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Molecular disruption through acid injection into waste activated sludge – A feasibility study to improve the economics of sludge dewatering

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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 use is currently 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 to 38% *(w/w)*. Various chemical or mechanical dewatering options exist; however, knowledge of the unique sludge composition and properties is essential to predicting how the product will react under each method. Sonication, Fournier rotary press technology, freeze/thaw cycling, and gravity drying were among the dewatering opportunities briefly explored outside of the chosen method, acidification. Notably, many industries utilizing dewatering technologies may not be producing value-added by-products, while geographic and climatic placement may limit processes which are possible for others. In the present study examining enhanced end-use value, further dewatering occurred through a comparative *in situ* experiment contrasting sulfuric acid and ferric sulfate acidification (direct acid injection into sludge). While both proton donors acidified the sludge and decreased moisture content, sulfuric acid was the more cost-effective option, yielding an ~4% increase in dryness, with commensurate economic and environmental benefits.

1. Introduction

Shifting market and environmental paradigms faced by the pulp and paper sector worldwide forces innovation not only with paper production, but also with energy management, environmental discharges, and fate of waste products. In the paper industry, mill residuals (or sludge) composition varies with the paper product manufactured, but is largely 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 paper mills and waste water treatment facilities, Port Hawkesbury Paper LP (PHP), 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, high moisture content sludge (25–38% *(w/w)* dryness, depending upon species and season) requires much of its contained energetic potential to evaporate off moisture as water vapour, thereby dramatically reducing its overall heat value. In some mills, financial losses due to low calorific value are also incurred for delivering sludge with dryness values < 30% to a local combined heat and power (CHP) facility as prescribed under agreement conditions regarding sludge incineration. Alternatively, landfilling options are limited and not considered best practice. On a national scale in Canada, while not all paper mills deposit sludge in landfills, even conservative estimates indicate landfilling requires a large environmental footprint, with long term implications.

Acidifying sludge is one mechanism for reducing moisture content by increasing constituent mobility, weakening binding forces, and facilitating chemical and metal releases. Such behaviour

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is consistent with the theory of biosorption, 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, which acts similarly to thickening chemicals used in typical treatment processes, by bringing zeta potential (reference point for stability within a mixture) of sludge flocs at or close to the point of zero charge (Mahmood and Elliot, 2007).

The primary objective of this study was to investigate acidification as a sludge drying method, and to determine the optimal acidifying agent to cost effectively reduce moisture content. Two acid combinations (93% sulfuric acid, and ferric sulfate with 10% sulfuric acid) were contrasted to determine the best dewatering performance that was economically achievable. Analyses include sludge pH change following acid addition, moisture release, and impacts on required polymer and coagulant use. The latter response is an important endpoint as acidification may decrease the need for these chemical inputs to current dewatering processes, resulting in cost savings. Further, the role of pH in modifying sludge Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) has yet to be properly documented, and this alone will be a valuable contribution to the literature. Improving sludge dryness in turn decreases sludge volumes, a beneficial property (both environmentally and economically) when landfilling or transporting is required, improving public perception of the pulp and paper or other sector by demonstrating an innovative approach to operational challenges. Hoffman et al. (2015) noted public perception of industries across sectors directly improved with the integration of more sustainable practices, transparency, and community involvement.

2. Materials and methods

2.1. Laboratory scale

The ability of acids to dewater sludge was first evaluated on a laboratory scale through titration-based acid additions using 60% ferric sulfate and 97% sulfuric acid. Ferric sulfate has a pH typically <2, while concentrated sulfuric acid typically exhibits a pH of 0.3. These acids were selected due to availability, cost feasibility, local regulations and safety objectives, while cognizant a higher hydrogen ion concentration would result in a greater pH change with less product consumed. Differences in concentration from the laboratory to industrial scale-up were negligible, although the laboratory scale experiments were purely to demonstrate capacity of these additions to dewater sludge. Titrants (acids) were diluted by a 1:10 ratio by volume (Table 1) and 100 mL of waste activated sludge (WAS) were used throughout the titration with pH measured with an ATI Orion perpHecT LogR Model 310 Benchtop Meter.

2.2. Preliminary in-situ trial

Prior to investing in permanent implementation, a preliminary, short-term manipulation of the secondary treatment process was initiated, and parameters to be measured across the mill process stream were selected (Fig. 1). Fennofloc XP 136H10 (ferric sulfate) was obtained from Kemira; the 93% sulfuric acid was obtained from ChemTrade.

To capture treatment effects over the ever-changing conditions of an operational facility, the addition of the two acids was alternated weekly to optimize acid concentration and thickening chemical use during subsequent system modifications. During the preliminary trial, acid was injected into WAS secondary sludge with an initial solids content of 2–3% *(w/w)* (in contrast, primary sludge is ~4% *(w/w)* solids content) (Fig. 1). The injection point was prior to mixing with the secondary sludge. The main parameter monitored was pH, which was typically measured at ~ pH 8 within the WAS prior to any acid addition. A final pH of 4 was selected following consultations with Canadian mill experts who indicated much

Table 1
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-value = 0.05.
Ferric sulfate t-based P-value ($\alpha = 0.05$), t-critical value = −1.72 and P-value = 0.05.

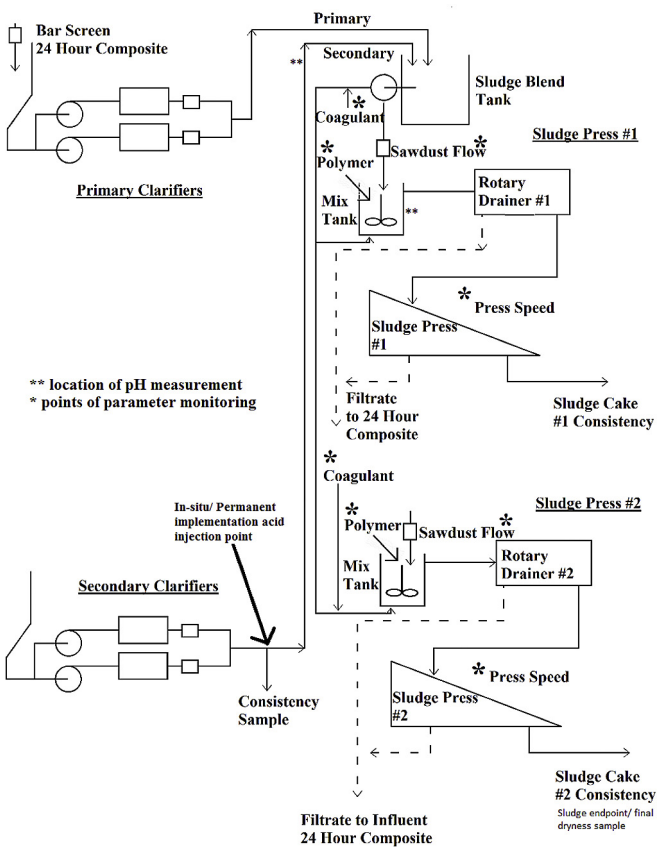

Fig. 1. Flow-based schematic of secondary treatment process monitored during acidification trial. (Adapted from Mitchell, 2015).