sample the water layer is clearly visible and could be decanted or siphoned in the case of laboratory work or on an industrial scale would be easily removed through drainers and presses.

0.152 mL of acid was added initially as the beakers seen in Figure 3 are representative of a trail performed at a second paper mill, Mill B. This value represents a comparison of the pH limits set forth by Mill B, in comparison to data obtained from Mill A's *in situ* trial.

Table 3 provides quantities of brought to surface following a 30 minute gravity settling period. The addition of 0.152 mL was not repeated due to the limit set forth by Mill B for acceptable pH production being well surpassed.

Table 3 - Water level formation following acid injection into paper Mill B sludge.

Volume Added (mL)	Water Level (mL)
0.00	12
0.05	15
0.05	14
0.10	22
0.10	18
0.152	23

Uncertainties *u*(Volume Added) = 0.01 mL, *u*(Water Level) = 1 mL

t-based *p*-value ($\alpha = 0.05$), t-critical value = -2.01 and $p < 0.05$

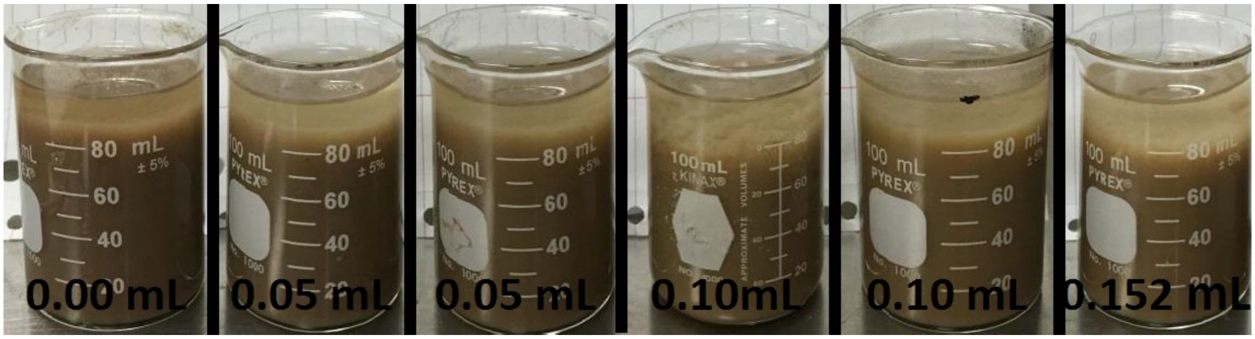

Figure 7 - Sludge samples taken from Canadian pulp and paper mill, Mill B with the addition of 93% sulfuric acid in varying volumes.

4.7.2 Industrial Trial Scale

The ratio between amounts of primary to secondary sludge (lower value representing a decrease in secondary sludge) and dryness of the output sludge over time is represented in Figure 8. The notable points on this graph are at the high points of the ratio line as here the ratio is 1.2 which represents a high/ 'worst case scenario'/ optimized value; to clarify, this refers to a greater amount of secondary sludge (more difficult to dewater) in comparison to its combination partner, primary. The ratio changes overtime, not due to acid injection, but due to presence of filaments of clarifiers due to seasonal and process conditions. This point is key as dewaterability decreases as ratio increases due to the excess of secondary sludge. When focusing on the optimized ratio values, dryness has been increased by approximately 4% throughout the trial.

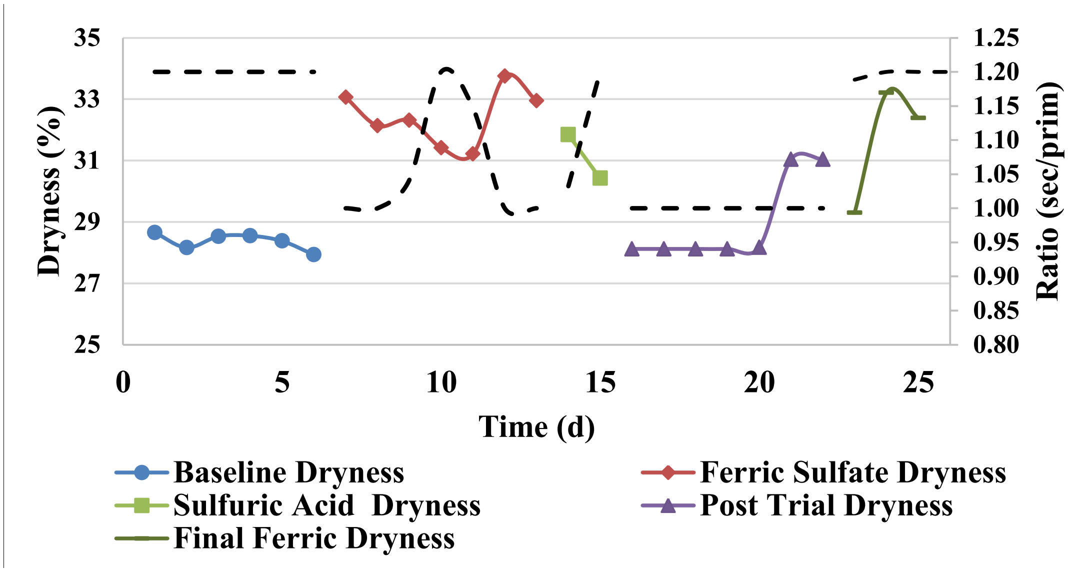

Figure 8 - Dryness and Ratio vs. Time for the trial duration. Colored lines represent trial segments as seen in the legend and the dashed lines represent the ratio of secondary over primary sludge.

The speed of the screw presses delivering sludge (to the endpoint of the process before leaving to landfill or incineration and the load leaving to the boilers (both expressed as percentages of operating capacity), are an operational surrogate demonstrating the ability of acid to decrease moisture content. Ideally, both press speed and load would be lowered with acid addition, which was the case during the latter portion of the trial (Figure 9). Both responses are due to decreased moisture content causing a decrease in the overall amount of sludge and difficulty to dewater.

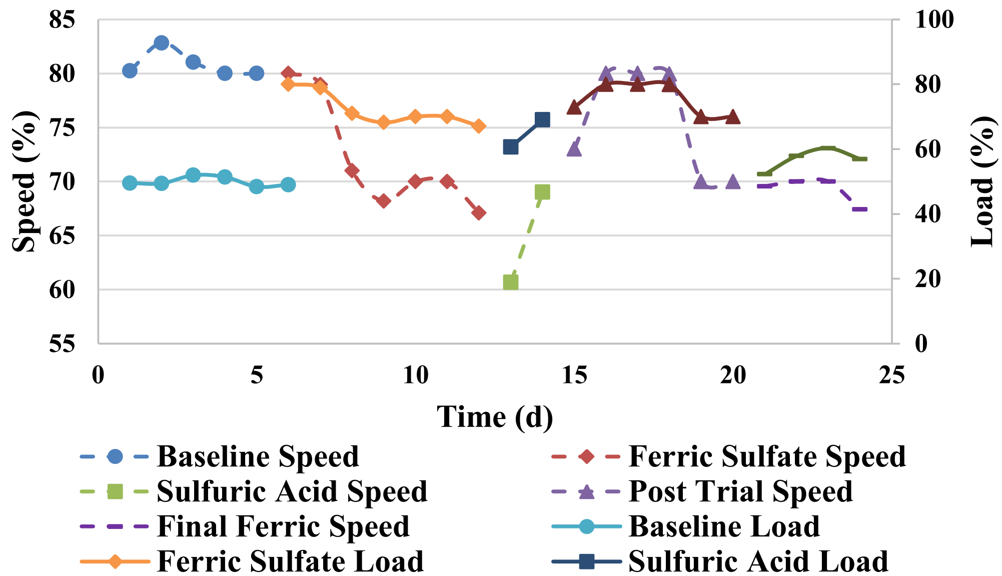

Figure 9 - Press speed (%) vs. sludge load leaving to the boilers (%). Dashed lines represent speed values and continuous lines represent load.

Weightometer readings represent the measured value of sludge output per hour; the addition of acid resulted in more than 1 ton/h less sludge output (Figure 10). The deviation between the first baseline and post-trial baseline are due to process parameter changes throughout those periods (due to dynamic processes), leaving the lowest points, and post-trial baseline, not representative of typical conditions. Reducing the output volume of sludge is an immensely important process parameter, ultimately a factor in determining potential sludge alternative usages. It should be noted that in comparison to literature trials, sludge volumes did decrease, potentially due to the fact that all measures were conducted following rotary drainer and screw press processes, which may reduce any gas or repulsive forces occurring.

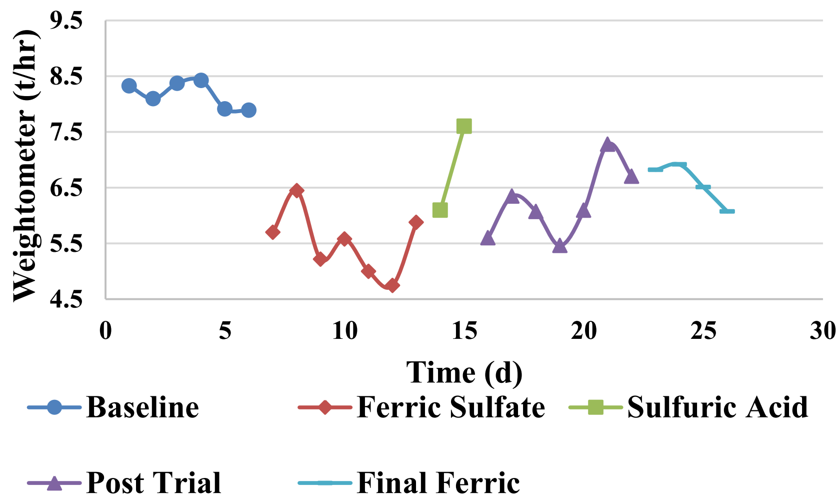

Figure 10 - Weightometer values of sludge output to boiler and/or site storage. Standard error values dependent upon trial stages are ±0.2, 0.2, 0.5, 0.2, and 0 t/hr. Overall, standard error for the complete data set is ±0.2t/hr.

Calorific value, a qualitative sludge fuel value measurement, increased following acid injection as dryness increased (Figure 11). The exact values are arbitrary and purely used as relative metric; based upon a typical dry basis of wood (COFORD, 2006). The biomass line represents an ideal, typical biomass value and would be the goal upon future permanent implementation. However, any caloric value increase is potentially advantageous to the consumer if sludge is used for burning.

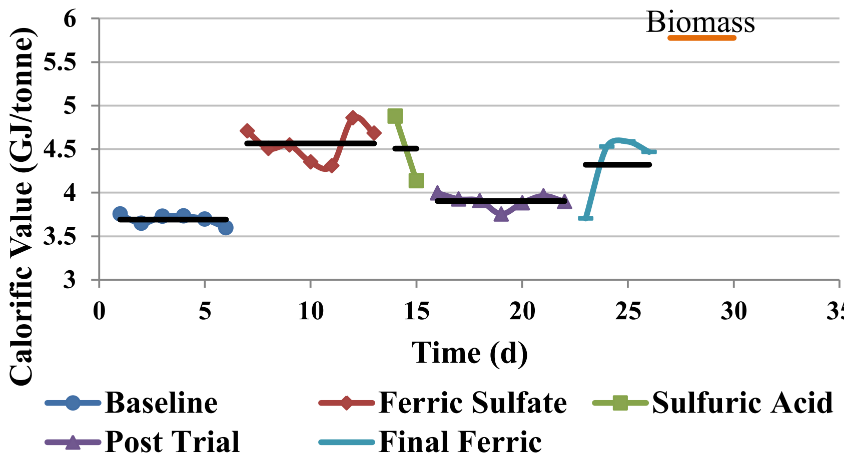

Figure 11 - Estimated calorific value of sludge based upon experimental dryness values achieved throughout trial. Lines with symbols represent experimental/estimated values while black horizontal lines are averages.

Sludge flows (m^3/hr) were held fairly constant throughout the trial, with outliers seen in the final ferric sulfate trials; however, this variation is negligible relative to the consistency of positive results throughout the trial (Figure 12). Not reflected in this graph are the myriad parameters affecting the ability of PHP to maintain a steady primary and secondary sludge flow, reflecting fluctuations in the paper making process. Our awareness of these fluctuations influenced our experimental methodology, in that the switching of acid types throughout the duration of the trial helped amortize variation across daily and weekly process changes to maintain overall consistency of operating conditions during experimental introduction of both acids.

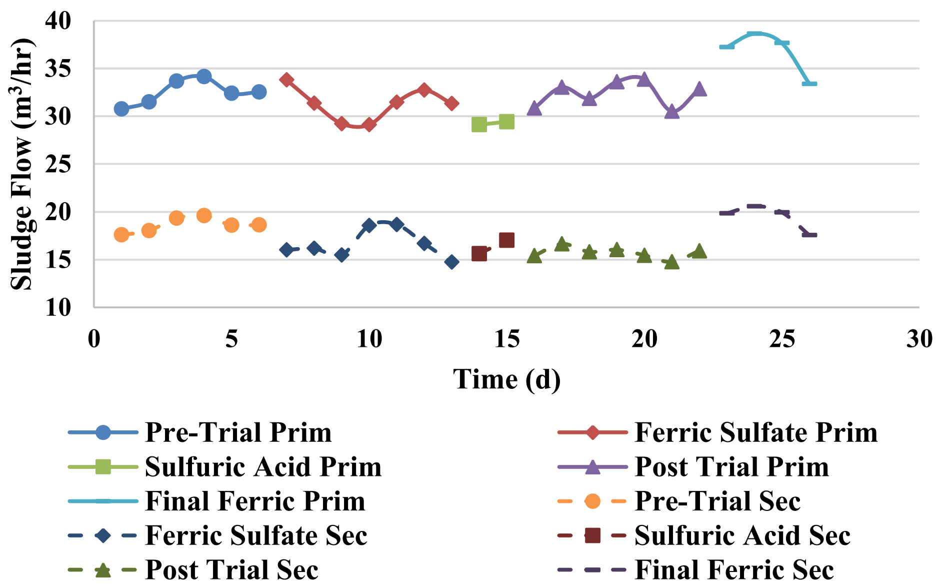

Figure 12 - Secondary and primary sludge flow rates throughout duration of trial.

Microorganisms (or "bugs") are regularly noted as a component of paper mill sludge, measured as mixed liquor suspended solids (MLSS) which are important for successful treatment of an organic waste stream. A desirable operational MLSS is between 2000-4000 mg/L (Mixed Liquor Suspended Solids (MLSS, 2017); with the addition of acid, the overall MLSS can be lowered to within the desirable range (Figure 13). MLSS fluctuations are to be expected as the loads and characteristics in a waste stream are ever changing. Notably, the MLSS trend with the 'Final Ferric' treatment indicates the drop in MLSS was continuing, signifying that over an extended period of time, MLSS could approximate that observed with the Ferric Sulfate and Sulfuric Acid trend lines. The MLSS values (Figure 9) correspond to COD and BOD (Figures 14-15), which are difficult to regulate during the winter months.

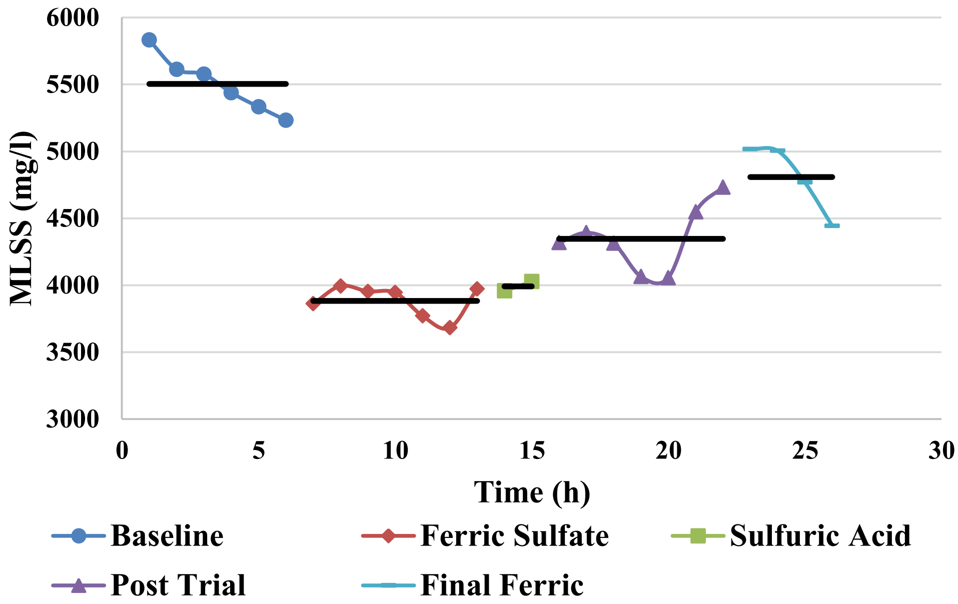

Figure 13 - Mixed Liquor Suspended Solids readings throughout duration of trial. Colored lines represent experimental values and black horizontal lines represent averages.

COD and BOD values (Figures 14 and 15), reflect both sulfuric acid and ferric sulfates' abilities to decrease these critical wastewater parameters values in the problematic winter season where demand for 'nourishment' is increased.

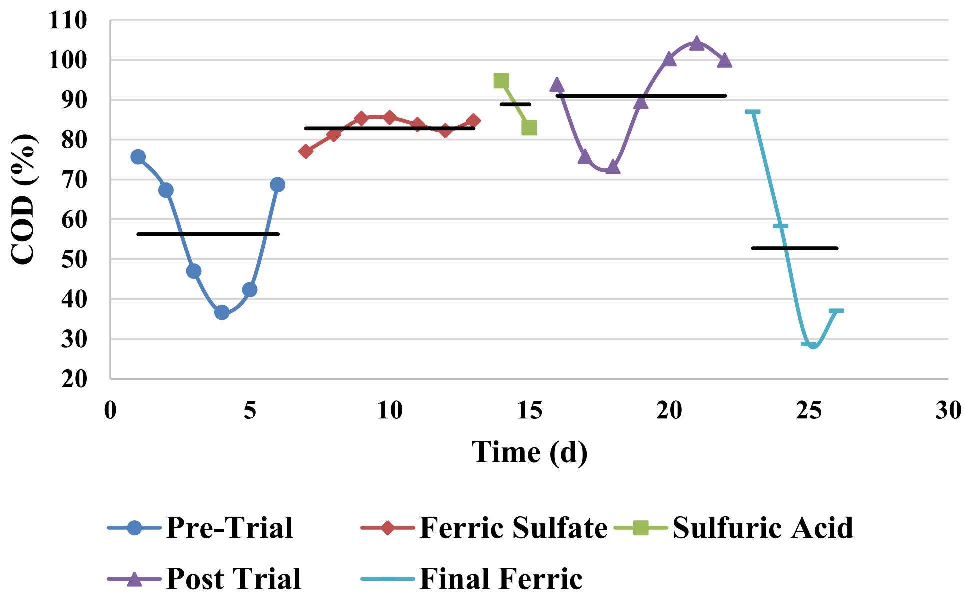

Figure 14 - Chemical oxygen demand values throughout duration of trial. Black lines represent average values across each trial segment.

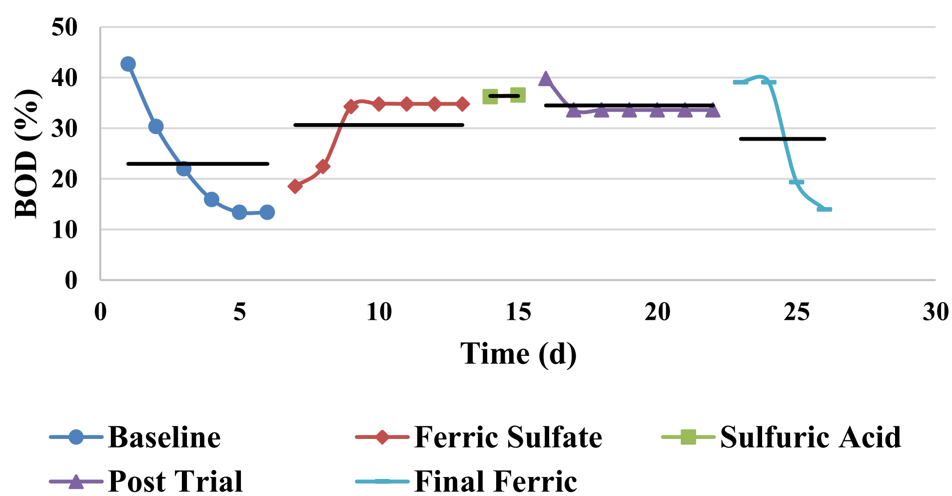

Figure 15 - Biochemical oxygen demand values throughout duration of trial. Black lines represent average values across each trial segment.

pH was one of the most important parameters in this trial and was monitored to ensure it was maintaining at a pH of less than 4. The pH was monitored approximately 10 min following initial acid injection, and again approximately 1 h following injection. The early data readings reflected initial 'large' changes in pH due to an unexpected waiting period prior to sufficient mixing of acid and sludge to produce a notable change on the pH meters, following this early period the addition rate was adjusted appropriately. Figure 16 represents this first pH measurement. The data on this chart indicates that small decreases were initially seen due to cautious addition to gain a general sense of the effects seen by the acid addition- overall, addition rate fluctuated throughout the initial portions of the trial. By the end of the trial, with the 'Final Ferric' the pH did meet PHP's goals, dipping below a pH of 3.8. The acid of choice for this portion of the trial is not to be confused with its' ability to decrease pH; rather, this chart's purpose is to display the potential of both acids to achieve a desired pH.

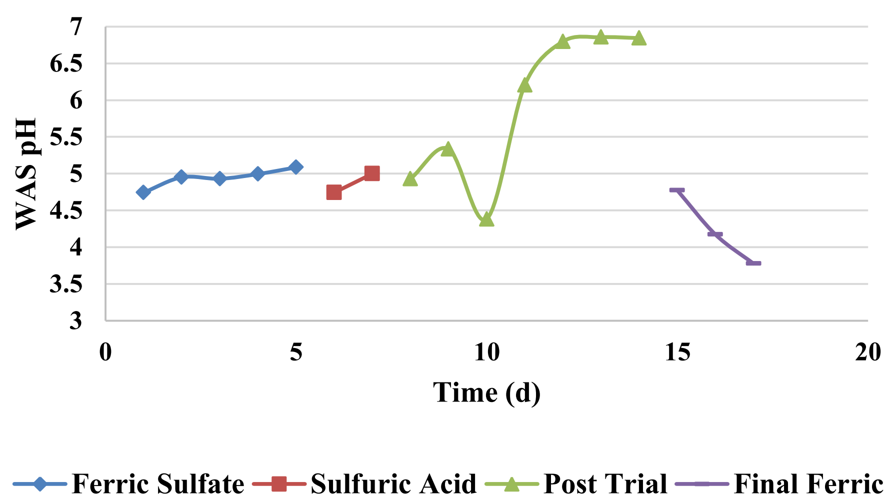

Figure 16 - WAS pH changes throughout the trial; readings were taken approximately 10 min following initial acid injection.

Moving to the next location for pH measurement, the blend tanks (Figure 17), this location reflects the process stream pH approximately an hour after injection. The amount of acid required to produce a change in pH is presented on the right vertical axis. The first four columns represent the final pH in the blend tank, demonstrating either ferric sulfate (10% sulfuric acid) or 93% sulfuric acid can achieve the same pH decrease, although a larger volume of ferric sulfate is required. From a cost savings perspective, sulfuric acid became a front runner. The orange bar represents predicted sulfuric acid usage based on estimates from laboratory data and the industrial trial, which is very similar to the actual sulfuric acid trial.

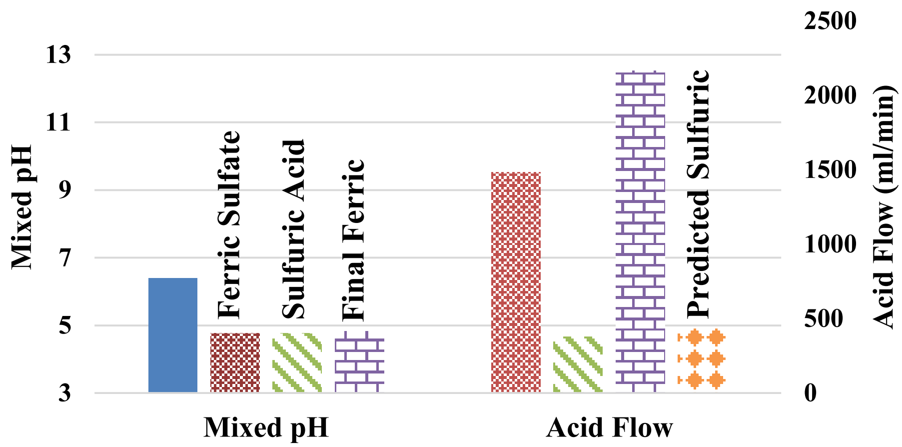

Figure 17 - Mixed WAS, primary, and thickening chemical pH values; readings were taken approximately 1 h following initial injection.

Initially, an increase in dryness of the sludge product was the sole goal of the experiment. However, it was observed that less costly thickening chemicals were required with acid injection, to the extent that polymer and coagulant may no longer be needed in excess. Mahmood and Elliot (2007) noted that there is great potential for cost reduction when thickening or preconditioning chemicals are replaced by an acid alternative. The bold black line in Figure 18 represents the ratio of secondary and primary sludge, our optimized 'worst case' occurs at a ratio of secondary: primary of 1.2:1. The areas without green bars (horizontal stripes) represent the baseline periods. The lowest overall cost is seen around the 8-9th of February, during the sulfuric acid portion of the trial. Looking towards the end of the chart, the last bar, as in the previous figure, represents a predicted value of sulfuric acid using the ratio of the two acids and the data obtained from the trial.

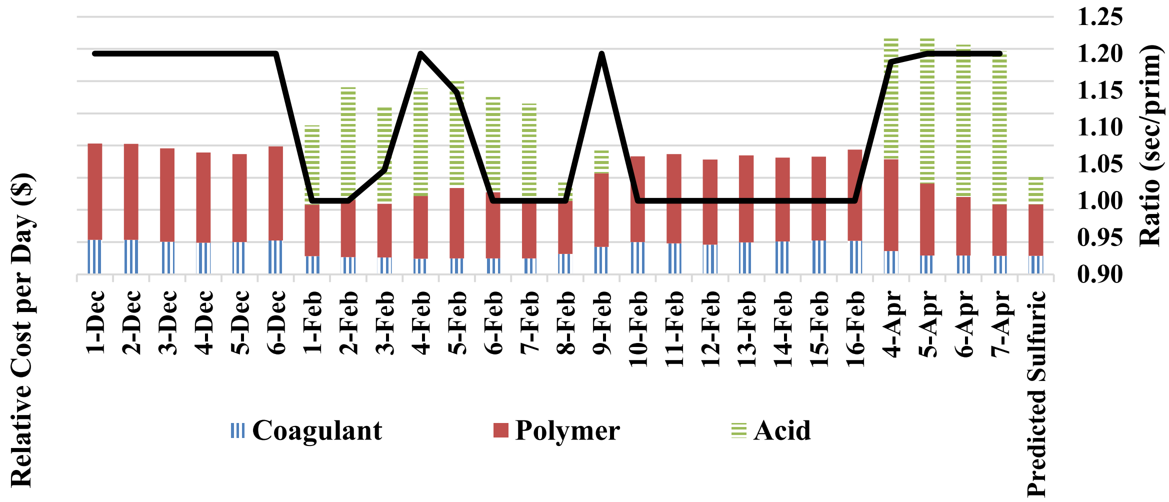

Figure 18 - Cost savings analysis of thickening chemicals throughout the duration of the trial.

Figure 19 presents the estimated savings and expenditures associated with the implementation of acidification on a full-time basis. The orange bar (checkered) represents a predicted sulfuric acid value in the case of each thickening chemical, penalty, and savings. Focusing on each set of columns, it is notable that in coagulant and polymer costs, and penalties, savings would likely be the same with each acid. However, a clear variation is seen in the acid cost column set, where the cost of ferric sulfate in both instances exceeds that of sulfuric acid.

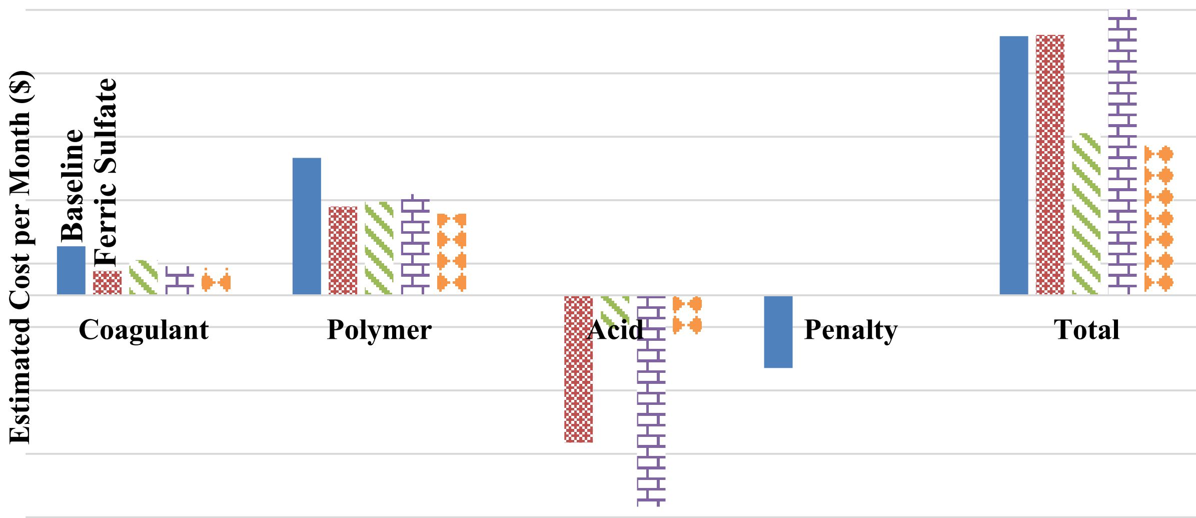

Figure 19 - Overall cost estimate and savings upon theoretical installation with the inclusion of penalty relief regarding sludge burned in biomass burners.

4.8 Conclusion

In conclusion, the addition of both ferric sulfate and sulfuric acid creates comparable ease of dewatering while allowing for decreased thickening chemical usage, decreased sludge pH and 4% increase in sludge dryness. The differentiating factor between ferric sulfate and sulfuric acid is the relative cost, making the selection for sulfuric acid moving forward obvious. With a savings estimated at ~$360,000 CAD /yr, this system can only become more beneficial with further optimization, as additional decreases in the use of coagulant and polymer are expected. The environmental benefits are also immensely promising as the drier sludge output has a higher end use value for burning, and erases the need to be landfilled – hence moving closer to the idea of a circular process with potential both within and outside of the mill. With regards to transfer of process, it is suggested that short-term industrial trials be implemented prior to full scale adoption as processes vary mill to mill, but that a prior inventory of areas available for alteration be considered in light of project goals. In the case of Mill A, the goal was to provide a minimum of 30% dryness for the final sludge product - regardless of seasonal influences. As a tangential benefit, the injection of acid produced cost-saving alterations in chemical additions, including the reduction of thickeners. As follow up, further efforts will be made once a permanent installation is completed, as well as experimentation with other methodologies for dewatering such as sonication which could work as an additional or replacement process. Future work will determine the threshold beyond which incremental acid injection no longer aids in dewatering or reducing thickening chemical requirements. Also, from a regulations perspective, the acid additions may reduce *E.coli* counts (Mahmood & Elliot, 2007) in residual sludge, which would prove valuable in broadening potential future sludge uses.

Remaining challenges include the creation of a composite data set incorporating the various possible systems of implementation, focusing first upon the pulp and paper industry, then expanding to any waste substance with a goal of decreasing moisture content. This strategic approach will require an extensive inventory of process data, and must provide user-friendly charts or correlations to allow industries to input data and receive an output savings estimate, or conversely, suggest regulation strategies or characteristics which can be implemented into processes on a trial or full-scale basis. Such a correlation or chart-based system would reduce the need for costly trials or unnecessary process flow disruption for common process scenarios.

At this time the project is in the early stages of testing at a second Canadian pulp and paper (Mill B). This will allow for the beginning expansion of a data set.

4.9 Acknowledgements

The Mitacs Accelerate program and Port Hawkesbury Paper LP have funding while Kemira has allowed for the use of equipment and troubleshooting assistance throughout the trial, specifically through representative Brad MacLean. FPInnovations worked collaboratively for acid preconditioning laboratory trials. Also, thank you to Ken Mitchell, Marc Dube, Bevan Lock, Clayton Carmichael, Bill Coady, Joe Allen, Glenn MacDonald, Derrick Cameron, Jason Spears, Krista Young, Floyd Fougere, Darren MacPherson, Bruce Embree, Phoebe Timmons, Jamie Smith, Devon Clark, John Campbell, Kevin Lee, Bill Campbell and all Port Hawkesbury Paper LP employees for the tremendous guidance and backing throughout this project.

Chapter 5: Further Acidification Results and Discussion

Additional work was completed that was not integrated into the previous chapter given the constraints associated the scope and length of journal articles.

5.1 Laboratory Scale

Laboratory work done in collaboration with FP Innovations resulted in an assessment of current cake consistencies in comparison to polymer and coagulant usage. Samples obtained from PHP included polymer, coagulant, primary sludge, and secondary sludge. Consistent with the remainder of the project, the primary and secondary sludge began at ~3 and ~2% solids content and at pH values of ~5 and 7, respectively. The results demonstrated a clear indication of acidification-based success when a combined (primary and secondary sludge) pH of 4.2 was produced from an initial pH 6.5. The total suspended solids values were also decreased to ~17% of the initial, non-acidified values. Overall solids capture increased nearly 4% and reduction in thickening chemicals was briefly tested showing that acid can replace (to an extent) the need for these costly additives (FP Innovations, 2015).

5.2 Preliminary *in situ* Trial Scale

It should be noted that the sulfuric acid data is limited due to a corrosion issue experienced during the preliminary *in situ* trial scale portion of the project. This resulted in the use of this acid being discontinued during the trial scale. Sulfuric acid is known produce corrosion issues at concentrations (above 60%) moves below 98% as illustrated in Figure 20.

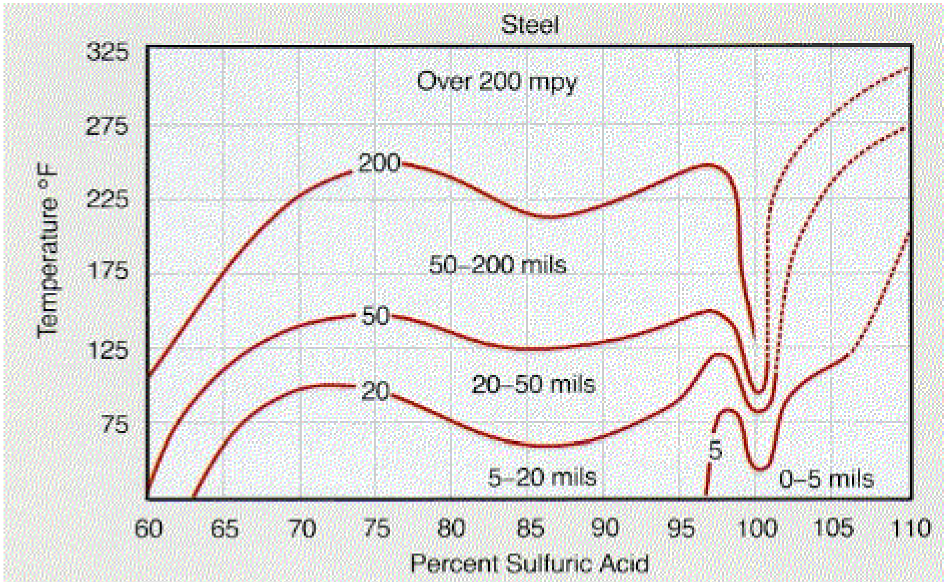

Figure 20 - Potential for uniform corrosion of steel when contacted with various concentrations of sulfuric acid (DKL Engineering, 2011)

The polymer (Fennopol by Kemira) used at PHP is a target for reduction as it is the most expensive thickening chemical used by PHP. As previously noted (Figure 19), acidification resulted in a reduction in polymer use. Figure 21 specifically shows that polymer usage was cut from an average baseline value of 1.9 to 1.0 m^3/hr. Standard deviations for each trial segment respectively are as follows: 0.07, 0.14, 0.29, 0.06, and 0.35. This creates a cost savings of approximately $18,000 per month on this chemical alone.

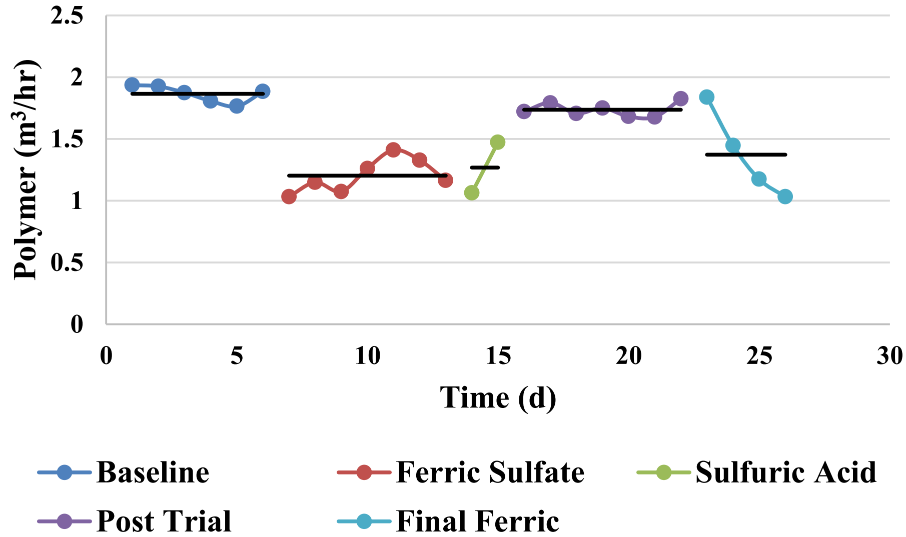

Figure 21 - Polymer usage data for duration of trial (black bars represent average values).

Similarly a reduction in the use of the partner thickening chemical, coagulant (Fennofix by Kemira) was observed, in this case from 137 to 68 mL/min. Standard deviations for each trial segment respectively are as follows: 4.95, 3.85, 20.67, 6.09, and 9.63. The savings, previously described in Figure 19 and again in Figure 22, is approximately $7000 per month.

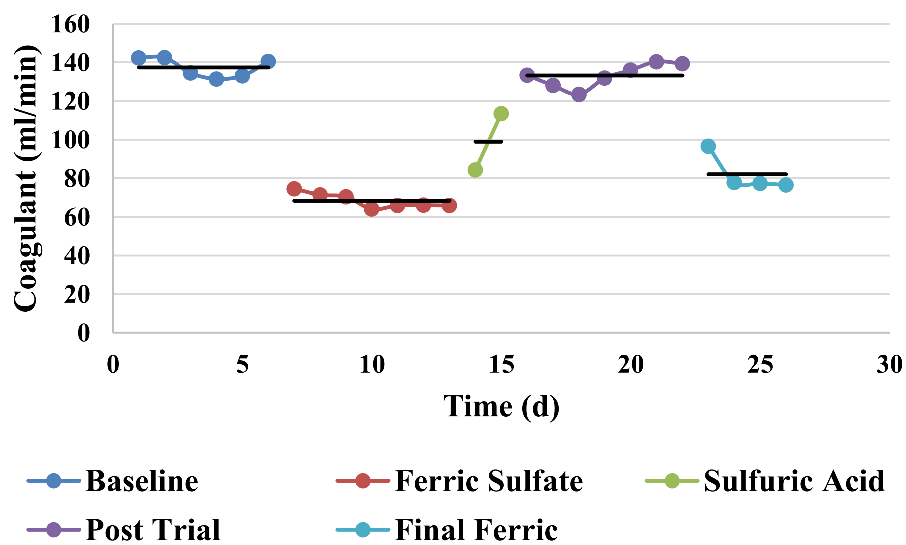

Figure 22 - Coagulant usage data for duration of trial (black bars represent average values).

5.3 Permanent Process Scale

Data gathered during the operation of the permanently implemented acidification system at PHP demonstrated the economic viability associated with the introduction of this process. This section will focus on the comparison to the *in situ* trial values (Final Ferric portion) and projected best case scenarios.

Data was collected over the first month of permanent operation to provide insight into the continued potential of the acidification process using sulfuric acid. Throughout the duration of the trial the mill experienced various process disruptions. Such disruptions are routine in an industrial setting, but may decrease the average values seen in this section; these disruptions are often seen in the latter portions of the reported data. Process conditions vary dependent upon variables such as economics, amount of orders, maintenance, and seasonal conditions (weather). Optimization will continue to occur on all fronts, taking into account seasonal change that results in lower secondary sludge lessens and thereby decreases further the need for costly coagulants, as well as acid volumes. Finally, note that the earliest data points of the *in situ* trial data represent initial acid addition which takes time to take effect following a baseline period. Therefore, these early data points may be slightly skewed; therefore comparisons are based on data collected later in the trial.

Also, when referring to the following figures, the quantity of *in situ* trial data is much smaller than that of the permanent trial scale; this is not believed to discredit the comparative results as the industrial process variation creates an immense difficulty in producing replicable data. This reflects again on the chosen season of trial operation being the problematic winter months to prove success potential in worst case scenarios. Figures 23-35 contain average values represented by black bars, clearly accompanied by a large deviation due to both the short data collection period as well as the variation as previously mentioned; again these bars simply act to represent a standard value for ease of reader review.

Observed dryness values (Figure 23) in the sludge samples evaluated from the operational setup are consistent with the *in situ* trial values, which boasted an increase in dryness of approximately 4%. Over the trial duration the PHP sludge stayed above the desired value of 30% dryness, except for minimal disruptions.

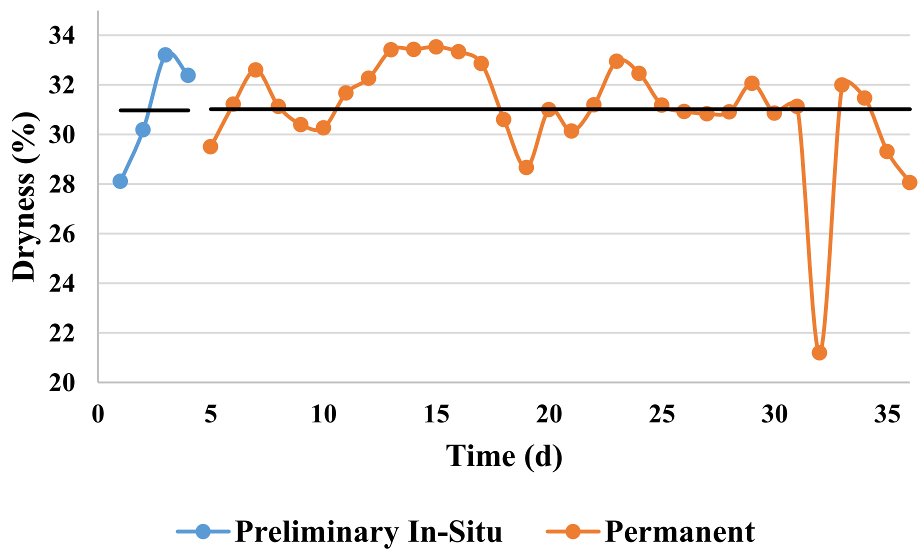

Figure 23 - Dryness (%) of permanent acidification process versus preliminary *in situ* trial stage.

The ratios of secondary to primary sludge have been regularly changing as the process stream changes regularly. A previously noted a ratio of 1.2:1 is the worst-case scenario and will be referenced throughout the rest of this section. These ratio fluctuations are seen in Figure 24.

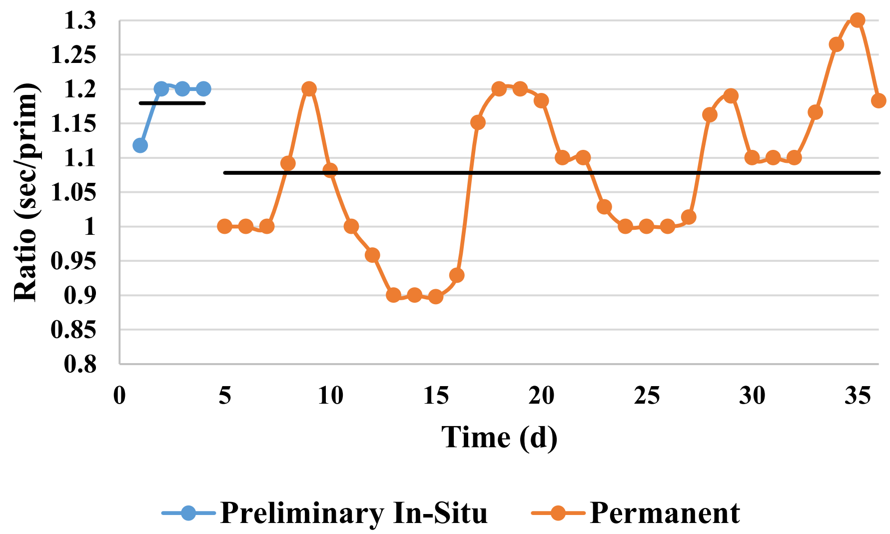

Figure 24 - Ratio of secondary to primary sludge flow of permanent acidification process versus preliminary *in situ* trial stage.

The load of sludge to the presses in Figure 25 has seen a decrease insinuating a lesser overall (mix of secondary sludge, primary sludge, thickening chemicals, etc.) volume of sludge leaving secondary treatment, over 10% is seen in this decrease. This, compounded with Figure 26, relating to speed, does in this case go against the trial results, due to the use of two presses by PHP and primary clarifier issues which caused the need for a quicker output/ removal (reason for drop in the latter data). This does not allude to a negative impact of the acidification process due to the previous decrease in load.

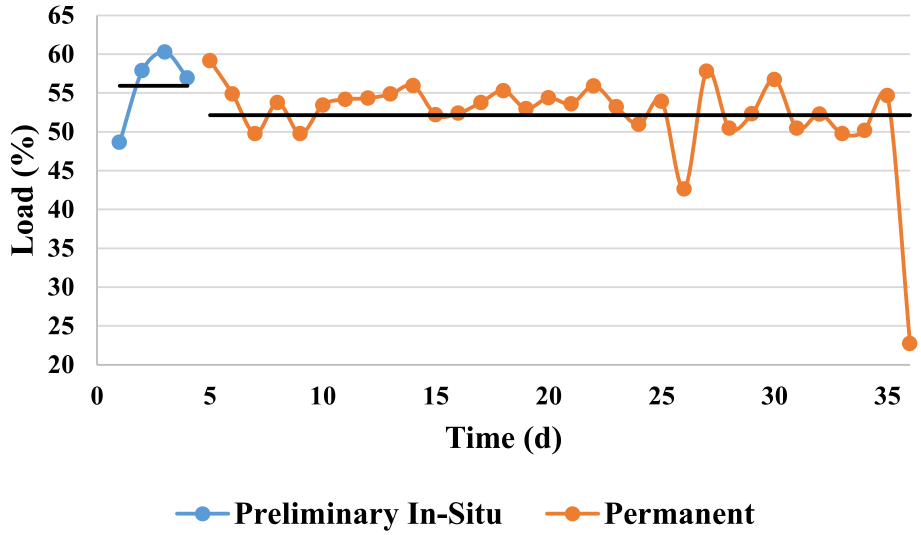

Figure 25 - Load to screw presses (%) of permanent acidification process versus preliminary *in situ* trial stage.

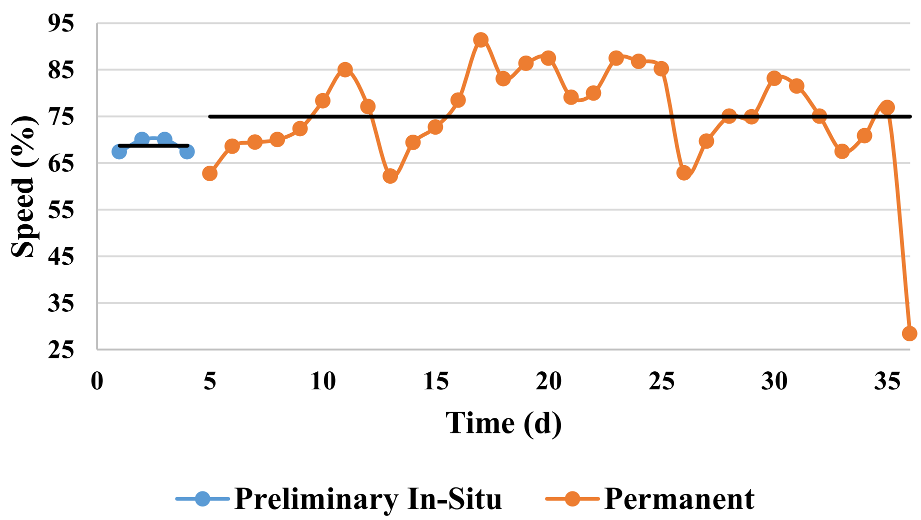

Figure 26 - Speed of screw presses (%) of permanent acidification process versus preliminary *in situ* trial stage.

Figure 27 depicts the usage of a thickening chemical, coagulant, which evidently has not been reduced. This is due to the now less hurried optimization process. Regarding dewatering chemicals PHP chose to first focus on polymer due to the greater purchase cost. Once fully optimized, the operators will begin to reduce the amount of coagulant as well. The dramatic decrease seen in the final data point represents a change in mill process due to shut down or alternation of press.

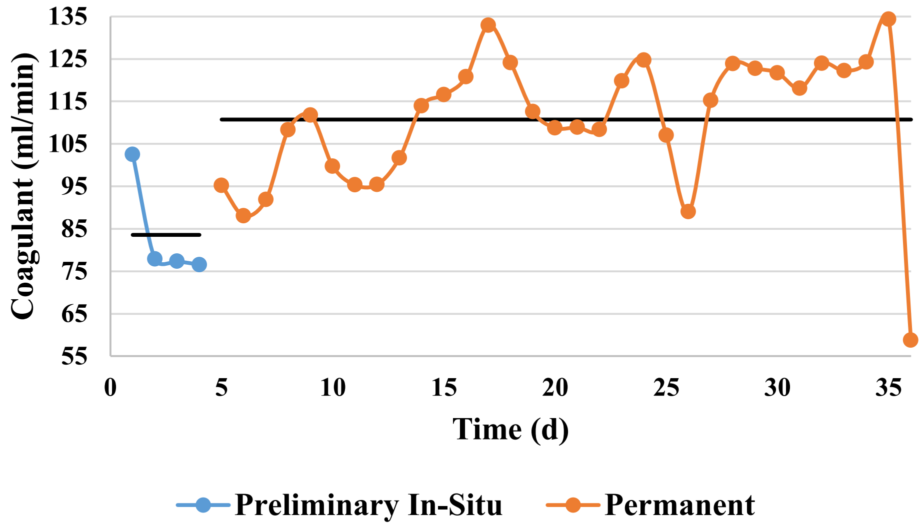

Figure 27 - Amount of coagulant added during permanent acidification process versus preliminary *in situ* trial stage.

Polymer data is found in Figure 28, where on average usage has dropped from 1.3 m^3/hr to less than 1 m^3/hr.

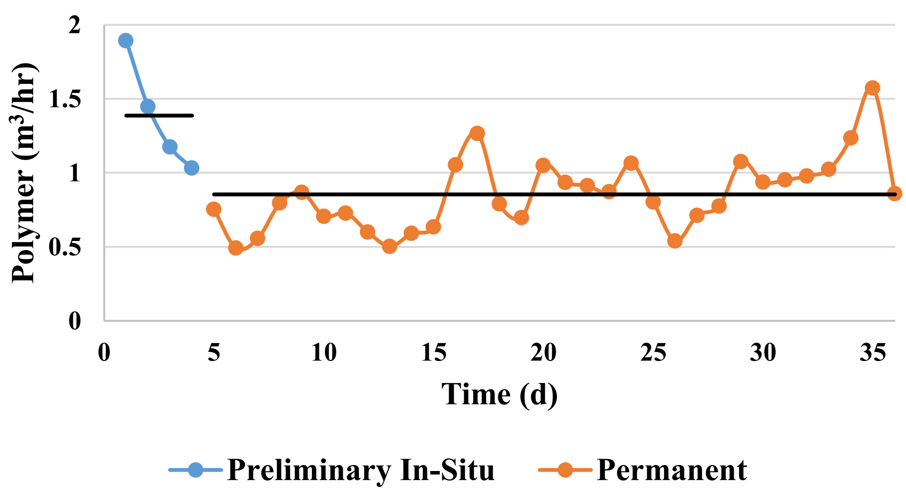

Figure 28 - Amount of polymer added during permanent acidification process versus preliminary *in situ* trial stage.

Primary and secondary sludge as seen in Figure 29 have shown consistency of operating conditions, again with few, but expected outliers.

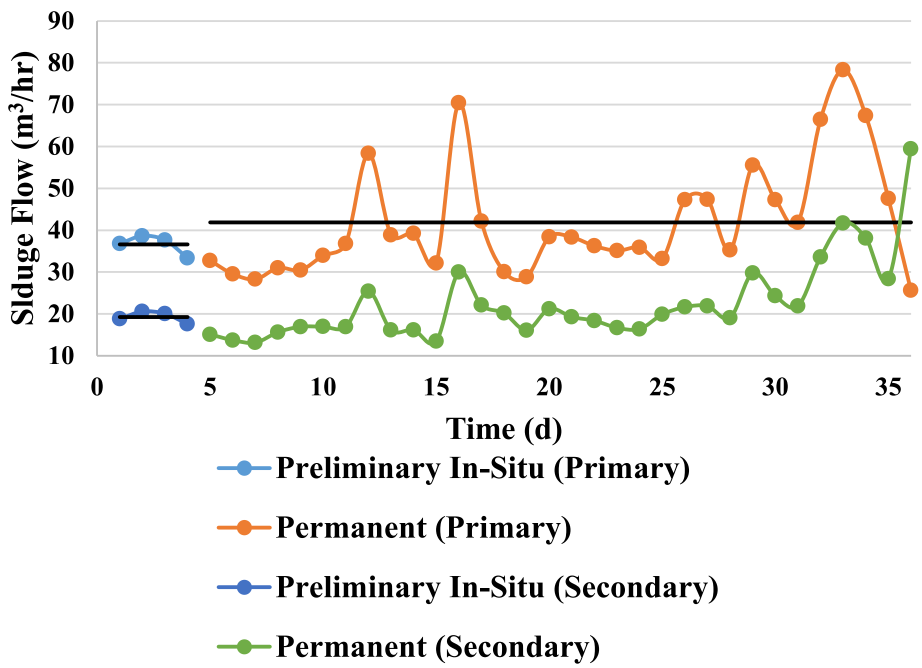

Figure 29 - Flows of primary and secondary sludge during permanent acidification process versus preliminary *in situ* trial stage.

pH values have not been measured for this portion of the trial due to technical difficulties regarding the tank probe operation. However, the WAS pH values have proven a sufficient comparison as seen in Figure 30. This change is quite notable; during the *in situ* trial the goal was to dip to a low 4 on the pH scale, but in the permanent process implementation PHP reduced the pH to a low 2 value. This change allows for a greater reduction in thickening chemicals without creating a risk to process operations. A notable point is day 30 (along the horizontal axis), where a minimum pH of ~1.5 was reached. This was due to a pump communication error which required switching an automated pumping system to a manual process. Prior to noticing the issue the pump was injecting acid at a much higher rate, over double that of the desired rate.

This occurred a few time, however this was the longest unnoticed occurrence; this issue is currently being investigated.

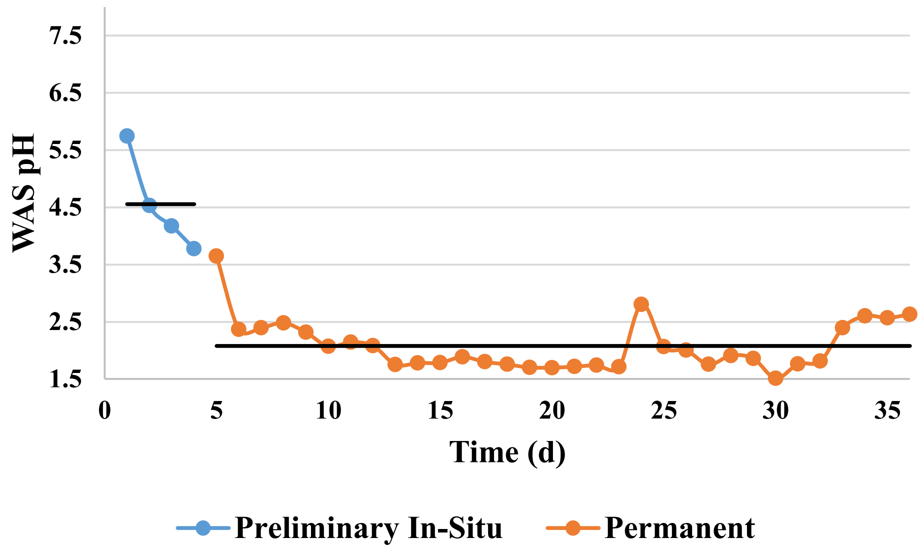

Figure 30 - pH changes of WAS during permanent acidification process versus preliminary *in situ* trial stage.

The average volumes changed from ~400 mL/min to ~600 mL/min (Figure 31). The elevated data points occurring after the 30^{th} day indicate a pump communication error which caused increase dosage not associated with the 60-70% ratio (0.6/0.7:1) acid in L/hr to sludge in m^3/hr.

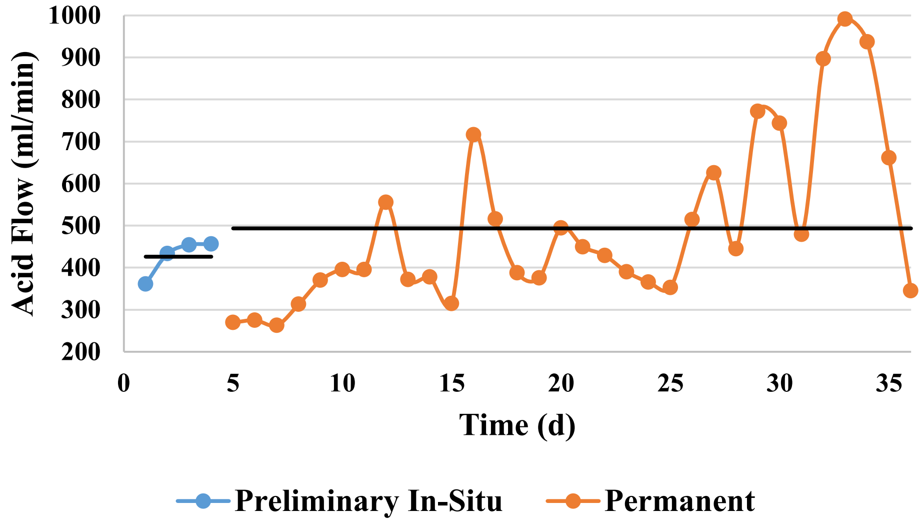

Figure 31 - Sulfuric acid flow rate during permanent acidification process versus preliminary *in situ* trial stage. *In situ* values are based upon an estimated 1:5 sulfuric acid to ferric sulfate ratio.

The weightometer values have seen a drastic decrease over the past month as exemplified in Figure 32, purely due to maintenance throughout the system combined with decreased output volume. The typical expected volumes through further operation will be much closer to those of the *in situ* trial.

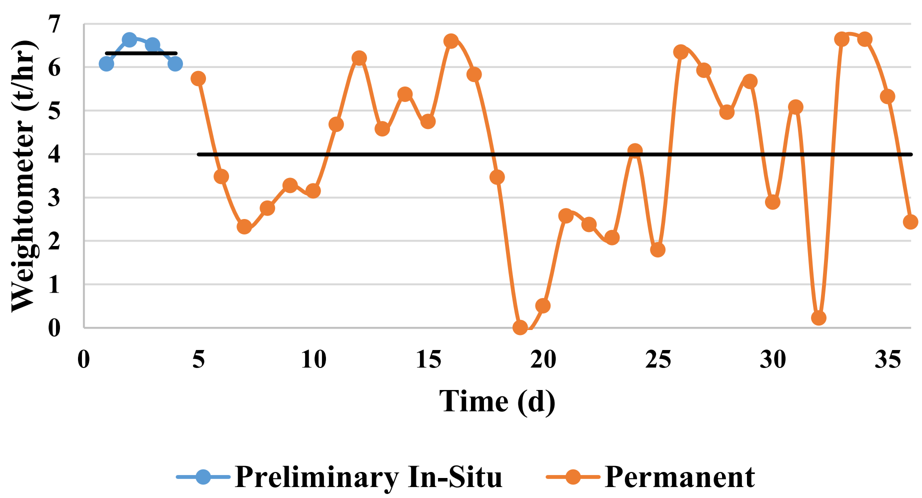

Figure 32 - Weightometer sludge flows of wet sludge during permanent acidification process versus preliminary *in situ* trial stage.

Mixed Liquor Suspended Solids (MLSS) values for this process showed increases following the *in situ* trial. However this was due to process changes and issues within the clarifiers, etc., these changes are expected to be mitigated over time (Figure 33).

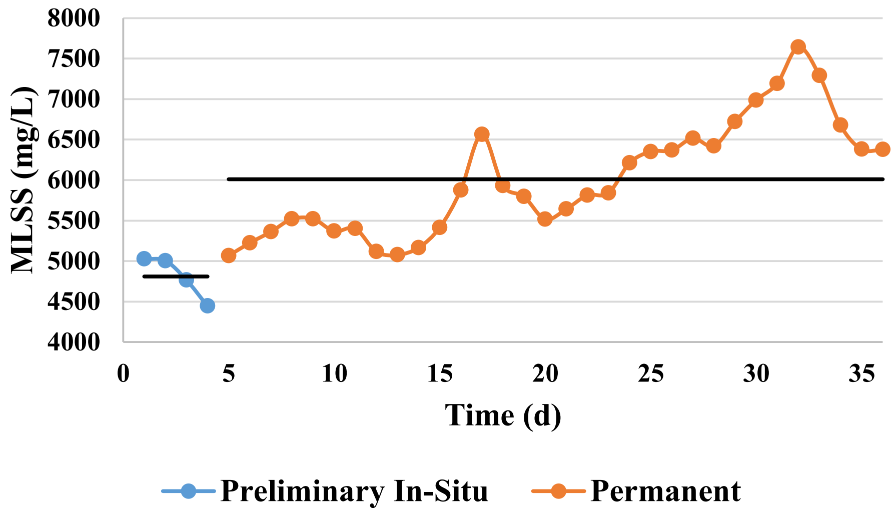

Figure 33 – Mixed Liquor Suspended Solids (MLSS) values during permanent acidification process versus preliminary *in situ* trial stage.

COD values remained steady throughout the month of monitoring with some observable fluctuations (Figure 34). Similarly, BOD was largely constant with some key observable fluctuations (Figure 35); in both cases these outlier values were due to a clarifier plugging issues. These issues have since been resolved.

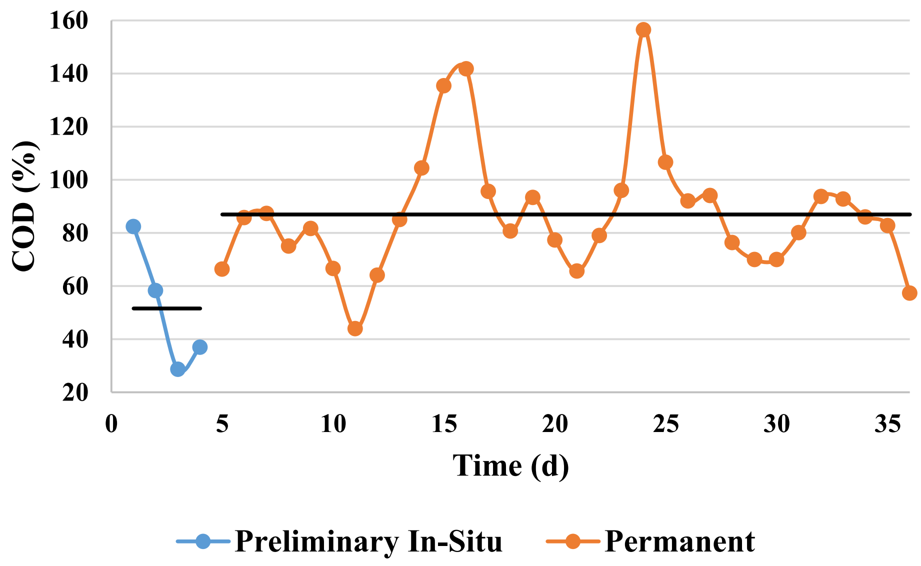

Figure 34 - Chemical oxygen demand (COD) during permanent acidification process versus preliminary *in situ* trial stage.

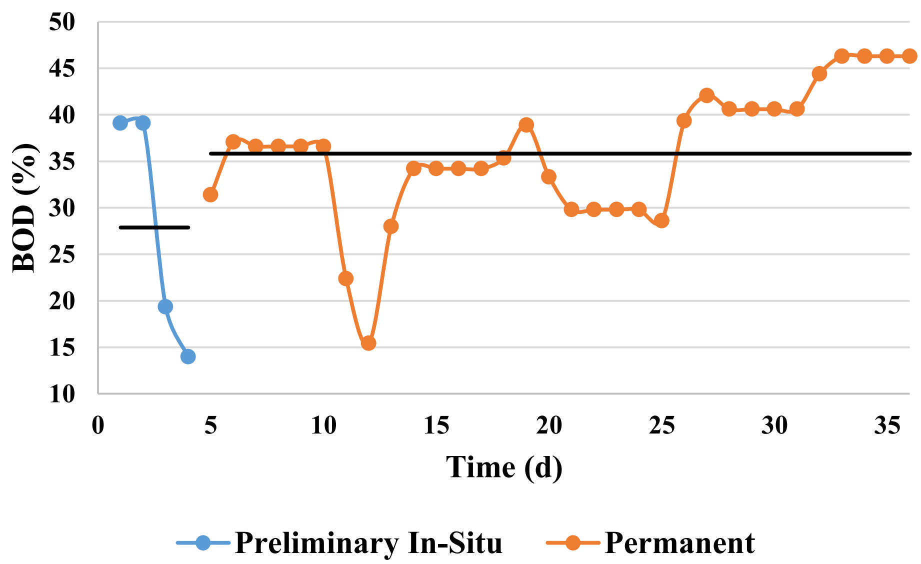

Figure 35 - Biochemical oxygen demand (BOD) during permanent acidification process versus preliminary *in situ* trial stage.

Finally, a cost analysis of chemical saving is found in Figure 36. Comparing the *in situ* trial and permanent implementation, the potential cost savings are shown to be similar. However, is previously noted, coagulant usage has not been altered to date in the actual mill operations. This will be a focus in the future.

The total estimated savings based upon the trial were that of ~$360,000+ CAD /yr; the permanent implementation has provided data supporting an estimate of ~$400,000+ /yr. This is based upon a savings of approximately $3,000/month on coagulant (yet to be optimized), $23,000/month on polymer, a cost of $13,000/month on acid, and an expected penalty savings of $19,000 ± $,6000 (for delivering sludge meeting the dryness requirements).

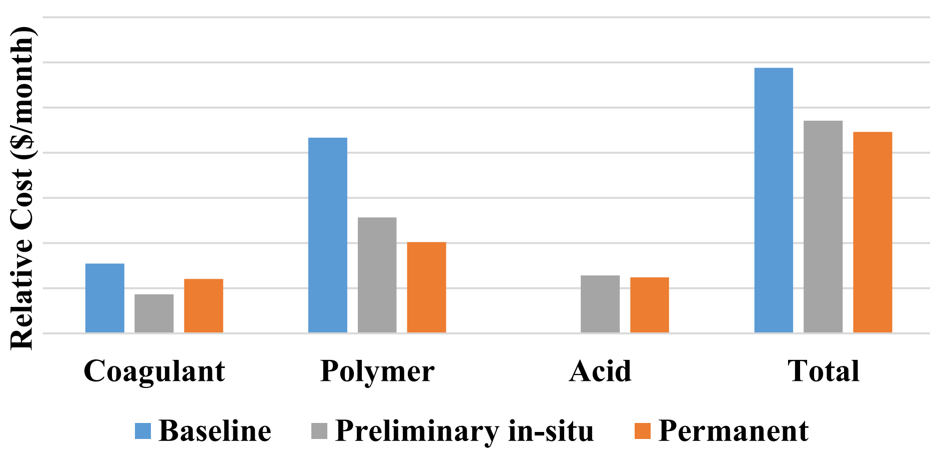

Figure 36 - Relative cost analysis for continuing acidification use through permanent implementation at PHP.

5.4 Environmental Considerations

It is important to ensure that the introduction of acid into the system does not negatively impact the environment through its presence in the leaving sludge and/or effluent water. Concerns typically surround "persistent toxic chlorine compounds like dioxins, organic materials that consume oxygen during decomposition, sulphur dioxide that contribute to lake acidification, and air-polluting nitrogenous compounds and phosphates that boost algae growth" ("WWF - Pulp and paper", 2017). The secondary treatment process ensures safety through addition of nutrients to the treatment reactors including: phosphorous from diammonium phosphate, nitrogen from urea, and oxygen from air. Nutrient deficiencies are easily identifiable through the presence of filamentous algae in the settling tanks (Environmental Leverage Inc, 2017). Two dominant species are *Nostocoida limicola* III and *Thiothrix defluvii* I (Mitchell, 2015). All acid injected into the WAS is neutralized prior to discharge to the Strait of Canso or - in the case of combustion - the concentration present in the sludge will be diminished through mixing and pressing options to provide a safe product with negligible change in characteristics apart from dryness. Overall, PHP completes a rigorous water treatment regime to ensure environmental compliance (Port Hawkesbury Paper LP, n.d.), mitigating potential harmful effects and monitoring input chemicals to estimate outgoing response whenever possible considering, again, chemicals causing growth and reproductive issues within fish are difficult to pinpoint at this time (Munkittrick *et al.* , 2013).

PHP regularly conducts testing to ensure environmental regulations are not exceeded; tests are run in adherence with Nova Scotia Department of Environment legal limits. These regular tests include BOD, Total Suspended Solids (TSS), and toxicity (LC50s). Toxicity is perhaps the most useful as *Oncorhynchus mykiss* and *Daphnia Magna* must survive in the effluent for 96 and 48 h respectively (Environment Canada[a,b], 2014; United States Environmental Protection Agency, 2002) . Five tests are performed with the goal of passing all five (*pers comm.*, Ken Mitchell, Port Hawkesbury Paper, Environmental Compliance Officer, 2015). Daily testing occurs as well, including tests of residual ammonia, dissolved oxygen levels, COD and BOD, settling abilities, clarifier blanket heights, and various microscopy examinations. Throughout the duration of the acidification trial, these values have not entered dangerous levels. Testing will continue to be monitored, with greater intensity, for the initial duration of permanent implementation and optimization of acid injection.

Regarding wastewater treatment, PHP has gone through a multitude of treatment classifications over the years, gaining excellence in this area, now classified as Class II (Nova Scotia Environment, 2009) since 2008; Classes are part of a point based system relating to types of treatment methods present along with chemicals used, etc.

PHP has a spill response procedure integrated new safety protocols to account for the introduction of liquid acid production to the mill's site. Chemical supplier ChemTrade Logistics works both with producers of acid as well as obtaining waste or by-products where available, and supported PHP to develop new safety protocols.

In a broader sense, greenhouse gas (GHG) emissions will be reduced not only through transport, which is more relevant in the case of mills transporting sludge for fertilizing purposes but in the case of PHP less sludge, if viewed comparatively to biomass, in turn lowers emissions; noting that wood contributes a large amount of CO_2 compared to other fuels (Partnership for Policy Integrity, 2011; "WWF - Pulp and paper", 2017). Increasing dryness not only will reduce emissions but will also reduce energy required to burn a product of low calorific value.5.5 Supplementary Early Business Opportunity Evaluation

Supplementing acidification as a means of dewatering, early in the study four plants were visited between August 25-26, 2015 to enhance the understanding of current waste treatment and dewatering processes in the local (provincial) industry. Below summarizes key information pertaining to each visit as well as relevant business opportunities for PHP.

1. Halifax Waste Water and Dewatering

This plant deals with sanitary sludge coming from humans, plants, digester, etc. All sludge began as sewage in this operation, commencing with sludge of 1-5% dryness concluding at an ideal/usual dryness of 25%, but on the particular day of the visit, dryness was at 18%. Polymer is added to the sludge to increase dewaterability- approximately 1 bag/day is added. This waste and dewatering plant has to date been using Cavity Pumps and Fournier Rotary Presses but plans to remove the presses and replace them with centrifuges. Aeration tanks will also be introduced to this process in the future. The dried sludge is then shipped to N-Viro for production of soil additives.

Business Opportunity

With the removal of the Fournier Presses, these pieces of equipment may come available for sale to be obtained in the future by PHP. This facility also had a moisture measurement balance which may be a purchase interest.

2. N-Viro – Walker Environmental Group – Soil Additive

Sludge from the Halifax Waste Water and Dewatering Plant is transferred to N-Viro where lime and cement kiln dust (obtained from Lafarge) are added – 30-35% added depending on incoming dryness. Following this addition the sludge is at approximately 45% dryness. The sludge at this facility is put through a natural gas drum dryer at a temperature of 400-700 ^{o}C to produce a product of approximately 55% dryness.

Business Opportunity

This experience has brought forth the potential of PHP working with local concrete suppliers where cement kiln dust is available to produce a similar soil additive for commercial sale.

3. Halifax C&D Tire Recycling

This facility creates tire derived aggregates (TDA) from waste tires. These materials can be used as the base for roads. The larger the material, the stronger the hold. An example of this was observed when an inspection of a well-used bus off ramp showed no cracks, sunken areas.

Business Opportunity

Use of the TDA as a base layer lay down area for offshore equipment after bark is removed near PM1. Also there is an opportunity trucked for a transport system – as TDA is delivered here, bark or other materials may be able to be back to Halifax.

4. SF Rendering

This plant extracts the oils from deceased animals and their waste to be used as fuel and other products. An expeller was used to dewater samples here which a technology that is comparable to dewatering presses except that the pressure is much higher in an expeller. The sludge from PHP began at a dryness of 34% (66% moisture). Upon exit from the expeller the dryness was found to be approximately 42-52% dryness. The sludge from PHP was also run through a pellet machine yielding pellets at 40% dryness with twice the density of the original sludge.

As previously noted, summarized results of trials at SF Rendering are found in Chapter 8, Table 11.

Business Opportunity

It has been concluded that pellets can be made from PHP's sludge; however, it is important to note that the pellet machine itself does not greatly increase the dryness of the sludge (what you put in is what you get out) - a further step is required as the sludge is thixotropic meaning that water is still present in the product regardless of its dry appearance (WERF - Innovations in

Dewatering Sludges, 2008). The expeller used at this facility may be worthwhile to look into obtaining a similar machine as the dewatering results were quite promising. From here the next step would be further pellet trials.

Chapter 6: Offsite Implementation at the Alberta Newsprint Company

Following the successful preliminary *in situ* trial scale application at PHP, the Alberta Newsprint Company in Whitecourt, Alberta expressed interest in the theory and requested an on-site visit take place as well as initial laboratory testing to determine the potential for dewatering their sludge via acidification.

The report provided to Alberta Newsprint can be found in Appendix F. The key findings are discussed below.

The Alberta Newsprint Company (ANC) has potential for drying success via acidification as was tested via laboratory scale experiments. Savings for this mill are based upon trucking costs as sludge product is trucked to farms for fertilizer; little cost can be saved in thickening chemicals. Savings are estimated within the range of $90,000-250,000 CAD /yr dependent upon the amount of trucks typically required.

It is recommended that ANC undergo an *in situ* trial similar to that of PHP to ensure that once implemented within the running processes of the mill, acidification will continue to dewater. Also there is a concern of residence time of acid prior to mixing which will also be investigated through an *in situ* trial.

Chapter 7: Reducing Water Content of Paper Mill Sludge: Comparative Study of Acidification and Sonication

This chapter will be submitted for publication in the near future. Therefore there will be some repetition of previous sections.

7.1 Abstract

Paper mill residuals (sludge) present a waste product with the characteristics and capabilities of becoming a valuable fuel or feedstock product. However, their typically high moisture contents hamper the incorporation of these sludges into valuable by-products, at least as currently produced by most contemporary industrial processes. Recognizing this challenge, Canadian paper mills are working to improve the value of their sludge products, with a Nova Scotia mill recently installing an acidification system. Sonication, in comparison to acid injection, uses variable frequency ultrasonic waves to cause disruption within material samples, which in the case of sludge, increases homogeneity and separation of water from solids. Acidification and sonication yield distinctly different products, with acidification producing the properties most attractive to further processing opportunities.

7.2 Highlights

- Acidified and non-acidified paper mill sludge is treated with sonication.
- Homogenisation of sonicated product occurs due to molecular disruption.
- Sonication is compared to acidification treatment.
- Sonication has potential as supplemental process to acidification.

7.3 Keywords

Sonication; Sludge; Dewatering; Acidification; Wastewater Treatment.

7.4 Introduction

Port Hawkesbury Paper LP (PHP), Port Hawkesbury, Nova Scotia, Canada, is a well-known producer of supercalendared paper; however, commensurate with this flourishing paper production is considerable volumes of product waste. In the case of PHP as well as many other mills across the globe, this waste is sludge comprised of wood fibers, clay and secondary treatment bio solids (MacDonald *et al*, 2017). Sludge produced varies in dryness by season, ranging from approximately 25 to38%. At lower dryness values, the calorific value of the sludge product is low, and with heat required to vaporize associated water, net fuel values are low. Within the last year, preliminary *in situ* trials followed by permanent implementation of an acidification system have taken place at PHP to prove the economic and dryness gains possible with this process. The new system delivers material with a minimum dryness of 30% to be obtained regarding sludge year round as well as providing economic value through reduction of costly dewatering chemicals (polymer and coagulant) (MacDonald *et al*., 2017). Where thickening chemicals typically act to disrupt particles and follow up with flocculation to separate out solids, acid can act to supplement this process with eruption of microorganisms and decrease water retention. Sonication is an alternative means of increasing dryness while having the added benefit of eliminating safety hazards associated with the storage and process addition of large volumes of acid. Sonication, with the provided temperature, pressure, and force changes, can reduce sludge volume outputs (Jin-song & Yu-feng, 2011) with a limited need for safety precautions; typically being hearing protection. Paper mills, as well as waste producers can be heavily safeguarded by regulations such as output product pH and in some instances this may prevent the integration of acidification into mills in some jurisdictions. This work investigates sonication on a laboratory scale to determine the potential of sonication for dewatering applications to compliment or replace acidification processes with the goal of increasing overall product value; not only for PHP but for industries with similar treatment situations.

7.5 Materials and Methods

This study was conducted in phases, the first phase examining the potential for physical change and water release through sonication vs. acidification, while the second stage optimized sonication procedures and parameters. Sludge used in this trial was a mixture of secondary, primary, and thickening chemicals (polymer and coagulant), with approximately 3% solids content.

7.5.1 Determination of Sonication Based Dewatering Capabilities

Initial testing evaluated the limits of mechanical removal of water through physical pressure exerted over a progressively thin mixture of sludge relative to impinging surfaces. Akin to wringing out a sponge, the water-holding capacity of sludge, before and following physical or chemical manipulation, would provide a baseline for improvements in manipulation on water release. As thicker sludge mixtures could re-absorb released water, making % moisture determinations problematic (using sponge analogy, released water during compression absorbed by adjacent non-compressed regions), it was deemed imperative to have complementary mating forces on compressive surfaces to prevent re-sorption of extruded moisture. Various paired products, which exhibited complementary tolerances and angles allowing thin sludge layers for compressive forces to act against, were evaluated in pairs, with a goal of over 50% insertion into one another to allow. The design must further allow reproduce-able application of consistent force, and for extruded water from a sludge sample to be released (*i.e.* mesh screening) for quantification while pressure is retained to avoid resorption. Products evaluated at the laboratory-scale included Tupperware containers, small traffic pylons, red Solo™ cups (Figure 37), and stacking trays; typically the lower positioned of the paired items required drilled holes to allow for water removal with screening to allow for retention of solids. While similarities with all devices were observed, and may facilitate rapid assessment and inexpensive assessment at many workplaces the most consistent and reproducible water-removing device was a cider press, and unless otherwise indicated, was used for results shown. Extruded water was collected in a Pyrex beaker. With sufficient replication to accommodate inter-trial human error regarding ability to exert reproducible force, this protocol would allow for the determination of physical and/or chemical influences on the potential for sludge dewatering on a gross basis.

Samples chosen for sonication were introduced into a SONICS Vibracell VCX750 Ultrasonic Cell Disrupter, using a 1/2” titanium alloy probe. Measurements of wet and dry mass, along with volume of water removed were taken prior to sonicating. Typical sonicating time was 10 min at an amplitude of 80% unless otherwise stated. Following sonication, samples were dried in a Thermo Heratherm oven for 12 h at 85^{o}C. Non-sonicated samples were handled in an identical fashion, but did not undergo the sonication process.

Figure 37 - Handmade small scale pressure exertion design using red Solo™ cups and screen mesh.

7.5.2 Determination of Sonication Parameters

A 4 gal Cider Press with stainless basket (Pleasant Hill Grain) was used for extraction of water; this allowed for a reproducible amount of force to be applied to each sample. A SONICS Vibracell VCX750 Ultrasonic Cell Disrupter, using a 1/2” titanium alloy probe was employed for sonication throughout the reported tests unless otherwise indicated.

For each trial, two sludge samples of each mass were weighed out; each sample was placed in the press and a complete; one sample for sonication, other samples should be used as benchmark, non-sonicated samples. With the non-sonicated sample, input into press and turn press handle until all threads have been used/ further immovable for exact pressure replication between trials. Measure amount of water removed and move retentate to oven. Sonication is then performed on 100 mL samples as previously stated for 5 min per sample unless otherwise stated in the results section. Following sonication, the cider press was again used to extract liquid, with retentate dried for 24 h at 95^{o}C in a Thermo Heratherm Oven. A post dry weight is finally obtained. Non-sonicated samples forgo the sonication process and go directly to the oven drying step.

7.5.3 Bench Scale Determination of Acidification Potential

Expanding upon the research completed by MacDonald *et al*. (2017), laboratory scale experiments were performed in beakers to determine potential for water removal upon acid addition; with the addition of a more precise de-watering evaluation by follow-up centrifugation. Also, the MacDonald *et al*. (2017) trial utilized Waste Activated Sludge (WAS), while in the present study, mix tank sludge was examined. The sludge composition differs somewhat in that WAS is solely comprised of secondary sludge; mix tank sludge is a mixture of both primary and secondary sludge. Mix tank sludge in the present study was selected due to ease of sampling and a desired focus on the material emerging from the newly implemented acidification at PHP. Mix tank sludge samples (30 mL) were injected with pre-determined aliquots of sulfuric acid, from 0 mL to 0.2 mL in 0.05 mL increments. Samples were placed into 50 mL Falcon^{TM} Conical Centrifuge Tubes and centrifuged at 3000 xg RCFfor 5 min in a Heraeus Megafuge 40 centrifuge. Water extracted as supernatant was measured following centrifuging.

7.5.4 Acid Effects on Sonication

Samples (40 mL) of acidified and non-acidified mix tank sludge (mix of primary and secondary sludge, ~3% dryness) were sonicated. Resultant sludge was tested for dryness consistent with section 7.5.2. Finally centrifugation was completed in a similar manner as noted in 7.5.3.

7.6 Theory/Calculation

Sonication is not typically used to dewater sludge; more often methods including freeze/thaw, gravity, and acidification are used. Options vary based upon expense, location, weather, and desired dryness. In this instance acidification is the main comparative method based on the theory of biosorption where paper mill sludge acts as a binding site for both heavy metals and large water containing molecules. The injection of acid breaks key binding sites both releasing heavy metallic components and causing eruption of water containing molecules. Data present in MacDonald *et al.* (2017) demonstrates various acids can provide comparable dryness values; however, economics favoured sulfuric acid as approximately 1/5 was required to produce the same results as ferric sulfate. Further, acidification also reduced costs of thickening chemicals such as polymer and coagulant; the resulting cost savings were well over $20,000 CAD /mthy, offsetting the approximate $14,000 CAD /mth cost of sulfuric acid addition (Macdonald *et al.,* 2017). When the acidification process is implemented on an industrial scale, payback period is immensely important. In addition to proof of concept, economic analyses must favor a 3 yr payback period, or better. Acidification delivers this result to PHP.

Alternatively, sonication uses rapid sound vibrations to initiate cell lysing that increases the ease that water is released from cells within sludge. Laboratory scale sonicators can cost between $3500-$8000 USD depending on the desired wattage and result; they also have limited safety challenges. When using this device the user simply requires ear protection to counter the high pitched sound. Such technology could reduce or eliminate the safety challenges associated with the use of concentrated acids. However, at an industrial scale such technology may not be cost effective, particularly as it would be a supplement to the mill's drying efforts – not a replacement. While there are gaps in the literature, research has shown an increase in total solids content up to 25000 mg/L when sonicated for a 35 min period at a power intensity of 125.8 W/cm^2 (Zhang *et al*., 2008)

Sludge sonication has been well documented, but the literature focuses upon sonication as a form of pre-treatment for anaerobic digestion, typically obtained from wastewater treatment plants. Our paper mill sludge differed in composition however from municipal wastewater sludge, being rich in clay, ash, pulp, and various thickening products. Sonication provides a very similar disruptive process to that of acidification, with flocculant disruption to release desired internal components, in this case, eruption for the release of water. Chu (2001) found that cavitation can occur readily, but the threshold at which it occurs could be considerably difference across test mediums;

> "the threshold was found to be 20–30 W/cm^2. This value should be applied with great cautions to other types of sludge since sludge characteristics as well as operational conditions affect the cavitation threshold (Chu, 2001)."

The Chu (2001) article suggested that the total solids amount can be positively affected through sonication with the best operating parameters are those of high intensity and short timeframe. Otherwise, the breakdown of flocculant space can allow for water molecules to actually adhere more efficiently, creating the opposite of the desired effect. One pulp mill study was reported using non-varying sonication as a pre-treatment for anaerobic digestion. Again, it must be recognized that results are highly dependent upon sludge sample characteristics (Wood, 2008); two phases may be present in processes utilizing sound waves, the first being disintegration of flocculant material, followed by solubilizing of remaining materials (Bougrier *et al*., 2007). A lack of dewatering ability has been seen in many cases due to overexposure at high frequencies. For example, Zhang and Wan (2012) reported that the optimal energy dose was 960 kJ/kgDS while an energy input higher than 1200 kJ/kgDS deteriorated the sludge dewatering capacity.

7.7 Results and Discussion

7.7.1 Determination of Dewatering Capabilities

Water removal via a pressure exertion technique (red solo cups, netting) followed by a measurement of solids remaining post pressure exertion indicates the adherence of water to the sludge prior to drying, as the mass of sludge post sonication drops to ~8% of its moist mass (Table 4). This table provides the moisture and solids contents of non-sonicated sludge on a percentage basis again demonstrating the hydrophilic nature of the sludge. Most paper mills use presses and drainers to enhance dryness values in the case of PHP, such equipment produces an output press with 25-38% dryness depending upon the season.

Table 4 – Characteristics of pressure exertion using non-sonicated, non-acidified sludge samples.

Trial	Water Removed (mL)	Solids Content (g)	Post Dry Mass (g)	Initial Moisture (%)	Initial Solids (%)	Post Dry Solids (%)
1	61.0	31.41	2.58	61	39	6.62
2	60.0	33.10	2.05	60	40	5.13
3	60.0	39.71	3.71	60	40	9.28
4	50.0	53.01	4.66	50	50	9.32
5	35.0	45.55	4.15	35	65	7.09

t-critical ($\alpha = 0.05$) = -2.13 and $p < 0.05$

There was considerable inter-trial variation in non-acidified sample water removal between trials (Table 5). Notably, sonication increases moisture content, the opposite of the desired result (Table 6), both Table 5 and 6 accompanied by t-based *p*-values ($\alpha = 0.05$). However, sonication did create a seemingly more homogenous mixture, which would facilitate water extraction under the right conditions, likely increasing the efficiency of various press technologies, although this was not specifically evaluated in the present study. Following the drying process the recovered sludge post-sonication is fairly moisture rich, dense, compact in formation, consistent visibly with water remaining in the sludge.

Table 5 – Sonicated, non-acidified sludge samples prior to and following sonication.

Trial	Water Removed Pre-sonication (mL)	Solids Content (g)	Water Removed Post Sonication (mL)	Post Dry Mass (g)
6	72	38.17	30	2.05
7	60	48.87	30	3.91
8	50	56.86	33	8.06
9	60	51.20	60	3.48

Uncertainties *u* (Water Removed Pre-sonication, Water Removed Post Sonication) = 1 mL, *u* (Solids Content, Post Dry Mass) = 0.01 g

t-critical value = -2.35 and $p < 0.05$

The values presented in Table 6's post sonication solids column does not represent oven dried sludge, but rather sludge immediately following sonication and manual dewatering (exerting pressure to remove residual water). Due to the increased homogeneity and macromolecular degradation within the sludge, potential for water removal actually decreases, causing a large increase in perceived solids content percentage as water remains within the sample.

Table 6 – Sonicated, non-acidified sludge samples initial moisture contents versus post sonication content.

Trial	Pre-sonication Moisture (%)	Pre-sonication Solids (%)	Post-sonication Moisture (%)	Post-sonication Solids (%)
6	65.45	34.55	27.27	72.72
7	60.00	40.00	30.00	70.00
8	50.00	50.00	33.00	67.00
9	60.00	40.00	60.00	40.00

t-critical value = -2.35 and $p < 0.05$

Overall, the comparison between the sonicated and non-sonicated samples, demonstrated that sonication does not increase overall dryness at the tested amplitudes, but instead homogenizes the composition to create a slurry which may be beneficial for treatment plants looking to reduce the volume of output and create ease of removal. Regarding power, the optimal operating conditions would be that of short duration and high intensity (Chu, 2001) if desiring a homogenous product, however, for the purpose of this study, ideally, mid-low intensity and time dependent upon degree of homogeneity desired. Table 7 draws attention to the changes in mass in sonicated and non-sonicated sludge; the physical appearance is distinct between the two, with the masses of sonicated sludge likely being higher as in Trial 3 than a true value due to the dense composition of the final product and its likelihood to contain water. Standard errors (SE) indicate greater consistency of dry mass values of sonicated samples (n=4).

Table 7 – Dry (final) masses of non-sonicated and sonicated sludge.

Trial	Non-Sonicated Dry Mass (g)	Sonicated Dry Mass (g)
1	-	2.05
2	-	3.91
3	-	8.06
4	-	3.48
5	2.58	-
6	2.05	-
7	3.71	-
8	4.66	-
9	4.15	-

Imprecision Uncertainties *u*(Non-Sonicated Dry Mass, Sonicated Dry Mass) = 0.01 g

7.7.2 Determination of Best Practice Parameters/ Data Collection

Initially, a high amplitude of 80% was tested (Section 7.2.1) quickly showing a change in physical appearance of the sludge, creating more of a slurry than the dewatered sludge product. As seen in Figure 38, the sonicated and non-sonicated dry samples are distinctly different, with the sonicated sludge drying in a uniform shape whilst non-sonicated sludge does not. Non-sonicated sludge however, in a short period of drying time (12 h) dries uniformly while sonicated sludge does not, with the center retaining moisture.

Figure 38 - Left to right, non-sonicated dried sludge versus sonicated sludge.

While sonication at high amplitudes creates a seemingly homogeneous mixture, the final solids content seems to be more dense, still exhibiting a moist overall composition due to its packed nature, leading to the assumption that the duration (12 h) provided for drying does not remove all moisture, again leading to the theory that sonication actually decreases dewaterability.

Visually, during sonication, amplitudes lower than 30% show no change/ disruption.

Tables 8 and 9 present an overview of the final data. This experiment demonstrates that sonicated samples tend to lead to a greater final sample mass, likely due to the drying time and temperature (12 h and 95^{o}C), which allows moisture to remain present in the sludge; this is seen in the dry mass. It is also suggested that much of the mass lost post sonication (prior to drying) is due to the mixing which occurs during sonication to create a more homogenous mixture and went placed into the apple press much of the smaller particles of sludge are able to escape through the grating. The data differs from Table 4 through the use of reproducible force exertion via cider press technology and also the exposure to varied amplitudes to further explore the extent of water retention. Table 9 also displays average power values which were obtained from acidified sludge samples assuming negligible variation in non-acidified samples. Tables 8 and 9 also include t-based *p*-values ($\alpha = 0.05$). Figure 39 displays the average mass difference produced by various amplitudes.

Table 8 – Non-Sonicated sludge sample characteristics.

Initial Mass (g)	Water Removed (mL)	Initial Dryness (%)	Initial Moisture (%)	Mass Difference (g)	Post Dry Mass (g)
111.87	50	55.31	44.69	50.69	3.56
112.04	50	55.37	44.63	57.53	5.62
108.03	50	53.72	46.28	64.2	7.41
116.17	59	49.21	50.79	51.62	3.85
110.20	50	54.63	45.37	66	3.61
102.71	38	63.00	37.00	60.91	1.95
109.62	40	63.51	36.49	75.28	5.79

Imprecision Uncertainties *u*(Water Removed) = 1 mL, *u*(Mass Difference, Post Dry Mass) = 0.01 g

t-critical value = -1.94 and $p < 0.05$

Table 9 – Sonicated sludge sample characteristics at various amplitudes.

Amplitude (%)	Average Power Required (W)	Mass Sonicated (g)	Solids Remaining Post Sonication (g)	Mass Difference (g)	Post Dry Mass (g)
80	71	108.24	28.30	79.94	10.76
		107.04	54.71	52.33	29.22
		102.41	78.60	23.81	26.80
70	47	113.82	29.90	83.92	9.90
		109.56	28.10	81.46	8.10
		112.17	30.76	81.41	12.27
60	42	114.65	32.60	82.05	12.60
		113.52	33.72	79.80	13.72
		109.97	35.05	74.92	15.05
50	36	112.40	92.90	19.50	18.82
		109.90	80.66	29.24	25.76
		103.85	84.14	19.71	24.30
30	19	107.98	78.00	29.98	24.56
		108.38	86.79	21.59	23.40
		105.65	88.44	17.21	25.10

Amplitude (%)	Average Power Required (W)	Mass Sonicated (g)	Solids Remaining Post Sonication (g)	Mass Difference (g)	Post Dry Mass (g)
20	12	105.72	90.91	14.81	18.84
		110.39	94.16	16.23	20.31
		101.46	86.30	15.16	11.02

Imprecision Uncertainties *u*(Mass Sonicated, Solids Remaining Post Sonication, Mass Difference, Post Dry Mass) = 0.01 g

t-critical value = -2.92 and $p < 0.05$

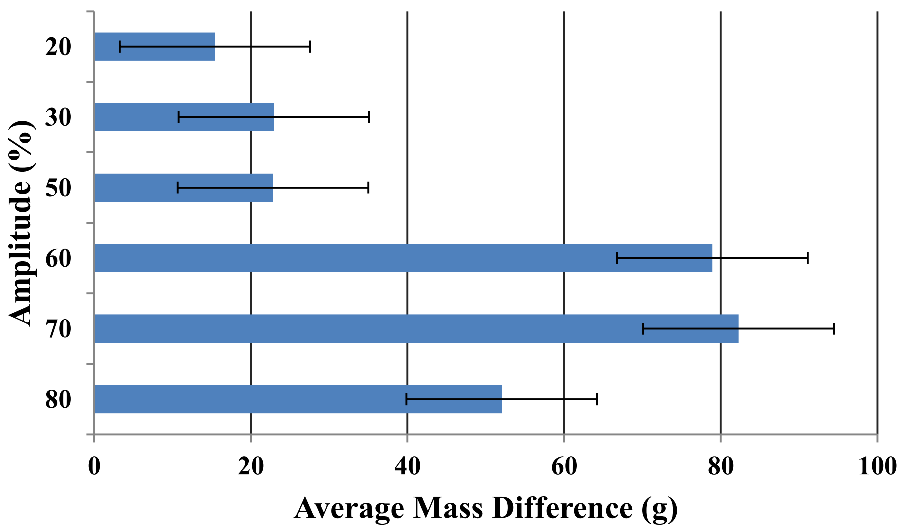

Figure 39 - Average mass difference at various amplitudes. Error bars represent standard error.

7.7.3 Determination of Acidification Potential on a Bench Scale

Following up on MacDonald *et al.* (2017), an initial test for potential of the dewatering potential through acidification on a biomass-like or waste material can be simply assessed through a visual analysis of gravitational separation as well as that accelerated by centrifugation. While keeping the mass of sludge constant, it is readily noticeable through gravity settling, albeit referencing the relatively imprecise beaker graduations, that an increase in acid increases the visible and easily removable water supernatant following centrifugation (Figure 40).

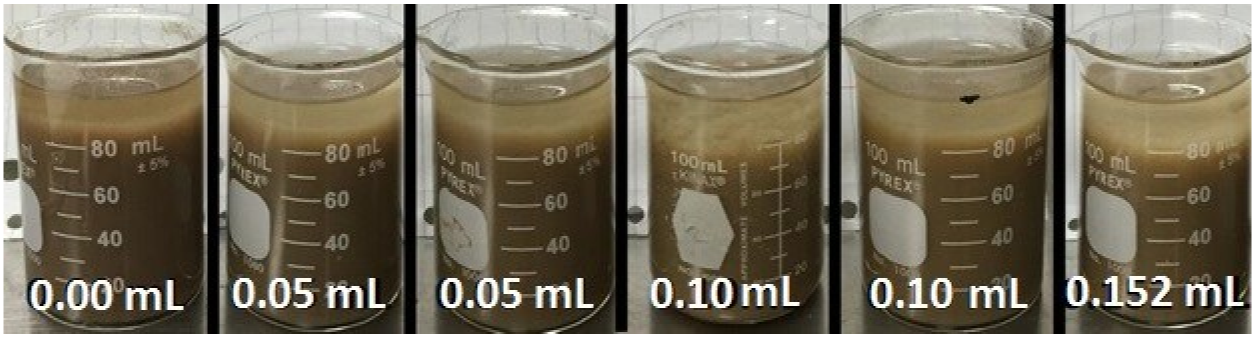

Figure 40 - WAS samples with increasing acid addition (left to right).

Similar trends seen by centrifugation (Figure 41) although visual determination of supernatant volumes is more difficult as the pellet: water interface is not level in each centrifuge tube. However, commensurate increases in respective water volumes yielded by acidification dose can be quantified (Table 10).

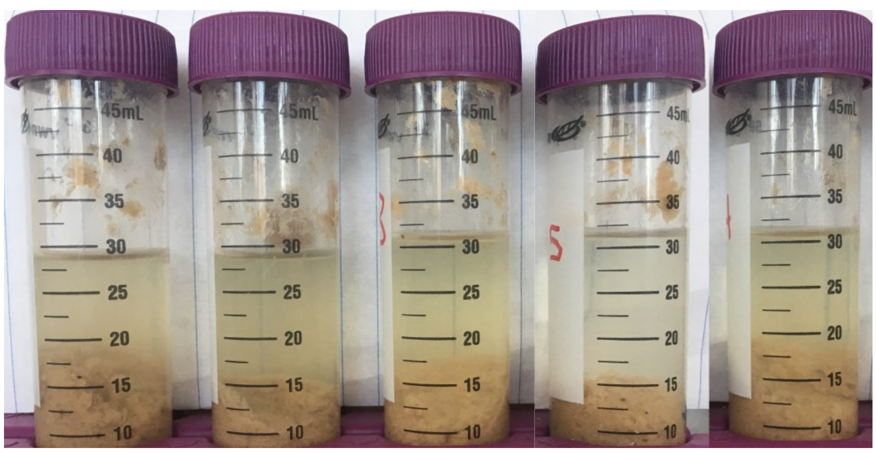

Figure 41 - WAS samples with ranging acid (93% sulfuric acid) addition volumes from 0 to 0.20 mL (left to right, 0.05 mL increments)

Table 10 - Volume of water removed through acidification with 93% sulfuric acid of paper mill sludge followed by centrifugation of samples.

Volume of Acid Added (mL)	Volume of Water Removed Following Centrifugation
0.00	13.0
0.00	12.5
0.05	13.5
0.05	13.9
0.10	15.0
0.10	15.0
0.15	16.0
0.15	15.9
0.20	17.0
0.20	16.8

Imprecision Uncertainties *u*(Volume of Acid Added) = 0.01 mL, *u*(Volume of Water Removed Following Centrifugation) = 0.1 mL

This experimental approach serves as a quick and simple method of determining sludge-acid dewatering capabilities, which can be implemented in any industrial context with minimal cost and effort. Notably, samples with 0.15 and 0.20 mL acid addition were significantly easier to extract water as the lower acid volume samples had a mid-level slurry whereas high volumes addition created a clear differentiation between water and pellet interface.

7.7.4 Determination of Acid addition on Sonication

To assess compatibility of acidification and sonication in liberating water from paper mill sludge, evaluations were completed using both non-acidified and acidified batches of sludge. Although the positive effect of acid addition on water removal from sludges have been demonstrated (MacDonald *et al.,* 2017), it is unclear what benefit the addition of a sonication process would yield. Due to the extreme homogenous changes associated with sonication observed in this study, an amplitude of 60% was chosen as a maximum. Outliers were found in various non-acidified samples which may be due to the trace presence of acid from the previous trials run at PHP and/or the age of the sludge (prior to initial acidification testing). All samples following sonication showed little change in volume of water separated from the sludge, regardless of amplitude. However, on a mass basis, lower amplitudes had a larger remaining mass of sludge after drying. Figure 42 presents the amount of water removed from the sludge and in combination with Figure 43, one can observe acidified sludge in combination with sonication is more amendable for water removal but also for the a more dense end product. The smaller mass difference at lower amplitudes relates likely to less mass lost due to mixing. Standard errors in both Figures 42 and 43 demonstrate the need for acidification prior to sonication, with greater deviation a greater change is seen such as in the case of water removal.

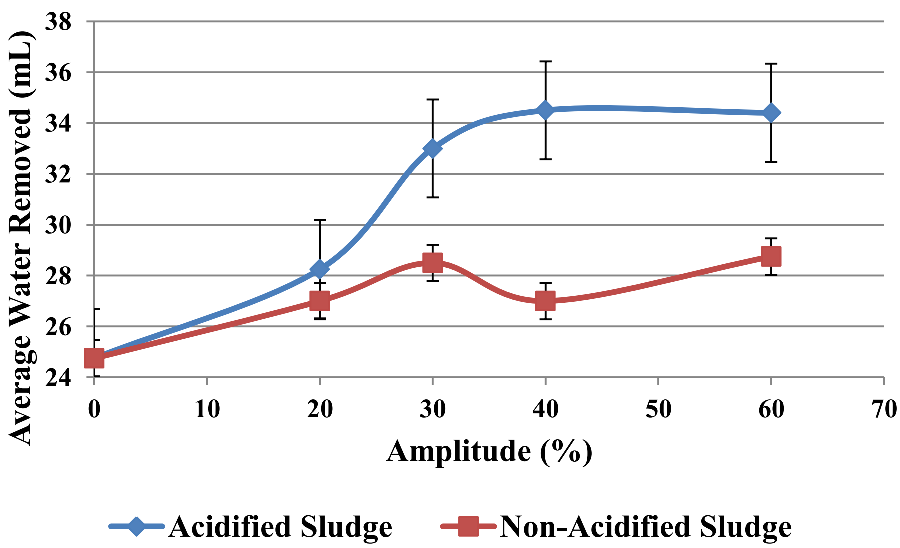

Figure 42 - Volume of water removed from sludge samples following acidification. Error bars represent standard error.

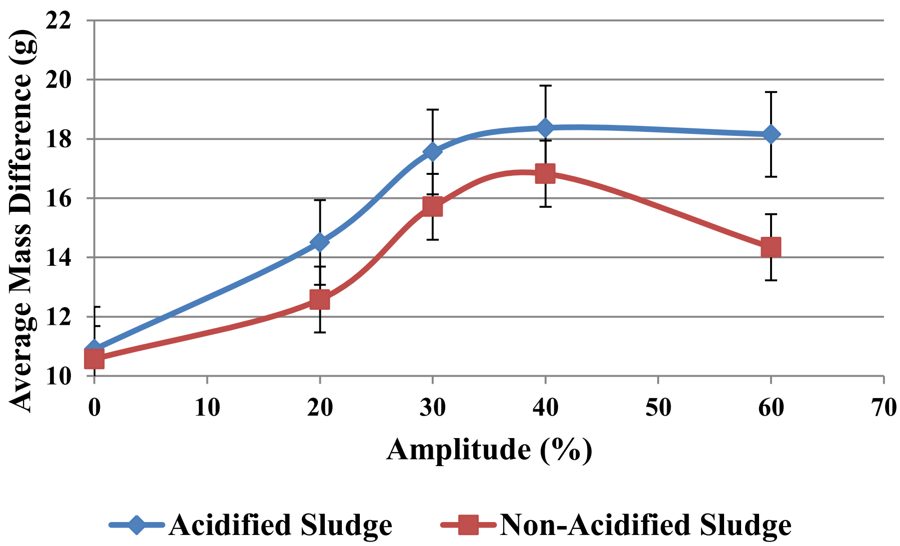

Figure 43 - Average mass difference of acidified and non-acidified sludge samples. Error bars represent standard error.

7.8 Conclusion

In conclusion, sonication, relative to acidification, efficiently homogenizes sludge, but contrary to expectations, inhibits water removal from sludge. Water removal, often the primary desired outcome of sludge treatment, may be inhibited by sonication through the re-sorption of water by macromolecular structures degraded by sonication that have heightened surface areas for binding water molecules. Also it should be noted that during sonication the sample volume was seen to slightly increase, commensurate with sonication amplitude, likely due to the presence of gas bubbles which was visibly monitored during the process. However, the slight increase in volume may be attributable to chemical changes produced by acidification, noted by Texier (2008).

The appearance of sludge dryness increase of is due to the packed composition following sonication (seemingly greater mass), which may aid in transport abilities but likely not aiding in the increase of value for final uses such as incineration.

While sonication removes the need for hazardous acid use, acidification, if conducted in a safe manner is the most viable method of increasing sludge dryness on an industrial scale. However, if reductions in overall waste amounts are the goal, sonication can provide desired results. Future work will involve expanding upon the data inventory to compare sludge from the base mill, PHP, and compare in all cases (acidification, sonication, etc.) to other sources of waste residuals and bio solids, including other pulp and paper mills. The potential exists for success on various levels of waste treatment as in areas valuing moisture, such as fertilizer augmenters which would benefit from water retention or industries looking to create a slurry.

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Chapter 8: Opportunities Through Sludge Pelletization

Trials were undertaken with the support of SF Rendering in Centreville, NS to determine the viability of using PHP's sludge as feedstock for biomass pellets – to be used either as fuel for combustion or as a soil amendment.

SF Rendering operates a large-scale pelletizer and agreed to process a specific amount of sludge to allow for testing linked to heat content and structural integrity of the resulting pellets. In addition, there was an interest in the potential for additional dewatering. The resulting pellets (Figure 44) were found to lose shape after a few days. Additional testing for moisture content are found in Table 11.

Figure 44 - Pellets produced at SF Rendering (August 25, 2015)

Table 11 – SF Rendering Plant trial results of pelletizing paper mill sludge (August 25, 2015)

	Moisture (%)	Dryness (%)	Increase in Dryness (%)
Original Sludge	**65.92**	**34.08**	**-**
Expeller Sample 9:30 AM	**48.80**	**51.20**	**12.76**
Expeller Sample 9:40 AM	**57.53**	**42.47**	
Average		**46.84**	
Pellet Sample 2:20 PM	**57.56**	**42.44**	**6.47**
Pellet Sample 2:30 PM	**61.34**	**38.66**	
Average		**40.55**	

Cellulose fiber (typically wood) pellets can be solid commercially; in addition a local CHP unit relieves the amount of waste to landfill from PHP. Typically, retail outlets such as Canadian Tire or Home Hardware sell ~18 kg bags of wood pellets at a price of ~$6.00. The initial target market for PHP pellets would be stores in Cape Breton; in recent years the region has experienced a shortage of available pellets (for combustion in pellet stoves, etc…) in the winter months. Pellet supply is outsourced to other provinces taking away from the local economy. Pellet producing plants in the province such as Eastern Embers has a high enough demand that the plant aims to run 24/7 to meet supply needs – however supply of biomass is sometimes a challenge. With a production option in Cape Breton pellets – if found to be acceptable to the retail sector – could be locally, with a potential for regional or international sales.

Alternatively, soil amendment is another salable product that could be introduced to the local retail market. Stores such as Canadian Tire sell such material for ~$10.00 for around 30 L of product. Animal bedding pellets is yet another product; current product is sold for around ~$6.00 for a 40 lb bag and would be popular again not only within Cape Breton but across the province.

Chapter 9: Conclusions

In conclusion, this research has demonstrated that acid can be a strong dewatering agent in the case of paper mill sludge as suggested by Mahmood and Elliot (2007). Data showed that both ferric sulfate and 93% sulfuric acid produce the same overall results as far as chemical savings and pH decrease. However, the cost associated with the use of sulfuric acid is considerably less expensive that the alternative due to the reduced volume required by the highly concentrated acid; ferric sulfate typically having a pH of less than 2 while sulfuric acid (93%) has a pH of 0.3Acidification overall acts as both a supplement and replacement for thickening chemicals (polymer and coagulant) as these chemicals act create flocculation, acidification acts to breakdown microorganisms and release water. Sulfuric acid and ferric sulfate are not the sole additives capable of injection, acidic compounds such as hydrochloric acid have also worked similarly (Devlin, Esteves, Dinsdale, & Guwy, 2011), the key component being hydrogen ions for donation.

Cost calculations based on the various trials show that savings of $30,000 per month is expected. This also includes avoided penalty costs due to the confidence in producing sludge of 30% dryness or greater. It is anticipated that savings will increase as the full-scale process continues to be improved and at this time the project is on track for a payback period less than two years.

Environmental benefits stemming from acidification are also broad, with a decrease in output waste volume PHP is able to easily transition away from the landfill topping project while also cutting back on the energy to burn through increased calorific value. Also, PHP, with economic success may have the potential to expand operations, for example, to anaerobic digestion which is an expensive process to implement, but may allow for production of methane which in turn can be used for heating (Mills *et al*., 2014; "Aerobic vs. Anaerobic Digestion: Benefits & Comparison", 2014). The addition of acid, also, does not negatively affect the burners or burning process as the small concentration of acid present in the final sludge product is negligible to the overall volume of sludge.

Pelletizing as a method of dewatering has minimum impact and the resulting pellets do not meet structural requirements necessary for retail sale. However, combined with further dewatering measures at PHP such as the Dryclone^{TM} technology currently under investigation, the opportunity to create a small-scale pelleting operation shows promise. Further, if the dried pellets can be consumed in greater quantity within the CHP unit, it will ease consumption of higher value hardwoods (a local point of contention), reduce shipping costs of biomass being trucked to the site as well as the GHG emissions associated with that shipping.

While not an intended result, the acidification step also reduced the count of coliform bacteria within the sludge, thereby improving market options. Additionally, a nearby gypsum plant could collaborate with PHP to produce a more holistic soil amendment. Gypsum pellets are readily used in soil; if mixed with the sludge from PHP it could provide a sludge/gypsum pellet that would also allow the gypsum plants to export some of its excess product for a reasonable price and the overall product would have a reduced moisture content. Gypsum has various benefits as a soil amendment, such as reduced risk of erosion (Hopkins, 2013). The gypsum represents only a small portion of the available material for consideration of mixed residual pellets at PHP. Further research into the opportunities for a mixed-residual pellet needs to be investigated.

Regarding other future work, PHP continues to investigate methods of further drying including continued discussion with Resource Converting, LLC regarding the Dryclone^{TM} system as the value of increasing to a desired value of approximately 60% would allow for PHP to expand business ventures into the way of commercial pellet production, fertilizer, or a burning to run on-site processes or co-operatively provide a fuel to another industry or business.

With the state of the paper industry wavering on a regular basis, PHP is working to innovate with focus on European strategies such as that of the Kalundborg industrial park in Denmark where an industrial symbiosis is created through resource, product, and waste sharing. PHP has this opportunity not only with sludge, but also with the large amount of waste heat produced by process streams (Kalundborg Symbiosis, 2017). The opportunity is also present to extract clean treated water, salt water, and process effluent.

Sonication is not currently plausible for use at PHP, due to the overall expected cost of implementation of an industrial scale device in conjunction with the likely negligible results seen during the test trials in comparison to current press technology used at the mill; however, if implemented this technology would work best as a supplemental practice to acidification. a slurry was created with assimilation increasing with increased amplitude; whilst PHP would benefit from a separation of solids and liquids, this technology could greatly benefit industries looking to retain moisture for transport.

pH being central to this study acts perhaps most notably in the sonication process regarding acidified samples as with the increased presence of hydrogen ions compounded with the available lone pairs on the oxygen portion of water molecules, attraction occurs (*i.e.* hydrogen bonding). Water retention results from these attractive forces which through the disruptive nature of sonication can be enhanced via mixing.

Finally, regarding potential for linkages to be made between sites, this will require further data inventory and will be likely presented in future work/publications. At this time the comparative test site, ANC, is updating various aspects of their secondary treatment regime prior to implementation of a trial.

Bibliography

A Rational Method for Sludge Dewatering via Freezing. (1986). Water Pollution Control Federation, 58(9), 911-916. Retrieved from http://www.jstor.org/stable/25043077

Aerobic vs. Anaerobic Digestion: Benefits & Comparison. (2014). *FOR Solutions*. Retrieved 12 February 2017, from http://forsolutionsllc.com/aerobic-vs-anaerobic-digestion/

Alturkmani, A. (2012). *Sludge Treatment. Environmental Engineering*. Retrieved 12 January 2017, from http://4enveng.com/edetails.php?id=61

Benchmarking Energy Use in Canadian Pulp and Paper Mills. (2015) Retrieved from http://www.rncan.gc.ca/sites/www.nrcan.gc.ca/files/oee/files/pdf/industrial/benchmark pulp-paper-e.pdf

Bougrier, C., Delgenès, J., & Carrère, H. (2007). Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge. *Biochemical Engineering Journal*, 34(1), 20-27. http://dx.doi.org/10.1016/j.bej.2006.11.013

Bruce, D., & van der Vooren, T. (2003). Trends in air emission limits for world class mills. Pulp & Paper Canada, 104(7). Retrieved from https://www.pulpandpapercanada.com/paptac/PDFs/July03/Regulations.pdf

CBC News, (2015). Wood pellet shortage hits Nova Scotia. Retrieved from http://www.cbc.ca/news/canada/nova-scotia/wood-pellet-shortage-hits-nova-scotia-1.2969870

Chemistry@Elmhurst. (2015). *Sludge Treatment*. Retrieved 20 November 2015, from http://chemistry.elmhurst.edu/vchembook/313sludge.html

ChemTrade, (2017). *Products. ChemTrade Logistics Inc.* Retrieved 23 January 2017, from http://www.chemtradelogistics.com/main/products/

Chiang, G., McMaster, M.E., Urrutia, R., Saavedra, M.F., Gavilán, J.F., & Tucca, F., Barra, R., & Munkittrick, K.R. (2011). Health status of native fish (Percilia gillissi and Trichomycterus areolatus) downstream of the discharge of effluent from a tertiary-treated elemental chlorine-free pulp mill in Chile. *Environmental Toxicology And Chemistry, 30(8)*, 1793-1809. http://dx.doi.org/10.1002/etc.573

Chu, C. (2001). Observations on changes in ultrasonically treated waste-activated sludge. *Water Research*, 35(4), 1038-1046. http://dx.doi.org/10.1016/s0043-1354 (00)00338-9

CTV News Atlantic, (2017). Closure of mill a blow to N.S. paper industry. Retrieved from http://atlantic.ctvnews.ca/closure-of-mill-a-blow-to-n-s-paper-industry-1.1020681

COFORD, (2006). *Wood Energy - Frequently asked questions.* Woodenergy.ie. Retrieved 6 January 2017, from http://www.woodenergy.ie/frequentlyaskedquestions/

Dahmer, S.C., Tetreault, G.R., Hall, R.I., Munkittrick, K.R., McMaster, M.E., & Servos, M.R. (2015). Historical decline and altered congener patterns of polychlorinated dibenzo-p dioxins and dibenzofurans in fish and sediment in response to process changes at a pulp mill discharging into Jackfish Bay, Lake Superior. *Environmental Toxicology And Chemistry, 34(11)*, 2489-2502. http://dx.doi.org/10.1002/etc.3126

Devlin, D., Esteves, S., Dinsdale, R., & Guwy, A. (2011). The effect of acid pretreatment on the anaerobic digestion and dewatering of waste activated sludge. *Bioresource Technology, 102(5),* 4076-4082. http://dx.doi.org/10.1016/j.biortech.2010.12.043

Diak, J. & Örmeci, B. (2016). Individual and Combined Effects of Freeze-Thaw and Ferrate(VI) Oxidation for the Treatment and Dewatering of Wastewater Sludges. *Water, Air, & Soil Pollution, 227*(9). http://dx.doi.org/10.1007/s11270-016-3039-0

DKL Engineering, (2011). *Storage Tanks. Sulphuric Acid on the Web*. Retrieved 13 January 2017, from http://www.sulphuric-acid.com/TechManual/Storage/storagetanks.htm

Environmental Leverage Inc. (2017). *Cold weather problems*. Retrieved 7 February 2017, from http://www.environmentalleverage.com/Cold_weather.htm

Electric Power Research Institute, (2002). *Task 2.6: Mechanical Freeze/Thaw and Freeze Concentration of Water and Wastewater Residuals: Status Report* (pp. 15, 21). EPRI, Palo Alto, CA: 2001. WO-671002 Retrieved from http://www.energy.ca.gov/reports/2004-04-02_500-02-019/500-02-019_A6.PDF

Elliot, R. *Rotary Press Revolutionizes Sludge Compaction*. Retrieved from http://www.tecumseth.com/documents/Rotary%20Press%20Revolutionizes%20Sludge 20Compaction.pdf

Elliot, R. (2014). Tecumseth Fournier Rotary Press Lab Trial.

Environment Canada[a],. (2014). *Biological Test Method: Reference Method for Determining Acute Lethality of Effluents to Daphnia magna.* Retrieved from https://www.ec.gc.ca/faunescience-wildlifescience/default.asp?lang=En&n=CF33F86F-1

Environment Canada[b],. (2014). *Biological Test Method: Reference Method for Determining Acute Lethality of Effluents to Rainbow Trout*. Retrieved from https://www.ec.gc.ca/faunescience-wildlifescience/default.asp?lang=En&n=F9AEDA4E 1

Epigentek.com, (2015). *EpiSonic Multi-Functional Bioprocessor 1100 | Epigentek*. Retrieved 20 November 2015, from http://www.epigentek.com/catalog/episonic-multi-functional-bioprocessor-1100-p2997.html?currency=ca&height=190&width=500& border=1&modal=true&random=1448048380653

Feng, H., Hu, L., Mahmood, Q., Long, Y., & Shen, D. (2008). Study on biosorption of humic acid by activated sludge. *Biochemical Engineering Journal, 39(3)*, 478-485. http://dx.doi.org/10.1016/j.bej.2007.11.004

Flaga, A., 2005. Sludge Drying. Institute of Heat Engineering and Air Protection, Cracow University of Technology, Krakow

FP Innovations, (2015). *Sludge Acidification - Port Hawkesbury*.

Frei, K.M., Cameron, D., Jasmin, S., & Stuart, P.R. (2006). Novel sludge drying process for cost effective on-site sludge management. *Pulp & Paper Canada, 107(4)*, 47-53. Retrieved from http://www.pulpandpapercanada.com/paptac/PDFs/Apr06/sludge.pdf

Haandel, A. & Lubbe, J. (2007). *Handbook of biological wastewater treatment.*

Hoffman, E., Bernier, M., Blotnicky, B., Golden, P.G., Janes, J.,Kader, A., Kovacs-Da Costa, R., Pettipas, S., Vermeulen, S., Walker, T.R.. *Environmental Monitoring and Assessment* (2015) 187: 766. doi:10.1007/s10661-015-4985-5

Hopkins, M. (2013). The Role Of Gypsum In Agriculture: 5 Key Benefits You Should Know. *Croplife*. Retrieved from http://www.croplife.com/crop-inputs/micronutrients/the-role-of gypsum-in-agriculture-5-key-benefits-you-should-know/

InyoProcess, (2015). *Concentrated Sulfuric Acid. Inyoprocess.com*. Retrieved 8 August 2016, from http://inyoprocess.com/chemicals-mainmenu-6.html?id=11

Irish, D. (2015). Port Hawkesbury Paper, government to file NAFTA appeal in tariff dispute. *CBC News Nova Scotia*. Retrieved from http://www.cbc.ca/news/canada/nova scotia/port-hawkesbury-paper-dispute-nafta-appeal-1.3324886

Jin-song, G. & Yu-feng, X. (2011). Review of Enzymatic Sludge Hydrolysis. *Journal Of Bioremediation And Biodegradation, 02(05)*. http://dx.doi.org/10.4172/2155-6199.1000130

Kalundborg Symbiosis. (2017). A circular ecosystem of economy. Retrieved 13 January 2017, from http://www.symbiosis.dk/en/system

Kim, J., Park, C., Kim, T., Lee, M., Kim, S., Kim, S., & Lee, J. (2003). Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. *Journal Of Bioscience and Bioengineering, 95(3)*, 271-275. http://dx.doi.org/10.1016/s1389-1723(03)80028-2

Kuhlberg, M. (2015). *Pulp and Paper Industry. The Canadian Encyclopedia.* Retrieved 15 January 2017, from http://www.thecanadianencyclopedia.ca/en/article/pulp-and-paper-industry/

Lee, D., & Hsu, Y. (1994). Fast Freeze/Thaw Treatment on Excess Activated Sludges: Floc Structure and Sludge Dewaterability. *Environmental Science & Technology, 28(8)*, 1444 1449. http://dx.doi.org/10.1021/es00057a011

Li, C., Lin, J., Kang, S., & Liang, C. (2005). Acidification and alkalization of textile chemical sludge: volume/solid reduction, dewaterability, and Al(III) recovery. *Separation and Purification Technology., 42(1)*, 31-37. http://dx.doi.org/10.1016/j.seppur.2004.06.001

Logsdon, G., & Jeffrey, E. (1966). Estimating the Gravity Dewatering Rates of Sludge by Vacuum Filtration. *Journal (Water Pollution Control Federation), 38*(2), 186-191. Retrievedfromhttp://www.jstor.org/stable/25035483

MacDonald, B., Oakes, K., and Adams, M. (2017). Molecular Disruption through Acid Injection into Waste Activated Sludge: A Feasibility Study to Determine the Economics of Sludge Dewatering. *Journal of Cleaner Production*. In review.

Mahmood, T., & Elliott, A. (2007). Use of Acid Preconditioning for Enhanced Dewatering of Wastewater Treatment Sludges from the Pulp and Paper Industry. *Water Environment Research, 79(2)*, 168-176. doi:10.2175/106143006x111970

Markovic, R., Gardic, V., Jugovic, B., & Stevanovic, M. (2014). Dewatering of sludge obtained by neutralisation from sulfuric-acid waste solutions. *Mining And Metallurgy Engineering Bor, (4)*, 125-136. http://dx.doi.org/10.5937/mmeb1404125m

McCarthy, M., Hafner, H., Simpson, J., & Fauci, M. (2009). *Air Toxics Around a Pulp and Paper Mill*. Presentation, National Ambient Air Monitoring Conference, Nashville, TN.

Mills, N., Pearce, P., Farrow, J., Thorpe, R., & Kirkby, N. (2014). Environmental & economic life cycle assessment of current & future sewage sludge to energy technologies. *Waste Management, 34(1)*, 185-195. http://dx.doi.org/10.1016/j.wasman.2013.08.024

Mitchell, K. (2015). Secondary Treatment Process Flow. Port Hawkesbury Paper LP.

Mitchell, K. (2015). *Welcome to Port Hawkesbury Paper*. Presentation, Port Hawkesbury Paper LP

Mower, B.F., Munkittrick, K.R, McMaster, M.E., & Van Beneden, R.J. (2010). Response of white sucker (Catostomus commersoni) to pulp and paper mill effluent in the Androscoggin River, Maine, USA. *Environmental Toxicology And Chemistry, 30(1)*, 142-153. http://dx.doi.org/10.1002/etc.364

Mukherjee, S., Mukhopadhyay, S., Hashim, M., & Gupta, B. (2014). Contemporary Environmental Issues of Landfill Leachate: Assessment and Remedies. *Critical Reviews In Environmental Science And Technology, 45(5)*, 472-590. http://dx.doi.org/10.1080/10643389.2013.876524

Munkittrick, K.R., McMaster, M.E, & Servos, M.R. (2013). Detection of reproductive impacts of effluents from pulp and paper mills: Shifts in issues and potential causes. *Environmental Toxicology And Chemistry, 32(4)*, 729-731. http://dx.doi.org/10.1002/etc.2143

NEBRA. (2017). *Pulp & Paper Residuals.* Prepared for North End Biosolids and Residuals Association. Retrieved 22 February 2017, from https://www.nebiosolids.org/pulp-paper-residuals/

Nhizou, J., Hamidou, S., Bouda, M., Koulidiati, J., & Segda, G. (2014). Using Dulong and Vandralek Formulas to Estimate the Calorific Heating Value of a Household Waste Model. *International Journal of Scientific & Engineering Research*, 5(1), 1878-1883. Retrieved from http://www.ijser.org/researchpaper/Using-Dulong andVandralek Formulas-to-Estimate.pdf

Novak, J., Sadler, M., & Murthy, S. (2003). Mechanisms of floc destruction during anaerobic and aerobic digestion and the effect on conditioning and dewatering of biosolids. *Water Research, 37(13)*, 3136-3144. http://dx.doi.org/10.1016/s0043-1354(03)00171-4

Nova Scotia Environment, (2009). *Facility Classification Standards*.

Ong, S., Toorisaka, E., Hirata, M., & Hano, T. (2010). Adsorption and toxicity of heavy metals on activated sludge. *Science Asia, 36(2)*, 204-209. http://dx.doi.org/10.2306/scienceasia1513-1874.2010.36.204

Partech Instruments. (2017) *Mixed Liquor Suspended Solids (MLSS).* Retrieved 10 January 2017, from https://www.partech.co.uk/measurements/mlss/

Partnership for Policy Integrity,. (2011). *Carbon emissions from burning biomass for energy.* Retrieved from http://www.pfpi.net/wp-content/uploads/2011/04/PFPI-biomass-carbon-accounting-overview_April.pdf

Port Hawkesbury Paper LP. *Description of Operations* (pp. 9-12).

Reed, S., Bouzoun, J., & Medding, W. (1986). A Rational Method for Sludge Dewatering via Freezing. *Water Pollution Control Federation*, 58(9), 911-916. http://www.jstor.org/stable/25043077

Resource Converting, LLC. (2017). Resourceconverting.com. Retrieved 2 December 2016, from http://resourceconverting.com/

Rotary-press.com, (2015). *Rotary Press Manufacturer of Dewatering Press and Wastewater Sludge treatment and dehydrator*. Retrieved 12 November 2015, from http://www.rotary press.com/

Sludge Treatment - Nordic Waste Water Treatment. (2008). Vantaa, Finland. Retrieved from http://www.greennetfinland.fi/fi/images/4/4b/Nordic_sludge.pdf

Smith, V. (2015). *How Paper is Made - WI Paper Council. WI Paper Council.* Retrieved 6 August 2015, from http://wipapercouncil.org/about-paper/how-paper-is-made/

Sonicators, Homogenizers, (2017). *Laboratory Sonicators & Cell Disruptors. Laboratory equipment.com*. Retrieved 13 March 2017, from https://www.laboratory equipment.com/sonicators/sonicators-x.php

Sonicator Safety | Lab Manager. Lab Manager. Retrieved 13 March 2017, from http://www.labmanager.com/lab-health-and-safety/1900/01/sonicator safety#.WMajBEszWM8

Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter. (2015) Retrieved from https://law.resource.org/pub/us/cfr/ibr/003/astm.d2015.1996.pdf

Streicher, D. *Sludge Treatment. Chemistry.elmhurst.edu*. Retrieved 5 November 2015, from http://chemistry.elmhurst.edu/vchembook/313sludge.html

Texier, P. (2008). Effect of Acidification on Sludge Dewatering Properties. Water and Environmental Engineering; Department of Chemical Engineering. Retrieved from http://www.chemeng.lth.se/exjobb/E493.pdf

The New Glasgow News,. (2014). Ministers to meet with “Clean Pictou Air” businesses. Retrieved from http://www.ngnews.ca/business/2014/7/7/ministers-to-meet-with-clean pictou-air-3790460.html

United States Environmental Protection Agency,. (2002). *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms*. Retrieved from https://www3.epa.gov/region6/water/npdes/wet/wet_methods_manuals/atx.pdf

Water Research Foundation, (2000). *Freeze/Thaw Conditioning of Water Treatment Residuals [Project #386]*. Retrieved from http://www.waterrf.org/ExecutiveSummaryLibrary/386_NON_profile.pdf

Water Environment & Reuse Foundation (WERF) - Innovations in Dewatering Sludges. (2008) (pp. 1-2). Alexandria VA.

Wood, N. (2008). *Pretreatment of Pulp Mill Wastewater Treatment Residues to Improve Their Anaerobic Digestion* (Masters). University of Toronto.

Woodbridge, P. (2015). *Nova Scotia's Pulp & Paper Sector … Back from the Brink of Disaster*. Retrieved from http://woodbridgeassociates.com/pdf/press/Nova%20Scotia%20pulp%20&%20paper%2 sector%20back%20from%20brink%20of%20disaster%20(Jan%202015).pdf

WWF - Pulp and paper. (2017). *WWF Global*. Retrieved 1 April 2017, from http://wwf.panda.org/about_our_earth/deforestation/forest_sector_transformation/pulp_ nd_paper/

Zhang, G. & Wan, T. (2012). Sludge Conditioning by Sonication and Sonication-Chemical Methods. *Procedia Environmental Sciences, 16*, 368-377. http://dx.doi.org/10.1016/j.proenv.2012.10.053

Zhang, G., Zhang, P., Yang, J., & Liu, H. (2008). Energy-efficient sludge sonication: Power and sludge characteristics. *Bioresource Technology*, 99(18), 9029-9031. http://dx.doi.org/10.1016/j.biortech.2008.04.021

Zhang, P., Zhang, G., & Wang, W. (2007). Ultrasonic treatment of biological sludge: Floc disintegration, cell lysis and inactivation. *Bioresource Technology, 98(1)*, 207-210. http://dx.doi.org/10.1016/j.biortech.2005.12.002

Appendix A: *in situ* Trial Operators Manual

WAS (Waste Activated Sludge) Acidification

Acid will be injected into WAS prior to mixing with the primary sludge. The pH of the WAS stream from the secondary clarifiers at present is ~8 and will be lowered to ~3.5-4. The purpose of lowering the pH is to burst the cell wall of the *bugs* in the waste sludge to release the water contained within them. This WAS is sent to the blend tank in the sludge dewatering building and mixed with the sludge from the primary clarifiers before it is sent to the sludge press. The overall goal is to increase the dryness of the sludge going to the boiler from its present value of ~30% dry.

Acid (ferric sulfate and sulfuric acid) will be added to thickened sludge pumps (WAS)

Pumps # 246, 247, 248 (will be added to two out of three)

Acid pumps (for ferric sulfate or sulfuric acid)

Only left hand pump is in use (right hand is spare)

Pumps are located in the room adjoining the sludge pumping building, opposite the old ammonia tank

Bottom 3 inch valve will be where the suction hose is for both acids

WAS acidification pump storage inside blue doors (ferric sulfate tanker to the left and sulfuric acid totes beside old ammonia tank (not shown here))

Safety gear cabinet located on top floor of the sludge pumping building

Safety shower and eyewash station located inside yellow door labeled ‘PUSH EMERGENCY SHOWER’

1. **<u>All</u> safety gear must be worn when entering room containing acid pumps**

Full rain gear, Boots, Gloves, Goggles, Shield

Safety gear cabinet located on top floor of the sludge pumping building

2. **Operator will notify security and the shift manager before entering the acid pump area**

3. **Shift manager will arrange for operator to be accompanied when entering pump area**

Safety shower and eyewash station located inside yellow door labeled ‘PUSH EMERGENCY SHOWER’

Eyewash station when used will activate an audible alarm which will ring in at the guard house as ‘EYEWASH SHOWER DEVICE SLUDGE PUMP BUILDING’

Appendix B: Operator Trial Data Sheet

Date mm/dd	Time	WAS Flow 1 (m^3/h)	WAS Flow 2 (m^3/h)	WAS pH	Acid Flow	Tanker Level (m^3)	Tote Level (m^3)	Mix Tank pH	WAS Ratio	Coagulant Flow (ml/min)	Polymer Flow (ml/min)	Saw dust (m^3/h)	Press Load	Press Speed
	8:00 AM													
	12:00 AM													
	4:00 PM													
	8:00 PM													
	12:00 AM													
	4:00 AM													
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Appendix C: Permanent Process Operators Manual

Purpose:

Acid will be injected into WAS prior to mixing with the primary sludge. The pH of the WAS stream from the secondary clarifiers at present is ~8 and will be lowered to ~3.5-4. The purpose of lowering the pH is to burst the cell wall of the bugs in the waste sludge to release the water contained within them. This WAS is sent to the blend tank in the sludge dewatering building and mixed with the sludge from the primary clarifiers before it is sent to the sludge press. The overall goal is to increase the dryness of the sludge going to the boiler from its present value of ~30% dry while decreasing thickening chemical usage (coagulant and polymer).

Safety Overview

**** In the case of leak, do not rely upon provided rain suit/ PPE. Contact a trained employee whom will be required to wear full chemical proof attire. Gear provided is to keep operator safe during initial contact, splash, etc. not for long durations of acid contact.***

If PPE is in contact with sulfuric acid, please contact Ken Mitchell before placing back into safety gear cabinet.

Acid Pump Room

Prior to entry into acid pump room, all PPE must be worn as found in the safety cabinet within the top floor of the WAS pumping building and contact must be made with supervisor prior to entry and exit.

PPE includes:

- Face shield
- Goggles
- Gloves
- Boots
- Full Rain Gear
- Etc. Please refer to 'Safety Cabinet' section

Unloading Area

Prior to engaging in unloading activities, all those involved must be dressed to the same specifications as in the acid pump room.

Signs must be placed in driveways adjoining acidification area to avoid thru traffic during unloading. Signs can be found to the left of the large blue double doors.

During unloading, one person present must have Transportation of Dangerous Goods (TDG) training – this will be the chemical supply truck driver. On-site personnel may also have TDG training.

Please refer to unloading procedures, Document Number: 11.81

WAS Pump Area

Upon entering the pump building and descending the stairs, one will approach yellow chains blocking further descent. Prior to removing these chains, the operator must be wearing long chemical coat, goggles, face shield, and gloves, which are located at the landing housing the fire extinguisher.

Berm Entry

If entering berm area for valve shut off or non-emergency work, enter from the south side where the ladder extends to the inside of the berm. All PPE should be worn as in the acid pump room and unloading.

In the case of a leak or emergency, chemical proof clothing (chemical suit – not found in safety cabinet) is to be worn by a trained employee.

Site Overview/ Photos

Safety Cabinet

1. All safety gear must be worn when entering room containing acid pumps

Full rain gear, Boots, Gloves, Goggles, Shield

Safety gear cabinet located on top floor of the sludge pumping building

2. Operator will notify supervisor before entering and after exiting the acid pump area

3. A second person must be present when operator is inside the pump area

Safety Shower

Safety shower and eyewash station located inside yellow door labeled 'PUSH EMERGENCY SHOWER'

Eyewash station when used will activate an audible alarm which will ring in at the guard house as 'EYEWASH SHOWER DEVICE SLUDGE PUMP BUILDING'

Acid Pump Room/ Area Overview

Pumps are located in the room adjoining the sludge pumping building, opposite the sulfuric acid storage tank (inside large blue double doors).

WAS acidification pump storage inside blue doors. Safety gear cabinet located on top floor of the sludge pumping building (single blue door)

Safety shower and eyewash station located inside yellow door labeled 'PUSH EMERGENCY SHOWER'

Entry into acid pump room

All PPE must be worn when entering through safety curtains

Acid pumps (011-291 on left, 011-292 on right)

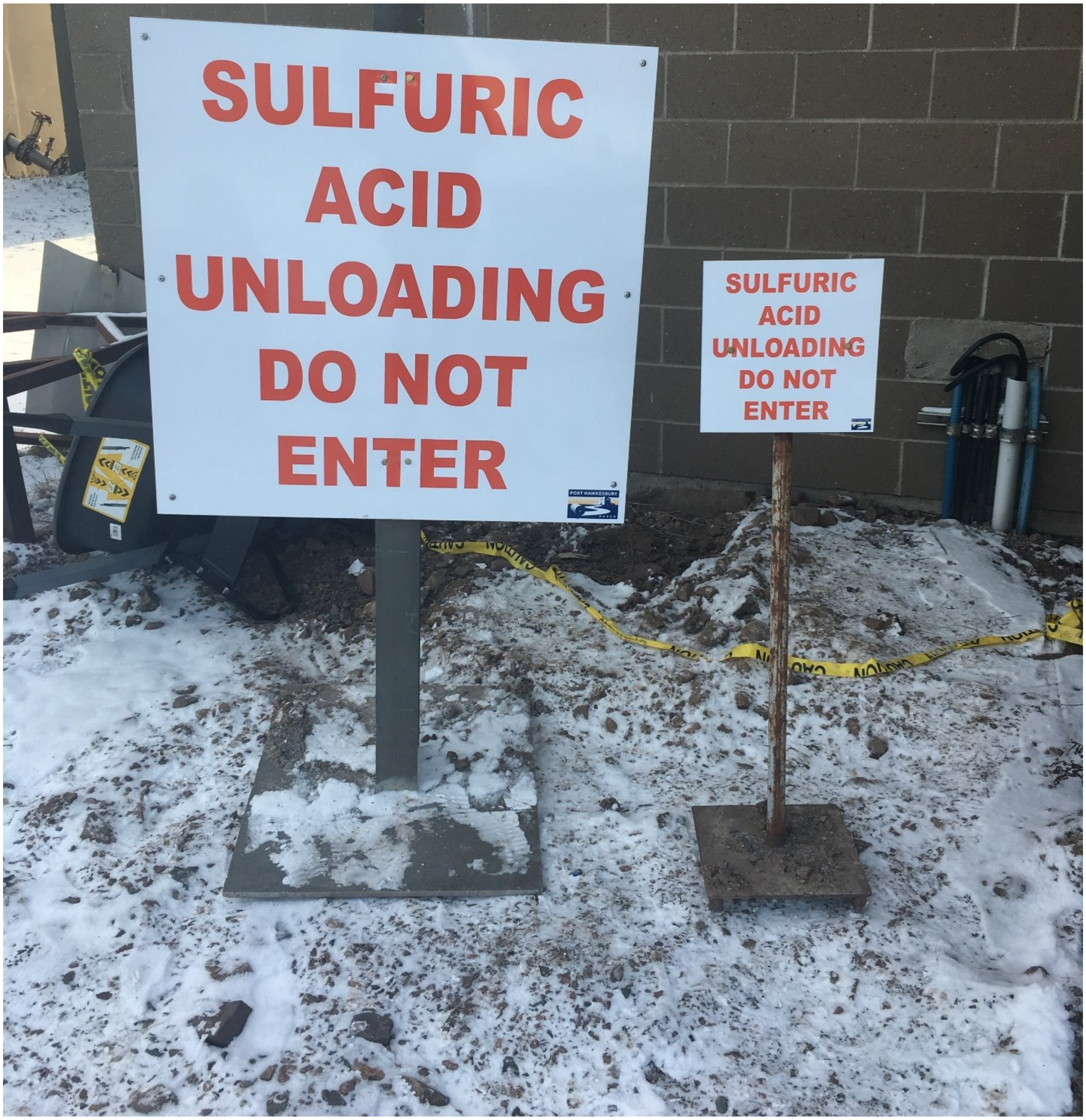
Only left hand pump is in use (right hand is spare)

Pumps are located in the room adjoining the sludge pumping building, opposite the sulfuric acid storage tank (large blue double doors)

Storage and Unloading

Sulfuric acid storage tank seen above, found opposite pumping building. Buried piping transports acid into pumps found within blue doors as in previous photo.

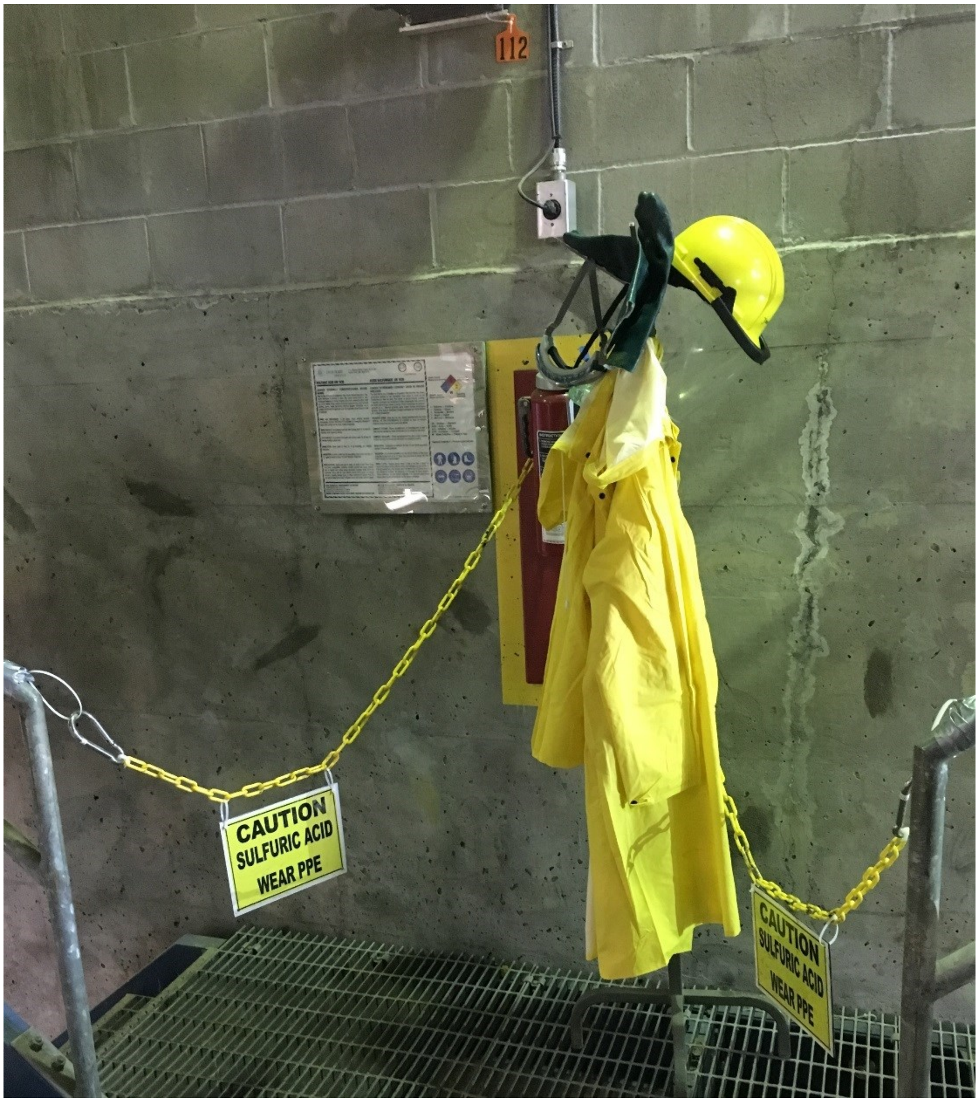
Sulfuric Acid unloading area is located on the north side of the tank as pictured above.



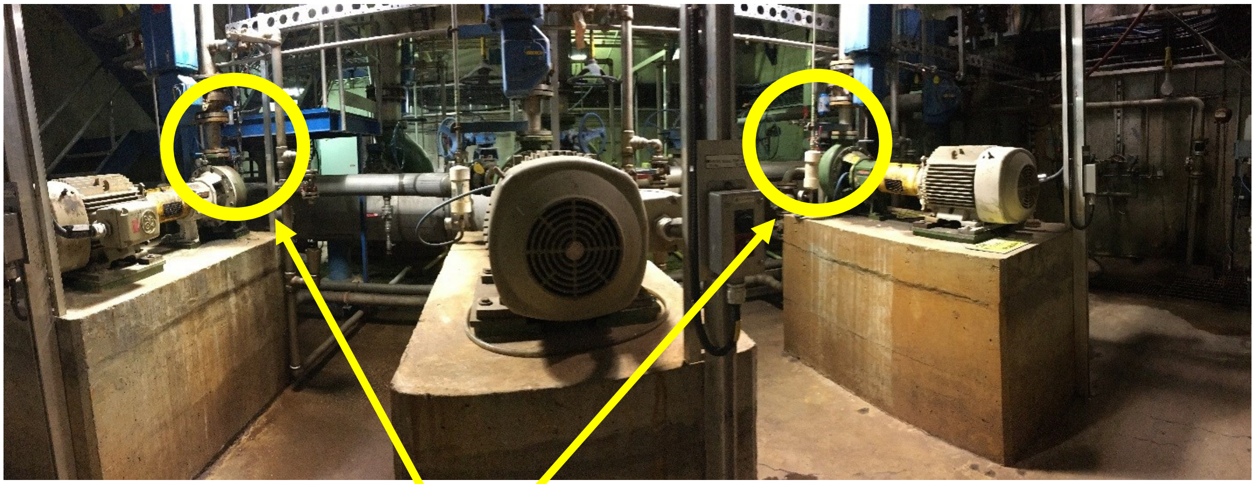
Signs above are to be placed in roadways between pump building and clarifiers during acid unloading processes.

If entering berm area, ladder on south side of berm are to be used for entry and exit.

WAS Pump Area



Mid-level landing where safety goggles, a long raincoat, face shield, and gloves can be found. If unavailable, revert to safety cabinet supplies or contact supervisor.



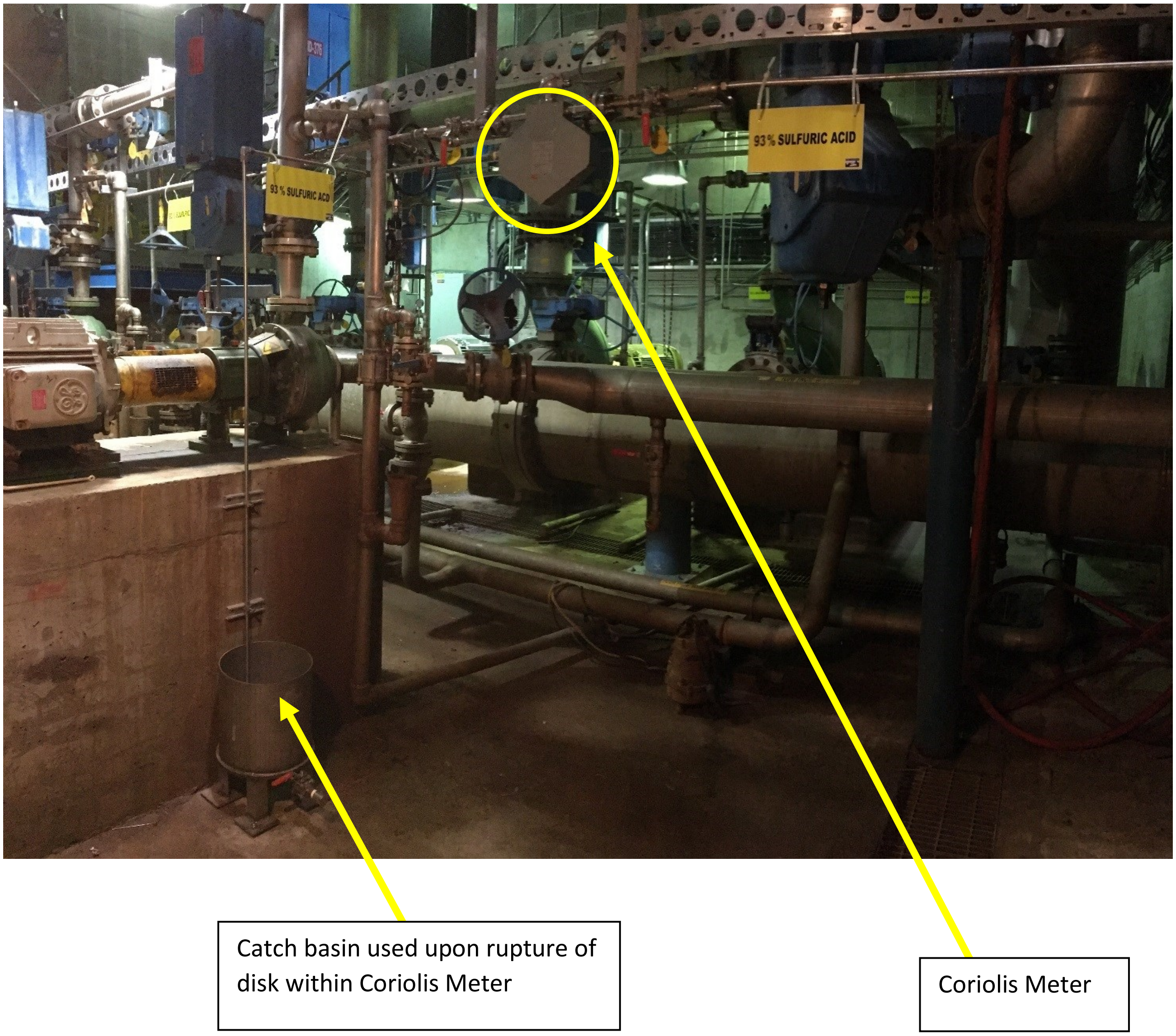
Acid Injection Points (seen up close in photo below)

Sulfuric acid will be added to thickened sludge pumps (WAS)

Pumps # 246 and 247

The following photo demonstates pipe wrap which is used as a leak indicator, if this wrap changes color (pink or red), a leak is present. This wrap is found on both injection areas as noted (unwraped) in the previous photo.

Coriolis Flow Meter Rupture Disk and Basin



Appendix D: RS View Operator View

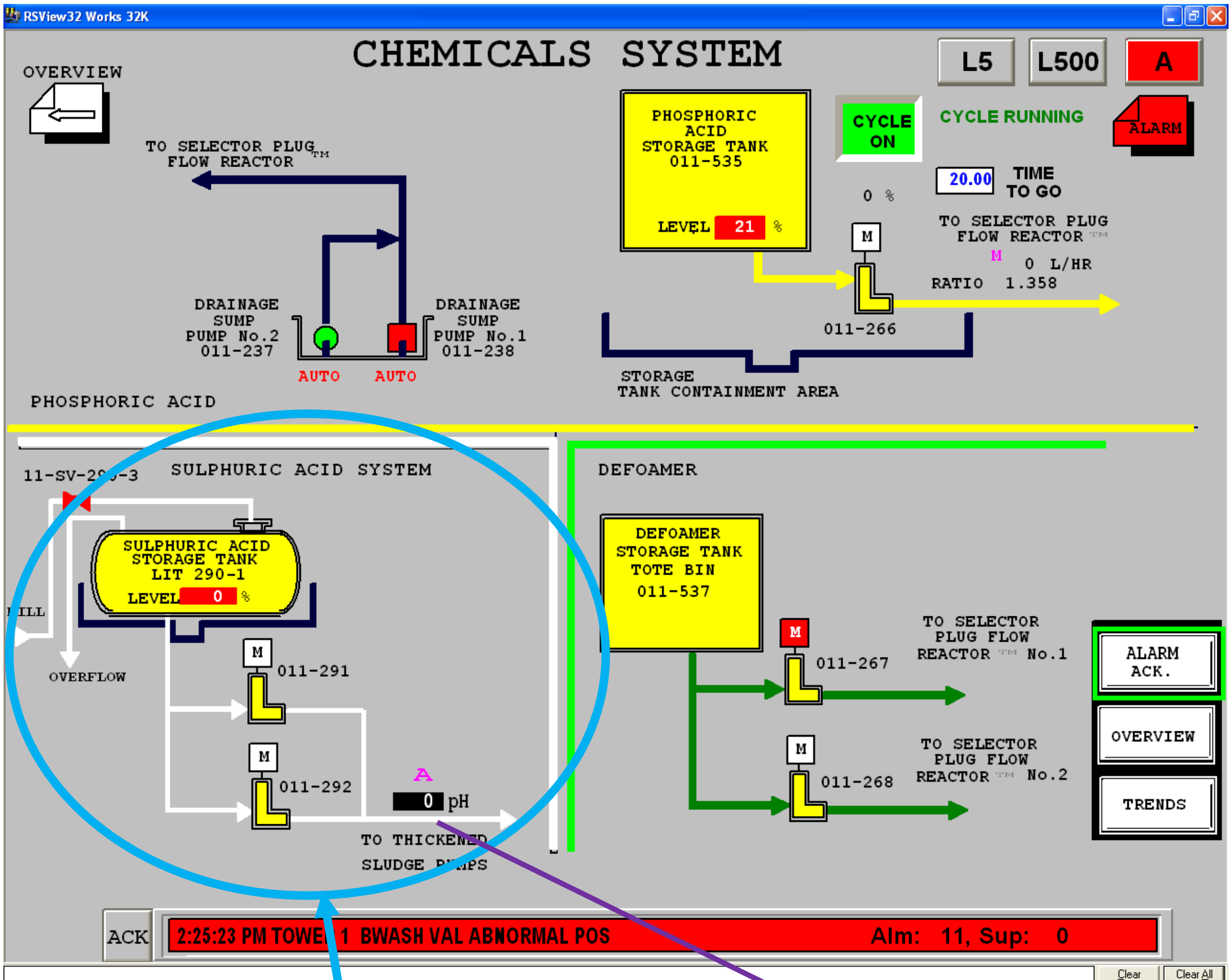
Sulfuric Acid started Jan 12, 2017 @ 10:100am

1. Do pH on WAS samples and do pH on sludge press drainer filtrate and sludge press filtrate samples.
2. Jan 12, 2017: Sludge press operation
   a) Reduced polymer ratio in sludge dewatering from 0.018 -> 0.008
   b) Reduced coagulant flow from 120 cc/min -> 90cc/min
   c) Sawdust at 4%

Goal: 1. Reduce polymer flow to < 0.8 m^3/hr

2. Run WAS to Blend Tank at pH at 3.5 to 4.0

3. Run Mix Tank pH at 4.2 – 4.9



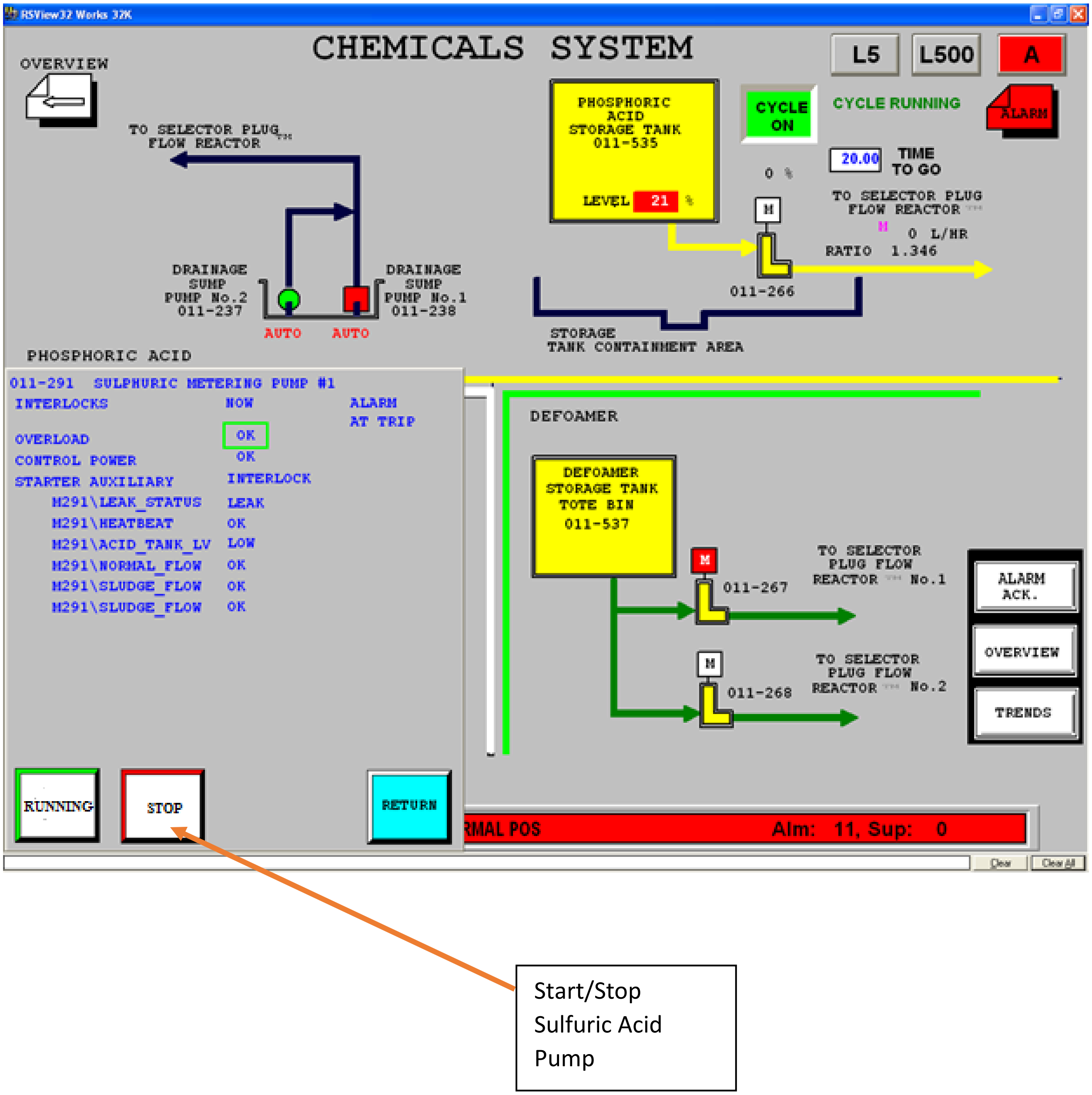
New 93% sulfuric acid system, 011-291 and 011-292 represent dosage pumps within the large blue building doors

***011-291 is operating sulfuric acid pump**

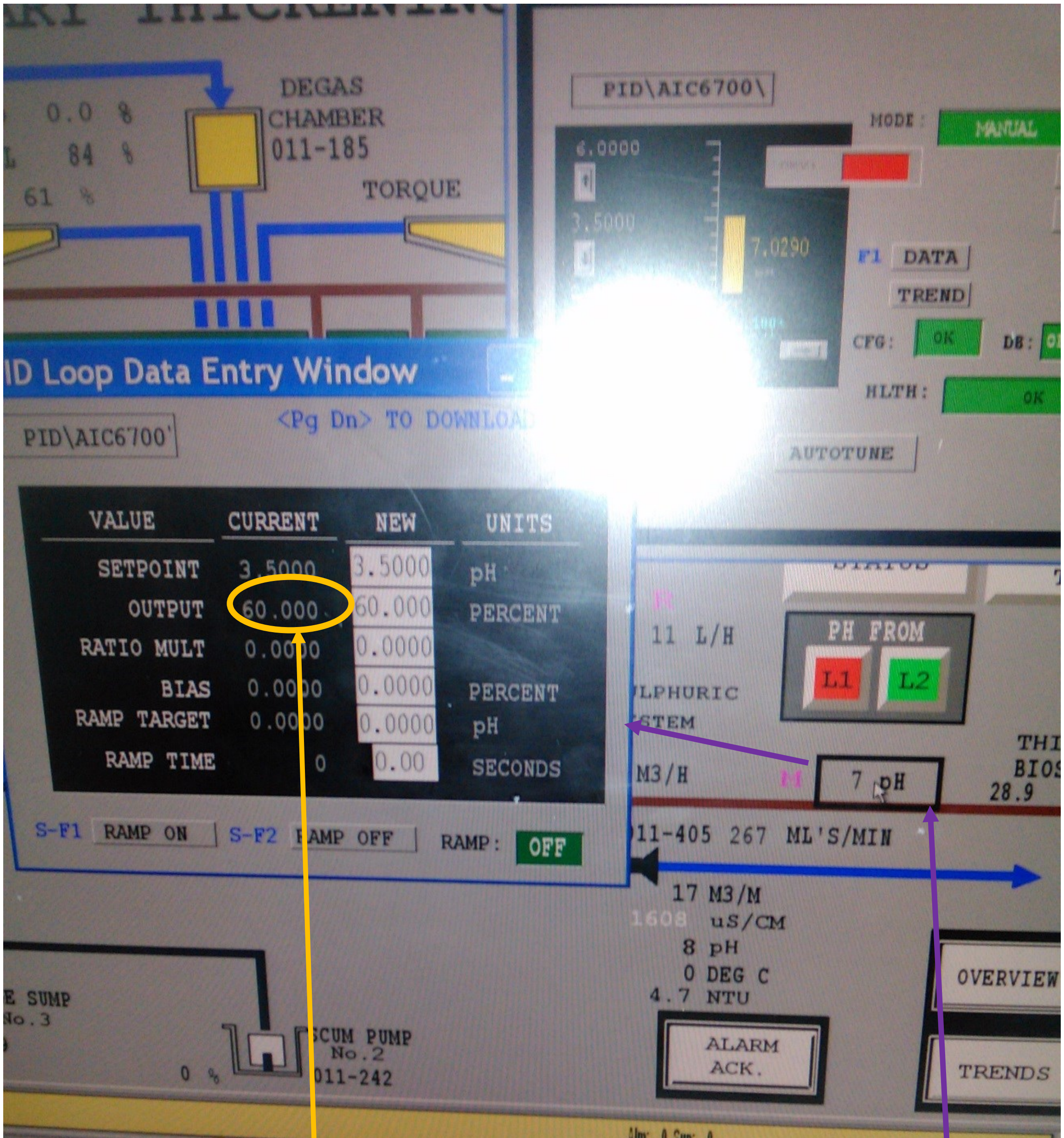
pH of WAS entering dewatering building on route for mix tanks

Next screen photo displays pop up found if acid pump 011-291 or 011-292 is selected.

1. Sulfuric acid pump 11-291 Start/Stop
2. Interlocks
   a) Pump will stop when WAS flow <4m^3/hr
   b) Pump will stop when WAS goes "Back to Reactor"
   c) Pump must be restarted by operator



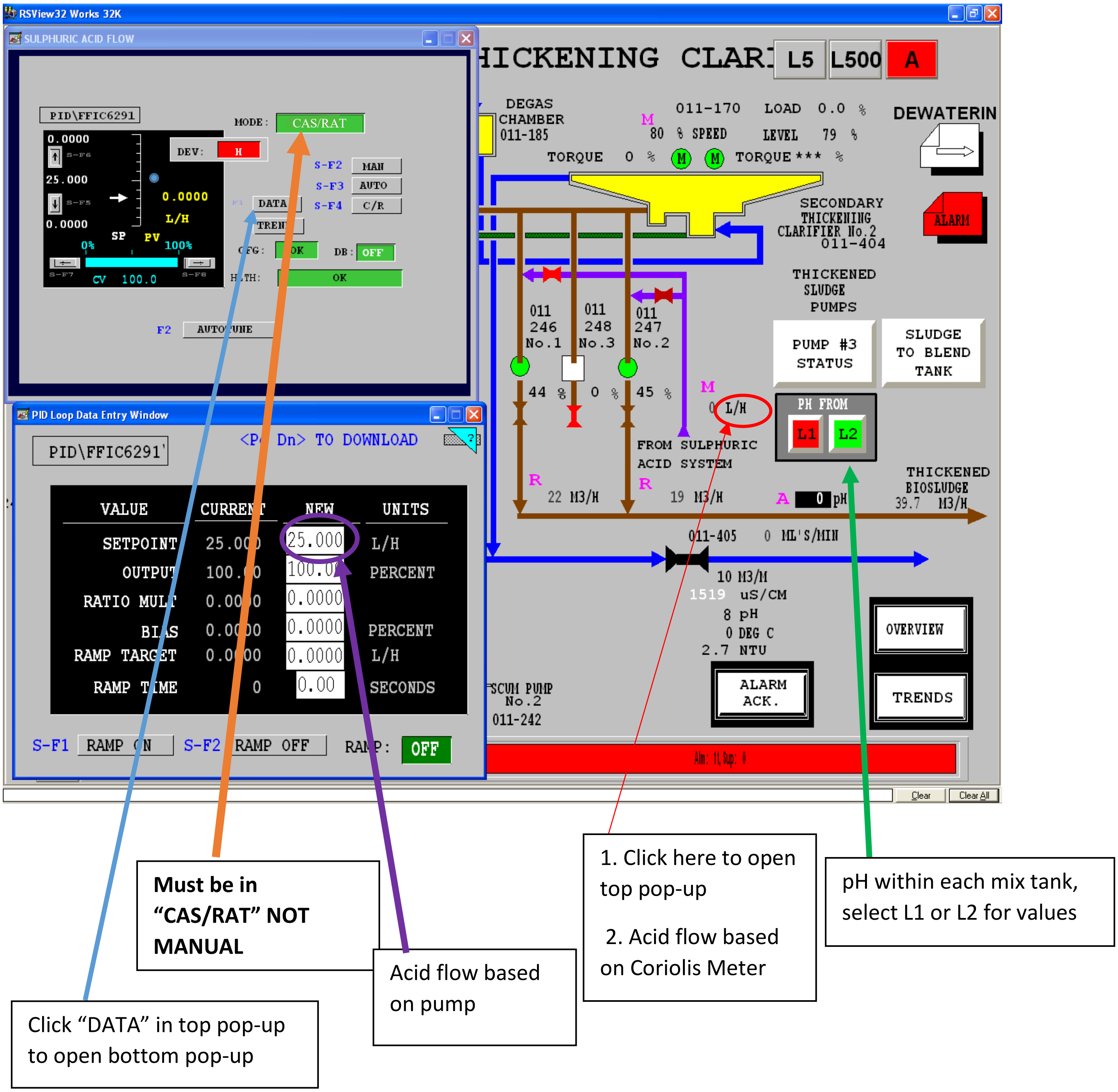
Bottom left hand corner displays pop up formed when clicking on a specific acid pump, in this case 011-291



pH control ratio set point 60% Acid Flow 60% of WAS flow

pH Control - WAS pH

Click here to bring up pop-up screen



Operator RSView screen– Acid flowrate is to be regulated based upon sludge ratio

Pop up screens on left display acid dosage

Appendix E: Sulfuric Acid Unloading Procedures

1.0 Purpose

The purpose of this procedure is to ensure the safe and proper unloading of Sulfuric Acid from a tanker to the new sulfuric acid tank (tank 11-290) located by the sludge pumping building.

2.0 Scope

The scope of this procedure is to cover off all the responsibilities associated with the receiving and unloading of Sulfuric acid.

3.0 General Introduction

Sulfuric Acid (H_2SO_4). Transportation of Dangerous Goods, Class 8, corrosive liquid, Placard UN 1830. Sulfuric acid at 70% - 100% concentration is a colourless to amber, slightly cloudy, oily liquid. It has a specific gravity of 1.84. Sulfuric Acid is utilized for acidifying the waste sludge to get better dewatering characteristics.

4.0 Safety and Training

All personnel should be trained in the following:

Proper use of personal protective equipment.

TDG Certification (Truck driver)

Handling and storage of dangerous goods.

Clean up of hazardous wastes.

Refer to MSDS for Sulfuric Acid, liquid, 70-100% for dangers associated with the handling of this chemical.

Conduct a risk assessment with the Truck Driver, highlighting the Plant Emergency Phone Number (222), location of the emergency eyewash and shower, and identifying the quick release shut-off point on the tanker and accessibility restrictions, before commencing unloading.

Sulfuric Acid, liquid, 70-100% is stable, but reacts with moisture very exothermically, which may enhance its ability to act as an oxidizing agent. Substances to be avoided include water, most common metals, organic materials, strong reducing agents, combustible materials, bases, oxidising agents. Reacts violently with water - when diluting concentrated acid, carefully and slowly add acid to water, not the reverse. Reaction with many metals is rapid or violent, and generates hydrogen (flammable, explosion hazard).

5.0 Tools and Equipment

Water wash down hose, cam-lock strap, rubber gaskets (for unloading hose) and the sulphuric acid chemical unloading hose.

6.0 Location

Sulfuric Acid unloading area is located on the north side of the tank.

7.0 Environmental Considerations

Reportable Release means a release to the environment, which meets or is in excess of those quantities, listed in Column II of Schedule "A", Emergency Spill Regulations. The reportable quantity for Sulfuric Acid and Caustic Soda is 5L or 5kg.

8.0 Responsibilities

When a tanker arrives at the main gate the Security Guard/Stores Receiving shall carry out the following:

Verify the contents by checking the documentation accompanying the shipment If there is a problem, the Security Guard must contact Day Supervision Effluent Treatment Plant.

Notify the Secondary Treatment Operator that a tanker is on route to the unloading area.

Direct tanker driver to the Unloading area.

It is the responsibility of the Secondary Treatment Operator to perform the following:

Verify the documentation of the truck

Unloading the bulk chemical tanker is the responsibility of the truck driver.

9.0 Procedure

9.1 Ensure truck driver has on personal protective equipment, rubber boots, rain gear, goggles and shield and rubber gloves.

9.2 Operator to wear all personal protective equipment, rubber boots, rain gear, goggles and shield and rubber gloves.

Check the bulk storage tank level, making sure there is enough capacity to receive tanker load. PHP tank (11-290) can hold three tanker trucks.

Show truck driver location of the eyewash stations and shower. Eyewash/Shower checks are to occur beforehand under normal inspection procedures.

Put out signage "Sulfuric Acid Unloading" signs at either end of the road that the truck is on, to ensure no one enters the area.

Have water wash down hose available.

Conduct a risk assessment with the Truck Driver, highlighting the Plant Emergency Phone Number (222), eye wash and shower and identifying the quick release shut-off point on the tanker and accessibility restrictions.

Guide tanker into position at unloading station.

Verify the chemical on board of tanker with truck driver;

Where at all possible the carrier's hoses should be used as they are regularly inspected. It is the truck driver's responsibility to check the chemical unloading hose for damage before making a connection.

Truck Driver must ensure:

Identify appropriate unloading point and connect female end of acid transfer hose to acid transfer line,

Make sure locks are securely fastened on all connections. It is a good practice to use cam-lock straps to secure locks closed.

Bulk tank vent must be clear

Begin to pressurize the tanker and have the driver set his supply regulator. This pressure must not be greater than that specified for a particular tanker.

The truck driver will line up the valves as required for safe unloading and watch for any leaks. Small drips may occur at connections. Any spill above 5 L or 5 Kg must be reported. In case of a line rupture or large leak, shutdown the unloading process immediately, shut off air to tanker, close tanker valve, and break off tanker quick shut-off (if necessary). Report spill to plant Emergency 222; refer to procedure Chemical or Hazardous Material Emergency Response Procedure (for additional information.

The chemical flow can be observed by watching the level on the bulk tank digital meter rise.

Monitor unloading continuously for leaks and for personnel who may stray into unloading area.

When the acid tanker is empty, the line will normally shake. Another way to determine if it is empty, is to lift the hose, it should be quite a bit lighter when it is empty.

Truck driver will shut off supply air and disconnect air from tanker to let depressurize.

Truck driver will shut off tanker chemical valve.

Truck driver will shut off plant chemical valve.

Truck driver will disconnect chemical hose.

Return any hoses and equipment to proper storage area if needed.

Take down signage.

10.0 Related Procedures

10.1 Mill Emergency Response Procedures.

Documentation

Copy of weigh bill and Dangerous Goods Certificate are filed at PHP.

Appendix F: Acidification Report Submission to Alberta Newsprint Company

Visit Dates: September 19-21, 2016

Report Submitted to Dan Moore and Kerilynn Hnatuk, Alberta Newsprint Company

Submitted by Brittany MacDonald, Port Hawkesbury Paper

Introduction and Purpose

Alberta Newsprint (ANC), like Port Hawkesbury Paper (PHP) produces a large amount of sludge particularly during the winter months when a greater amount of secondary sludge is produced. With this high secondary sludge production, there is a related increase in moisture/ decrease in dryness. In the case of PHP, the sludge produced augments a nearby biomass burner, which requires 30% dryness to avoid a moisture penalty. Comparatively, at ANC the sludge produced is trucked away from site for land use and farming. While land application may not be as stringent regarding dryness, the space and weight consequences associated with the shipment of un-necessary water is a concern.

PHP implemented an acidification trial on an industrial scale which yielded savings in many areas such as chemical cost and moisture penalties. Acidification allowed for the eruption of water containing microbes and molecules which when moved to the drainers and presses improved ease of dewatering and yielded an overall ~4% drier product.

It is the goal with this trial set to provide evidence suggesting acidification would create separation of solids to increase dryness while also decreasing costs of additivities or transport.

Comparative Qualities

Measurable	Approximate PHP Value	Approximate or Estimated ANC Value
WAS Flow	18 – 30 m^3/hr	54 m^3/hr
Primary Sludge Flow		60 m^3/hr
Polymer Flow	1.5-2 m^3/hr (during acidification)	0.9 m^3/hr
Coagulant Flow	3960 m^3/hr (during acidification)	-
WAS Initial pH	6.4	~6.5
Primary Initial pH	~6.2	~6.5-7.5
MLSS	From ~3600 – 5000 mg/L during acidification	4000-4800 mg/L
WAS Consistency	~2%	~1.4%
COD	70-90 t/d	28 t/d
BOD	25-30 t/d	13.5 t/d
Overall Sludge Output		36 BDT/d
Dryness (prior to acidification)	25%-35%	~20%
Dryness (following acidification)	Upwards of 34% (expected to increase)	19-24%

Note that the comparative trial values regarding PHP reference the winter months where dryness is difficult to obtain, leading to the assumption that a greater increase will be seen in the warmer months.

Materials and Methods

Dilution

Sulfuric acid supplied by ANC was 95-97%. Two separate dilutions took place assuming 95% and the second assuming 97%. The variation in acid had the potential to cause errors throughout the trial due to the unique characteristic changes of the acid at different percentages.

Mixing

Each sample was mixed to the ratios found in Table 1. Addition of acid took place under fumehood conditions and using a dropper. To ensure ample mix time, magnetic stir bars were used to simulate process mix conditions. Timing for mixes was based upon PHP trial timing for pH readings; approximately 10 minutes for WAS alone and 40-60 minutes for mixtures of WAS and primary sludge.

Measurement

pH was taken with supplied pH meters and cleaned/ calibrated in a pH 4 buffer solution between each sample.

Outside of pH COD and BOD measures were taken by ANC.

Initial Findings

Table 1 - Sample results presented as mixtures and isolated substances.

Sample Number/ Date	Date	Amount Secondary Sludge (g)	Amount Primary Sludge (g)	Amount Acid (mL)	pH	Assumed initial acid percentage prior to dilution to 93% (%)
1	Sept 20	0	100	0	6.12	95
2	Sept 20	100	0	0	6.70	95
3	Sept 20	100	85	0	6.42	95
4	Sept 20	100	85	0.152	1.77	95
5	Sept 20	100	0	0.152	1.99	95
6	Sept 20	100	0	0.5	1.64	95
7	Sept 20	100	0	1	1.52	95
8	Sept 20	100	0	5	1.4	95
9	Sept 21	100	0	0	6.72	97
10	Sept 21	100	0	0.152	2.44	97

11	Sept 21	100	0	0.05	4.70	97
12	Sept 21	100	0	0.10	2.51	97
13	Sept 21	100	0	0.05	3.73	97
14	Sept 21	100	0	0.10	2.32	97
15	Sept 21	850	0	0.425	3.49	97
16	Sept 21	0	100	0	7.35	97
17	Sept 21	0	100	0	7.33	97
18	Sept 21	100	0	0	6.70	97
19	Sept 21	100	0	0	6.45	97
20 (composed of 16 and 18)	Sept 21	100	100	0.10	5.28	97
21 (composed of 17 and 21)	Sept 21	100	100	0.05	6.33	97

Observations

The trials which took place on the 20th showed extreme pH reduction with minimal acid addition, well below that of PHP's trial. It was expected that pH would be within the range of 4-5, but results in samples 4-7 showed a resulting pH of less than 2. A notable difference between PHP and ANC sludge is that the ANC primary sludge includes a lime addition to increase basic pH properties as well as mitigate undesirable chemical omissions. With this added basic component an attempt was made in sample 4 to counteract the harsh effects of the sulfuric acid, however, this was not seen as the pH continued to dip below 2. Figures 1-6 display visually, sample comparisons from ANC on-site trial.

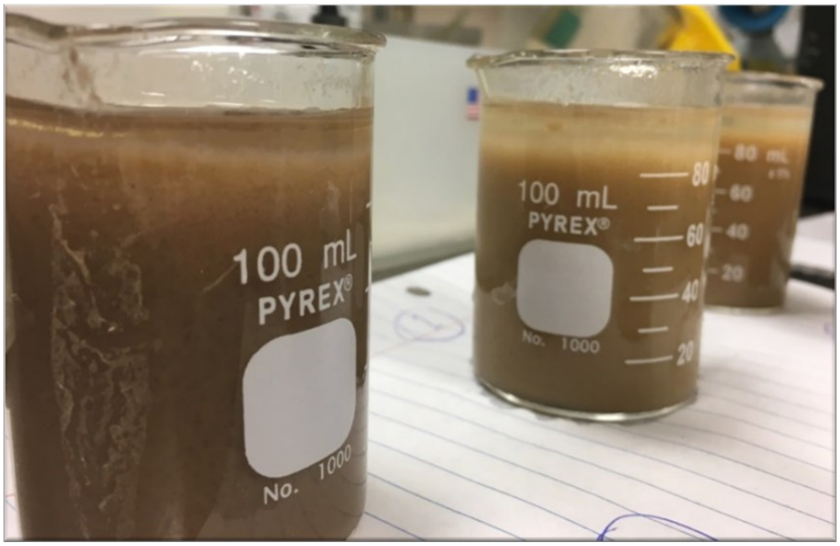


Figure 1 - Left to right, samples 2, 5, and 6

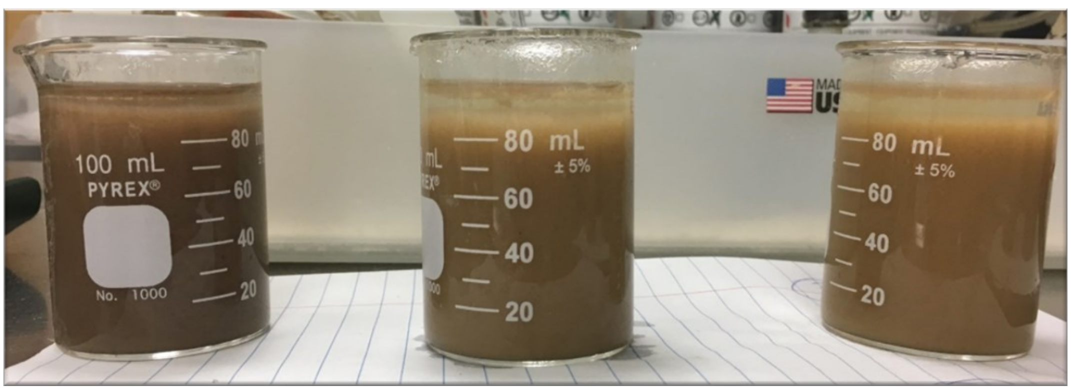


Figure 2 – Left to right, samples 1, 5, and 6.

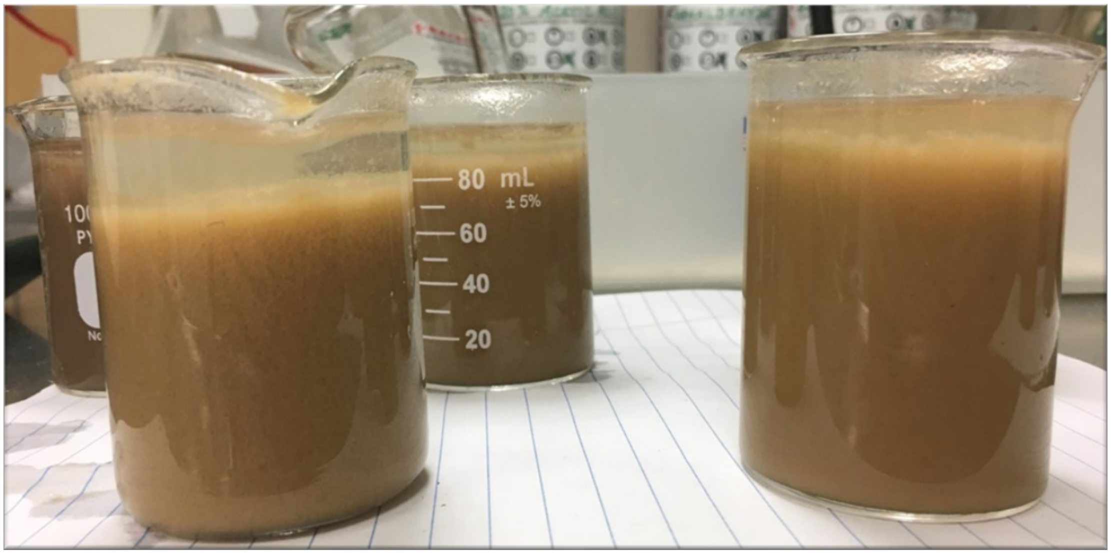


Figure 3 – Left to right – Back: Sample 2 and 5, Front: Sample 7 and 8.

The next set of trials were performed under the assumption that the acid had not been diluted heavily enough, meaning that the acid obtained was on the higher end of the scale (97%). Again, separation was evident, but without the intense drop in pH. Also, in this second trial the, pH of primary was higher than the previous day allowing for a more preferable equalization of the overall sludge output.

As seen in Figures 4-7 below, the beakers containing two drops of acid showed significant separation in the beakers with two drops of acid; however the acid drop is cause for concern due to ANC's output regulations of 5.1 as a pH.

Figure 4 – Left to right, samples 9-14.

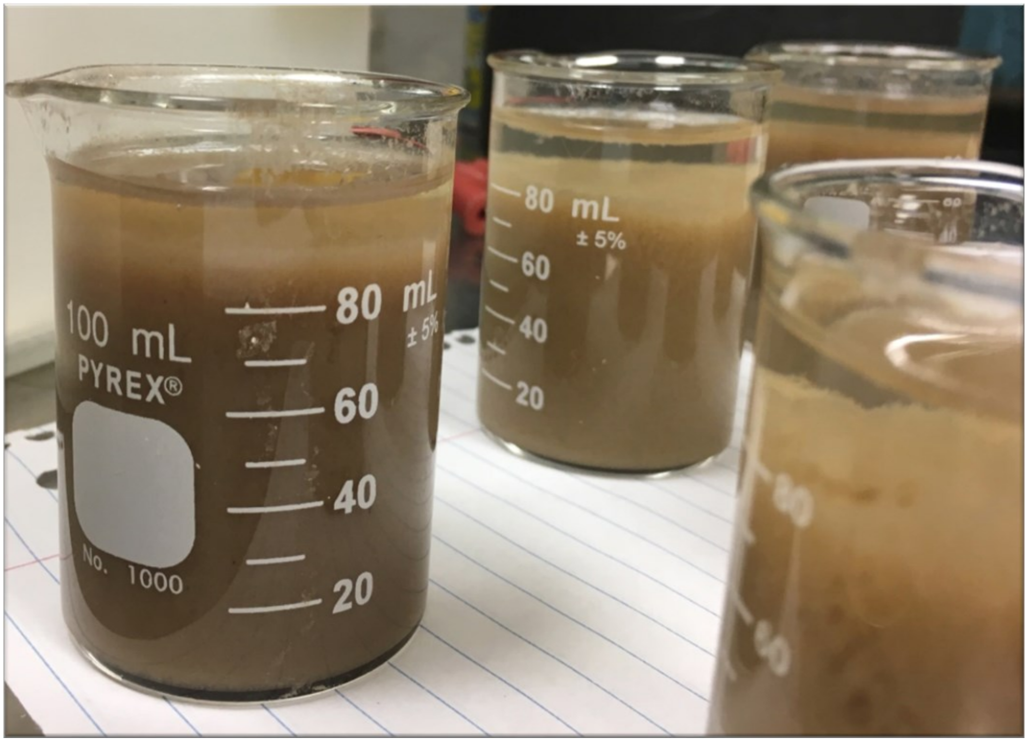


Figure 5 – Left to right, samples 9, 10, and 11.

Figure 6 – Left to right – Front: Samples 12, 13, and 14, Back: Samples 9, 10, and 11

Discussion/ Cost Analysis

Based on the figures in the previous section, there is clear evidence acidification is working to remove/ separate water from the moisture-rich sludge.

Table 2 presents the economic situation facing ANC with regards to trucking. Relating to the acidification project this is also where focus should be placed as with the presently low use of chemicals, trucking decides if addition of acid is economically plausible.

Table 2 - Sludge Haul Costs to Farms vs. % Solids

% Solids	Tonnes/load	Current $/tonne	Winter/ Road Bans $/Tonne
15	4.7	53.76	72
20	6.2	40.32	54
25	7.8	32.25	*45
30	9.3	26.88	36
35	10.9	22.94	31

*This rate of $45 at 25% solids seems out of place.

When also reflecting upon the trial aspect of acidification, in the case of PHP, much of the system was made readily available as a package deal, *i.e.* pumps, equipment, expertise, etc. Overall, not including in-house maintenance, less than $40,000 was required to complete this trial. Taking into account the larger picture, permanent implementation, costs are still growing at PHP to include revamping of a pre-existing ammonia tank to house sulfuric acid, intense changes within the existing control logic, etc. These must be considered by ANC. Also, process flow differs with a thickener, which when turned on (necessary for mixing as retention time can be vast) may create an additional operating cost.

In Table 3 below, costs are compared to amount of trucks (estimated at 8) required with increasing dryness. Assuming a dryness gain of 4% (as seen at PHP) the calculations provided savings of $100,000+/ year without the inclusion of acid.

Table 3 – Projected sludge haul costs and savings with the implementation of acidification. (Savings estimated if rounding number of trucks up and down)

% Solids	Tonnes /load	Current $/tonne ($)	Winter/ Road Bans $/Tonne ($)	Estimated Winter Cost/ Truck ($)	Estimated Warm Months Cost/ Truck ($)
15	4.7	53.76	72	591.07	252.67
20	6.2	40.32	54	584.78	249.98
25	7.8	32.25	45	602.55	251.55
30	9.3	26.88	36	584.78	249.99
35	10.9	22.94	31	587.95	250.05
19	5.92	42.40	57.29	590.16	251.03
24	5.92	33.54	45.44	467.53	198.54

Assume 8 trucks per day
Assume start 15% Dry
Assume 4 Months Winter

% Solids	Tonnes / day	# Trucks Req (rounded up)	Winter Cost/ Day ($)	Non-Winter Cost/ Day ($)	Cost/ Year ($)	Savings/ Year ($)
15	37.6	8	4728.58	2021.38	1052559.00	135102.80 – 266168.00
19	47.36	7	4131.12	1757.18	917456.60	

Assume 8 trucks/ day
Assume start 20% Dry
Assume 4 Months Winter

% Solids	Tonnes / day	# Trucks Req (rounded up)	Winter Cost/ Day ($)	Non-Winter Cost/ Day ($)	Cost / Year ($)	Savings/ Year ($)
20	49.6	8	4678.27	1999.87	1041362.00	107581.20 – 211334.00
24	47.36	9	4207.74	1786.88	933780.80	

The preceding tables simply describe savings based upon the amount of trucks required to transport sludge. The following, Tables 4 and 5 provide savings with an estimated acid usage value. Usage value determined by taking PHP trial value and halving due to the comparative supply costs of PHP versus ANC and either again divided by 3 following tests performed at ANC the week of September 19th, or using the amounts required in PHP's trials as it is assumed that when implemented in the physical process, the amount required will increase. Also, this will provide a worst case scenario cost and savings. The savings seen here have greatly decreased, especially when beginning at 20% dryness. Also it is important to account for the typical number of trucks needed as the following tables estimate a large range from 5-8 trucks.

Table 4 – Cost savings estimated with the implementation of acidification – 8 trucks/day.

Dryness Change (%)	Savings/Year ($)	Acid Cost (PHP Acid Amount) ($)	Acid Cost (ANC Trial Acid Amount) ($)	Savings/ Year (incl. acid) PHP Acid Amount ($)	Savings/ Year (incl. acid) ANC Trial Acid Amount ($)
15-20	271537.92	76800	25600	194737.92	245937.92
20-25	245293.92			168493.92	219693.92
15-19	266168.00			189368.00	240568.00
20-24	211334.58			134534.58	185734.58

Table 5 - Cost savings estimated with the implementation of acidification – 5 trucks/day.

Dryness Change (%)	Savings/Year ($)	Acid Cost/ Year (PHP Acid Amount) ($)	Acid Cost (ANC Trial Acid Amount) ($)	Savings/ Year (incl. acid) PHP Acid Amount ($)	Savings/ Year (incl. acid) ANC Trial Acid Amount ($)
15-20	137168.64	76800	25600	60368.64	111568.64
20-25	120139.20			43339.20	94539.20*
15-19	133588.70			56788.70	107988.70
20-24	132084.11			55284.11	106484.11

*Based upon ANC Sludge Haul Costs to Farms vs. % Solids chart (Table 2). The winter rate of $45/tonne at 25% solids seems out of place.

It is highly recommended that if ANC is interested in pursuing acidification further that a trial system similar to that used at PHP be input prior to permanent implementation.

With input on an industrial scale it is expected the results will differ slightly from estimated values due to an array of conditions which cannot be simulated on a laboratory scale. For maximum separation, mixing of acid with the secondary sludge prior to contact with primary sludge should be no less than 10 minutes (maximize retention time if possible). In the case of ANC where a thickener holds the mixture, agitation is necessary to ensure ample mixing of primary and secondary acid containing sludge to see overall separation.

For this trial period 93% sulfuric acid could be shipped in totes to the desired location and added through pumps of the mill's choice (however, note that these should be pumps capable of use at a small capacity so not to harm the pump itself). pH probes should also be installed in 1-2 areas throughout the path of the acid addition; ideally one probe should be placed shortly following injection and another on the blend tank – this may differ at ANC if injection is close to the thickener, 1 probe on the blend tank may be all that is needed.

The estimated dosage would be ~0.05L/t with room for optimization if a trial is implemented. A decrease in polymer may be possible; however, this is difficult to estimate at this time as the polymer dosage presently used at ANC is less than the optimized value used by PHP.

Further Work

ANC will be installing an industrial scale acidification trial into their secondary treatment process soon. Likely, the results will be similar to those presented in 20% starting dryness option due to the potential implementation of new press technology on-site which will act as an additional method of increasing dryness.