Vermont Phosphorus Innovation Challenge Business and Market Development Plan

Pe^{-}Phlo

September 30, 2019

Pe^{-}Phlo VPIC Project Partners:
UVM Department of Civil & Environmental Engineering
Village of Essex Junction
Efficiency Vermont
Chittenden Solid Waste District
James W. Morris & Associates, Inc.

Vermont Phosphorus Innovation Challenge

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Project Overview

The need for small-scale Phosphorus reduction technologies is a growing market in the United States. Improved water quality standards for compliance with EPA TMDL (Total Maximum Daily Limit) nutrient management requirements on the state and federal level have raised the compliance bar at the local level. This has occurred at a time where there are few mechanisms to fund the development and implementation of processes to meet these needs.

Many developing commercial Phosphorus removal nutrient solutions are only economically feasible for larger scale applications. In rural settings, these solutions are often not financially viable. The **Pe^-Phlo** (pronounced P Flow) is a mobile, flexible and scalable solution for Phosphorus capture and removal. **Pe^-Phlo** applications focus on reduced installation and operational costs without the investment needed for conventional Phosphorus removal "brick and mortar" approaches.

Proprietary pipe descaling technology (PDT) is widely used throughout the United States in thousands of successful scale formation control applications. This technology may well prove cost effective for Phosphorus removal in Vermont sized wastewater applications. The technology induces an oscillating electric field of variable amplitude and specific frequency that promotes formation and precipitation of crystalline minerals (i.e. Struvite) without dangerous and damaging adhesion normally associated with the formation of these compounds. **Pe^-Phlo** uses PDT coupled with an electric-filtration membrane filtration cell, to enhance Phosphorus capture and removal from the waste stream. Early data indicates an enhanced purity of the material formed by this process. The innovative **Pe^-Phlo** pretreatment and electric enhanced ultrafilter process operates at a lower pressure and improved reliability over other similar processes.

Research by the University of Vermont has confirmed the viability of applying descaling technology to aggregate dissolved Phosphorus in waste streams into particulate or crystalline forms for capture and removal. Work is ongoing to optimize laboratory parameters needed for full scale application required to prove out the innovative application of this technology.

Description of Project

Struvite (magnesium ammonium phosphate hexahydrate or $MgNH_4PO_4 \cdot 6H_2O$) is a crystalline compound formed when magnesium ammonium phosphate ions are dissolved in a waste stream's water phase above saturation concentrations. In many instances, Vivianite or hydrated ferrous phosphate; $Fe_3(PO_4)_2 \cdot 8H_2O$ may also be formed. Both of these compounds can be present in a wastewater treatment system's unit processes. Left unchecked, the formation of these crystals can lead to problematic scale formation on treatment plant surfaces clogging pipes, fouling valves and otherwise creating severe maintenance problems. The **Pe^-Phlo** system allows for controlled formation and removal of Struvite and Vivianite outside of the treatment process. The collected Struvite can be processed as a fertilizer resource outside of the wastewater facility and outside of the Lake Champlain Basin.

Struvite generation systems are employed to remove Phosphorus from waste streams. Commercial scale proprietary Struvite generation systems on the market are geared towards larger farm and municipal wastewater systems. Their profitability is based on a scale 10 times (or more) larger than applicable to the majority of facilities in Vermont. **Pe^-Phlo** is viable on a small scale application because it uses an innovative application of pipeline descaling technology (PDT) as a means of enhancing crystalline Struvite generation and Phosphorus removal. This makes it cost-effective for smaller facilities. **Pe^-Phlo** also couples an innovative oscillating electric-field assisted membrane filtration technology to capture and recover Struvite and/or Vivianite from the stream exposed to PDT. Re-processing the treated **Pe^-Phlo** provided a more complete removal of nutrients captured by this process.

Pe^-Phlo enhanced Struvite generation and capture improves the scalability to Vermont-sized water resource recovery facilities and Vermont sized farms. It does this at lower capital, operating and chemical costs than conventional innovative or proprietary systems. **Pe^-Phlo** does this at lower pressure to operate, reducing operating costs.

<u>Pe^-Phlo</u>

The **Pe^-Phlo** technology is a start-up-business in this quickly developing market. Process scale-up will determine the final configuration and capital equipment necessary for installation. Most potential installations are retrofits. The installations will utilize existing buildings and ancillary equipment, when feasible, to keep capital costs down. Typical installations are shown in Figure 1 below. **Pe^-Phlo** can be sold directly to a facility or installed by a general contractor. Start-up services and warranty included in the purchase price.

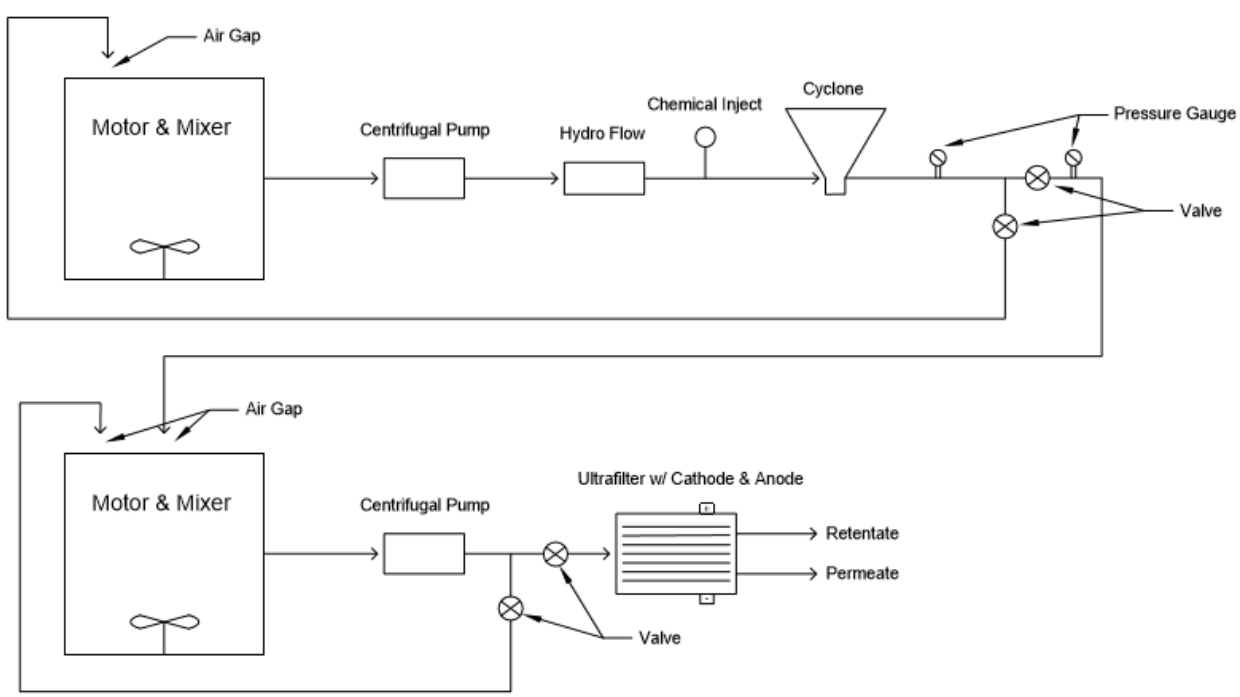

Figure 1: **Pe^-Phlo** Process Flow Schematic
(UVM Capstone Team Schultz, Hugo, Hancock)

The **Pe^-Phlo** application is unique in that the final installations can be very flexible and take advantage of underutilized space or equipment. This flexibility gives **Pe^-Phlo** a competitive edge over conventional P removal technology. Its low operating cost and reduction of Water Resource Recovery Facilities (WRRF) sludge generation provides additional benefit and reduced lifecycle costs, making this installation highly cost competitive.

Market Niche: DEFERRED WRRF CAPITAL

There are over 15,000 Water Resource Recovery Facilities (1), many of which use industry specific conventional biological, physical and chemical processes to remove Phosphorus. These processes generate increased amounts of sludge for further treatment and disposal. Greenhouse gas reduction potential is important to many potential end users of the **Pe^-Phlo** system. Chemical coagulation and flocculation of Phosphorus is also costly to the facility and to the environment. The coagulants used to bind and remove Phosphorus generate proportionally large amount of greenhouse gas emissions during the manufacture of these chemicals. (WRRFs are in the top ten of energy consumers and greenhouse gas producers.)

Biological treatment processes use “mixed liquor” or naturally occurring micro-organisms that collect Phosphorus and Nitrogen as part of their metabolism. When the treatment process is complete, waste micro-organisms are removed as sludge and then digested or forced to decompose, releasing a significant portion of those nutrients back to the process for treatment again. The constant recycling of P within conventional wastewater facilities is squandering valuable treatment capacity and increasing operating costs.

Pe^-Phlo breaks this vicious WRRF nutrient re-cycle by:

- Removing the Phosphorus from the digested sludge and frees Phosphorus and Nitrogen treatment capacity at the same time.
- Reduces sludge production
- Reduces the chemicals needed for Nitrogen and Phosphorus treatment
- Improves the process reliably for maintaining effluent Phosphorus concentrations below regulatory limits (0.2 mg/L Total Phosphorus in VT Lake Champlain basin).

At the Essex Junction, VT WRRF, sludge production and chemical use have increased ±30% since running at a discharge of 0.2 mg/L total Phosphorus. This costs the facility approximately $150,000 per year. As flows and pollution loads increase, more sludge will be produced and the cycle continues with decreasing potential for reliable effluent Phosphorus compliance. By application of the **Pe^-Phlo** process, we interrupt this expensive nutrient re-cycle with a unique Phosphorus separation and isolation process that preserves valuable existing treatment capacity and stabilizing sewer user rate. Additional treatment capacity could then become available for the processing of high strength wastes generated by Vermont’s expanding food and beverage facilities or ensure that there is sufficient capacity to treat the waste from our connected and growing communities.

Many WRRFs are nearing the end of their design life cycle and need capital maintenance or process improvement. Even more WRRFs are approaching organic treatment capacity at a faster rate than they are approaching their hydraulic capacity. Nearly all facilities are facing increasingly stringent discharge requirements for Phosphorus and Nitrogen. Over time, the **Pe^-Phlo** process is one inexpensive tool for process enhancement that may have broad and innovative application in the hands of WRRF engineers and operators.

Food and Beverage Production

Vermont has the highest per capita density of breweries and microbreweries in the country with over 100 microbreweries, wineries, meaderies and distilleries (2). These breweries and distilleries generate a high Phosphorus waste stream that gets further treatment at WRRFs or co-digestion with cow manure treatment systems on farms.

Vermont is also home to many value-added food and dairy product manufacturers that convert raw milk to cheese, ice cream and many other consumer products. These large manufacturers often rely on farm-based digesters for management of their manufacturing byproducts. While Vermont leads the country in farm-based anaerobic digestion per capita (3), there is diminishing capacity to handle these high Phosphorus waste streams with seasonal farm nutrient spreading restrictions. With added farm nutrient management planning requirements and a trend towards increased farm herd density on large farms, the capacity to handle these waste supplemental waste streams can be impacted. **Pe^-Phlo** nutrient removal system expands capacity where it is applied. Further work is needed to determine if **Pe^-Phlo** may well be a viable pretreatment system at the point of food waste generation.

Often, food manufacturing wastes generated by these producers introduce up to 400 ± ppm soluble (dissolved) Phosphorus to WRRFs and farm-based digesters. These facilities are often designed for 5-7 ppm. This concentrated Phosphorus waste increases the total mass load of Phosphorus in the digestate which is most often applied to the land as a fertilizer on farms or turned into a value-added fertilizer for specific markets. Farms have been identified as a significant source of Phosphorus in the Lake Champlain TMDL. As noted earlier, farms are required to develop nutrient management plans that require close monitoring of Phosphorus in the soil and fertilizer applied to fields. Importing additional Phosphorus to the farm by accepting food and beverage waste may create nutrient limits to the farm.

DEFERRED CAPITAL EXPENDITURE

The primary markets for the **Pe^-Phlo** installation are deferred capital expenditure and process Phosphorus removal enhancement. The **Pe^-Phlo** process is also less energy intensive and less land intensive than conventional treatment approaches. A secondary market is installation into existing facilities to aid in Phosphorus control within existing operations. Other markets to be explored include but are not limited to pretreatment of farm manure pit treatment, farm yard and silage nutrient treatment and Phosphorus removal at food and beverage manufacturers.

Municipal and agricultural pollution control installations often use similar equipment from the same manufacturers for environmental mitigation work. Conventional municipal mechanisms for Phosphorus removal often employ expensive technologies in a redundant manner to reduce Phosphorus concentrations to meet more stringent environmental discharge requirements. As agriculture is increasingly regulated, equipment technology is being used to further process animal waste to remove Phosphorus and reduce soluble Phosphorus on agricultural fields for environmental compliance.

Both municipal and agricultural applications often result in high capital expense and labor-intensive operations that generate more waste byproduct in order to achieve Phosphorus reduction targets. The **Pe^-Phlo** process provides an alternative Phosphorus removal mechanism in a cost-effective way.

Reduced capital and operational savings are the market niche for **Pe^-Phlo**. A potential revenue from sale of Struvite collected in a **Pe^-Phlo** installation is added incentive. The Phosphorus market is based on the sale of sequestered Phosphorus as an offsetting revenue to operation. These emerging Phosphorus markets are not yet considered a reliable revenue source. However, as the markets mature, revenue from Struvite sale will reduce the overall life cycle cost of a **Pe^-Phlo** installation

MARKETING PLAN and IMPLEMENTATION STRATEGY

The marketing and application of this technology will be similar to many other industry standard process equipment suppliers. WRRF design engineers will work with the **Pe^-Phlo** design team manufacturer's representative as Engineers would with other industry equipment manufacturers' representative. A 'job' shop will assemble the components as designed for each specific application and ship them to the purchasers site for installation by the project general contractor. Startup services will be provided by **Pe^-Phlo**.

The use of a manufacturer's representative is anticipated to be the primary product education and outreach mechanism for sales. This follows the WRRF and agriculture industry path with technical information provided to WRRF design engineers and facility managers. Prepared specifications will be developed to aid potential customers in developing requests for proposals.

Mobile point of use application is also a strong potential market. P&H Senesac Environmental Services, a Milton Vermont Environmental Services company with extensive experience in the fitting and application of mobile technology in the water quality industry. Senesac has expressed interest in teaming up with the **Pe^-Phlo** project team for the in-field application. P & H Senesac Environmental Services provides water and wastewater dewatering services throughout the country. They have extensive experience in the setup and application of mobile environmental services, thus have the experience and knowhow in full scale field applications. They also demonstrate the flexibility needed to apply technology at a wide assortment of facilities and based on the individual application needs.

Early stages of market development for the **Pe^-Phlo** system is based on sludge generation reduction, enhanced treatment capacity and avoided capital costs. Over time the sale of Struvite captured to fertilizer blenders will offset facility capital and operating costs.

EMERGING PHOSPHORUS MARKETS

Phosphorus (P) and Nitrogen (N) fertilizers have revolutionized food production creating farm enhanced crop yields. Production of both P and N fertilizers require raw materials and energy to create these valuable crop nutrients. The scientific community has recognized that Phosphates used as fertilizer are a finite source. Markets for recycling Phosphorus as a nutrient are seen as unreliable at this time. As the market develops, revenue estimates for the sale of struvite are estimated to be $100 to $600 per ton depending on the area of the country.

Struvite derived from WRRF processes may require certification as an alternative process to achieve Class A status for unregulated distribution and marketing of the **Pe^-Phlo** Struvite. Class A determination is important in improving direct marketability of the captured Struvite. However, one regional biosolids processer has expressed interest in **Pe^-Phlo** Struvite as a tool to provide custom fertilizer blending options for them in their Class A products. This blending option would provide the further treatment needed for distribution.

A third marketing tool for consideration of some is the green environmental sector for environmental credit trading. Climate change, local agricultural movements and environmental compliance converge to develop an emerging market for Phosphorus supplemental sources. Unlike energy carbon offset markets, this nutrient trading commodity is in its infancy and experiencing ebbs and flows in pricing. Over time and as reliable rock phosphate reserves diminish, the market for P derived from Water Resource Recovery Facilities (WRRF) and agriculture will improve. Revenue from this emerging market is not a factor for consideration in this implementation plan.

Interest to farms, tax payers and rate payers

Vermont is a small state in terms of population, but a BIG state in terms of innovation and problem solving. Vermont interest in a market-based approach to Phosphorus reduction is huge in applying cost effective solutions for small facilities. The technology is transferrable to thousands of small facilities throughout the country.

Vermonters also have significant challenges in meeting the requirements of the Lake Champlain TMDL. The Vermont Phosphorus Innovation Challenge recognizes that small size does matter in addressing Phosphorus removal challenges. EPA focus is on all sectors of pollution identified including but not limited to farms, timber operations, stormwater discharges, WRRF discharges, etc. That noted, EPA's only direct permit enforcement capability is to those entities with an NPDES Point Source Permit, which are municipal stormwater permits and WRRF discharge permits.

During a series of public hearings prior to release of the Lake Champlain TMDL, Stephen Perkins of EPA (retired) made it abundantly clear that if Vermont efforts for TMDL compliance did not meet the mark, the only recourse the EPA has is to tighten standards on NPDES point source permit holders. These two sectors are heavily invested now in Phosphorus reduction and will reach diminishing return for dollars invested per pound of P removed. **Pe^-Phlo** provides an alternative for consideration.

Effective and cost-efficient removal of P and resale of waste products derived will greatly reduce the application cost per pound of Phosphorus removed. Many of the TMDL non-point Phosphorus removal projects are based on derived calculated Phosphorus values, not hard quantifiable and verifiable Phosphorus removal numbers. The **Pe^-Phlo** process generates a measurable and quantifiable product removed from the waste stream. **Pe^-Phlo** offers a potential offsetting revenue to support operations.

Should Vermont continue on a path of aggressive Phosphorus removal via offset and trading, the opportunity for a flexible and low implementation cost installation such as **Pe^-Phlo** can be very desirable. A sewer district that installs **Pe^-Phlo** would have less capital for rate payers to absorb. **Pe^-Phlo** technology may potentially be applied in two general approaches. One approach could be retrofitting to existing WRRF operations as noted earlier. There is also potential for regional distributed application. A group of small operations, perhaps a group of small WRRF's and/or several on-farm operators with or without digesters in an appropriately defined area could form a Co-Operative. A Co-Op approach or a shared **Pe^-Phlo** unit could be used by nearby municipalities or a collective of nearby farms for use of a mobile version of the installation.

The municipal and farm market are highly competitive and funding constrained. Profitability would be based on industry averages of 10% net margin for the total design and installation package. Experience with the development and installation of multiple units would allow for some increase in margin up to 20% by means of increased performance and more market share as a result of successful installations. The **Pe^-Phlo** benefit is reduced capital, reduced energy cost and potential revenue from sale of collected struvite.

Business Launch (needs and hurdles)

Currently the project requires migration from the UVM laboratory to the Essex Junction WRRF for **Pe^-Phlo** scale-up application. A scaled up version of the application will allow the research team to analyze performance in a commercial application while allowing for a lot of process variables that are not typically encountered in a laboratory setting.

A project time line for further product and market development can be established after successful completion of this first application scale-up. The budget presented is to scale up the application with installation and product monitoring at the Essex Jct. VT WRRF for a period of up to 6 months.

This business plan will be updated after successful field demonstration. A budget for the next stages of **Pe^-Phlo** is attached for the VPIC consideration.

Budget: Attached

1. One Water for America State Policymakers' Toolkit, US Water Alliance and The Council of State Governments
2. BrewVeiw Vermont, 2019 Issue 2
3. www.NEWMOA.org

UVM, Essex Jct WRRF et al.

	Overall Budget	Next Stage Grant Request	UVM et all Match
Laboratory Testing	$6,000	$3,000.0	$3,000.0
Membrane purchase	$12,000	$6,000.0	$6,000.0
Ultrafilter Equipment Rental	$27,600	$13,800.0	$13,800.0
Ultrafilter micron filters	$5,000	$2,500.0	$2,500.0
Frac Tank Rental	$5,000	$2,500.0	$2,500.0
Miscellaneous	$1,000	$500.0	$500.0
Outside Consulting Services	$6,000	$3,000.0	$3,000.0
UVM Grad Student Stipend (X-Months salary +12% Fringe + Tuition)	$44,094	$22,047.0	$22,047.0
UVM F & A Charged at 25%	$11,120	$5,560.0	$5,560.0
Total	$117,814		
50% Match		$58,907.0	
Grant Total Request		$58,907.0	

Vermont Phosphorus Innovation Challenge
Final Technical Report

Pe^{-}Phlo

September 30, 2019

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1.0. INTRODUCTION

The investigation activities described herein were conducted by Civil and Environmental Engineering graduate students and the PIs from the University of Vermont, Essex Wastewater Resource Recovery Facility (WRRF), James Morris & Associates Inc., Efficiency Vermont, and Chittenden Solid Waste District.

The purpose of this investigation was to develop and test an innovate phosphorus recovery device (Pe^-Phlo) for phosphorus reduction in wastewater streams in a cost-effective manner. The Pe^-Phlo device is composed of two units that are critical for successful recovery of dissolved phosphorus: 1) commercial particle descaling technology a.k.a. "*Hydro*Flow", and 2) a custom-built electric filtration cell. These units can be operated individually or in tandem as per treatment requirements dictated by dissolved phosphorous, ammonia, and magnesium concentrations, and the size of colloidal phosphorus-containing crystals formed during the treatment. In addition, the pulsed-electric fields generated by *Hydro*Flow should avoid scale build-up in distribution pipes carrying the wastewater streams. The enhanced phosphorous recovery in the form of struvite or struvite-like minerals (i.e., magnesium ammonium phosphate (MAP) hexhydrate or $MgNH_4PO_4 \bullet 6H_2O$) using Pe^-Phlo device would improve the scalability to Vermont sized water resource recovery facilities and Vermont sized farms.

The hypothesis of this study is that the *Hydro*Flow coupled with oscillating electric-field assisted membrane filtration can precipitate struvite, and consequently enhance the phosphorus removal from wastewaters. In addition, the wastewaters treated with *Hydro*Flow exhibit a lower tendency to generate hard scale on surfaces of the conduits (or distribution pipes and membranes). To test this hypothesis, a bench-scale Pe^-Phlo device was developed and tested in the batch as well as continuous mode treatment using dewatering centrate obtained from Essex WRRF. Additionally, the role of seed additives (e.g., magnesium ions) on struvite precipitation was examined. The seeding approach was employed to induce precipitation and thereby enhance struvite recovery efficiency. The dewatering centrate samples before and after treatments were analyzed using APHA Standard Methods (SM), Environmental Protection Agency (EPA) methods, colorimetric assays, and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The struvite crystals formed under various treatments were characterized using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) spectroscopy, X-ray fluorescence (XRF) spectroscopy, and brightfield microscopy.

2.0. LABORATORY METHODOLOGY

2.1. Raw Source Water: The dewatering centrate was obtained from the Essex WRRF located at Essex Junction, Essex, Vermont. 10 L of centrate was collected and transported to Dr. Badireddy's laboratory within 1 h and stored at 4 ºC until further experimentation. The centrate sample was settled and stored at room temperature prior to the experimentation. At the time of sampling, a portion of the sample was sent to Endyne Inc. laboratory (Vermont) for the chemical composition analysis. A duplicate sample was also analyzed in Dr. Badireddy's lab at UVM. Table 1 shows the chemical composition of the centrate employed for this investigation. The results showed the presence of magnesium (21 mg/L), ammonia (990 mg/L), and phosphorus (130 mg/L, dissolved) in the centrate sample. These three components are collectively known as MAP and are responsible for struvite precipitation under appropriate conditions. The centrate has a pH of 7.54 at 22.7 °C.

Table 1. The characteristics of centrate sample obtained from the Essex WRRF on 03/13/2019

Parameter	Result	Units	Method
BOD-5 day	99,000	mg/L	SM 5210B(11)
COD	110,000	mg/L	Hach8000/EPA410.4
Conductivity at 25 °C	8,720	μmhos/cm	EPA 120.1
Ammonia as N	990	Mg/L	EPA 350.1, R.2
pH	7.54	SU at 22.7 °C	SM18 4500- H B
Phosphorus, Total Dissolved	**130**	mg/L	EPA 365.1, R.2
Phosphorus, Total	150	mg/L	EPA 365.1, R.2
Solids, Total Dissolved	1,690	mg/L	SM 2540C-97
Solids, Total Suspended	220	mg/L	SM 2540D-97
Metals Digestion	Digested		EPA 3015A
Calcium, Total	48	mg/L	EPA 6010C
Iron, Total	7.1	mg/L	EPA 6010C
Magnesium, Total	21	mg/L	EPA 6010C
Potassium, Total	170	mg/L	EPA 6010C
Sodium, Total	150	mg/L	EPA 6010C

STAGE I

Pre-development stage includes the purchase of particle descaling technology (*Hydro*Flow Inc. USA) and building a custom-designed electric filtration cell. These two units were assembled and developed into an innovative **Pe^-Phlo** technology for the VPIC project**.**

2.2. Development and Operation of Pe^-Phlo device: The Pe^-Phlo device is composed of two units that are critical for successful recovery of dissolved phosphorus: 1) commercial particle descaling technology (PDT) a.k.a. "*Hydro*Flow", and 2) a custom-built electric filtration cell. The description and working principle of the components is described below.

2.2.1. Commercial particle descaling technology a.k.a. "*Hydro*Flow": *Hydro*Flow is powered by the patented Hydropath technology. When properly installed on any type of pipe material (Figure 1), it induces a ±150 kHz, oscillating sine wave, alternating current (AC) signal. The electric induction is performed by a special transducer connected to a ring of ferrites. The unit attaches around an existing pipe made of any material and no plumbing or cutting of the piping system required (Figure 1a). It uses 120 V power and consumes less than $10 of electricity per year. The pipe and the flowing fluid act as a conducting medium, which allows the signal to propagate. The induced AC signal is believed to cause the mineral ions that make up **struvite** to form **loosely held together clusters**. When certain conditions are created (e.g., pressure change, temperature change, and high mixing intensity (i.e., turbulence or shear forces)) the clusters precipitate out of solution and form stable crystals of struvite that remain in suspension. The crystals are not stable to adhere to surfaces as hard scale and are carried away with the flow. Because hard scale no longer accumulates, the shear forces created by the flowing liquid erode and soften existing scale deposits over time. **It is important to note that constant liquid flow is required to remove scale deposits from a system**. The bench scale *Hydro*Flow device used in this investigation is shown in Figure 1b.

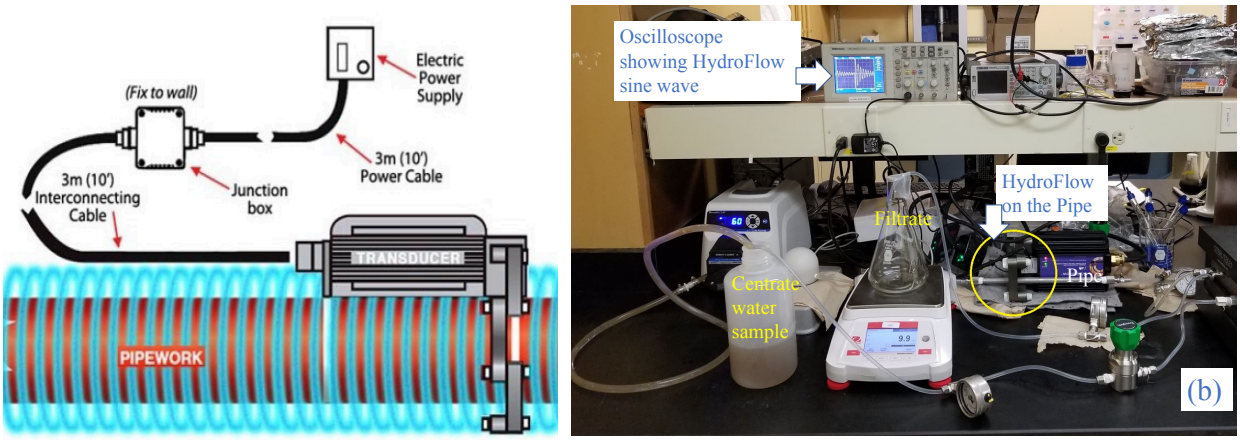

Figure 1. The pipe and flowing liquid act a conducting medium, which allows the electric signal generated by the *Hydro*Flow device to propagate in the liquid (a); the electric signal interacts with the ionic species present in water to induce particle cluster formation. A bench-scale Pe^-Phlo device with the *Hydro*Flow installed on the pipe is shown in (b).

<u>2.2.2. Custom-built Electric Filtration Cell</u>: A bench-scale electric filtration cell was developed at UVM. This filtration cell is designed to withstand transmembrane pressure up to 70 psi, which means microfiltration or ultrafiltration can be implemented depending on the treatment requirement. The filtration cell was equipped with two graphite electrodes with one on the feed side (wastewater) and the other on the permeate (filtered water or filtrate) side. A membrane is situated between the two electrodes separating the feed and permeate side (Figure 2a). The platinum wire leads connect the electrodes with the external power source (alternating or direct current) through the alligator clips. Each electrode was located at a distance of 1 cm from the membrane surface. The schematic and actual electric filtration cell set up used in this investigation is shown in Figure 2a and 2b, respectively. All crossflow microfiltration experiments were carried out using 0.22 μm pore-size polysulfone membrane.

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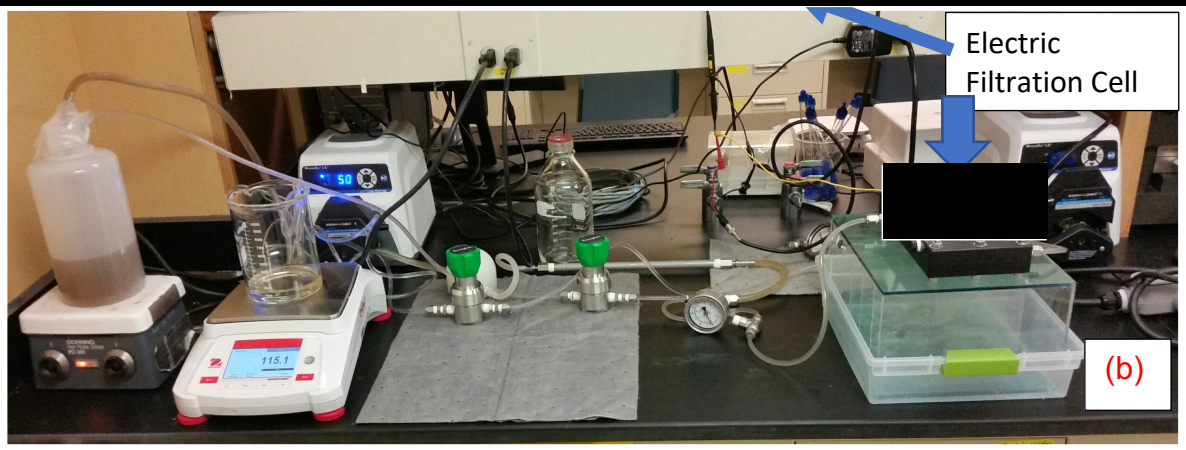


Figure 2. The schematic (a) and actual set up (b) of the custom-built electric filtration cell. Note PDT refers to particle descaling technology, a.k.a *Hydro*Flow.

STAGE II

P*e*⁻Phlo technology development stage includes testing the technology's ability to recover dissolved phosphorus in the form of struvite or struvite-like crystals (P-product) from dewatering centrate water. In addition, develop business model and identify the market opportunities for the P-product.

3.0. TEST PROCEDURE AND DISCUSSION

The dewatering centrate was studied for struvite precipitation and recovery under the experimental conditions described in Table 2.

Table 2. The experimental test conditions investigated in this project.

	Test Condition 1		Test Condition 2		Test Condition 3		
	Control	*Hydro*Flow	Control	*Hydro*Flow	Control	*Hydro*Flow + Electric field filtration OFF	*Hydro*Flow + Electric field filtration ON
	Batch + Dead-end Filtration	Batch + Dead-end Filtration	Batch + Dead-end Filtration	Batch + Dead-end Filtration	Batch + Crossflow Filtration	Batch + Crossflow Filtration	Batch + Crossflow Filtration
	Time (h)= 4	Time (h)= 4	Time (h)= 1, 4, 24	Time (h)= 1, 4, 24	Time (h)= 0-6	Time (h)= 0-6	Time (h)= 0-6
Centrate	√	√	√	√	√	√	n/a
Centrate + Mg^{2+} ions	n/a	n/a	n/a	n/a	√	√	√

3.1. Centrate sample preparation: 1 L of raw dewatering centrate sample was taken out from 4 °C storage and kept on the workbench for an hour to allow the centrate to reach ambient room temperature. Meanwhile, the settleable solids in the centrate sample settled to the bottom of the bottle and the supernatant was transferred to a clean beaker. The collected supernatant centrate sample was used for further experimentation under the test conditions described in Table 2.

3.1.1. Test Condition 1: Batch mode treatment without and with *Hydro*Flow for 4 h and dead-end filtration.

The experimental set up for the batch treatment with the *Hydro*Flow is shown Figure 3. A 40 mL of centrate sample in a 50 mL polypropylene vial was treated under batch conditions for 4 h without (control) and with ±150 kHz *Hydro*Flow electric field signal. The samples were then filtered using 0.22 μm-pore size polycarbonate filter to recovery precipitated crystals. The filters were air dried and the retained solids were analyzed for elemental composition using energy dispersive X-ray spectroscopy and X-ray fluorescence spectroscopy. The crystal morphologies were examined using the scanning electron microscopy.

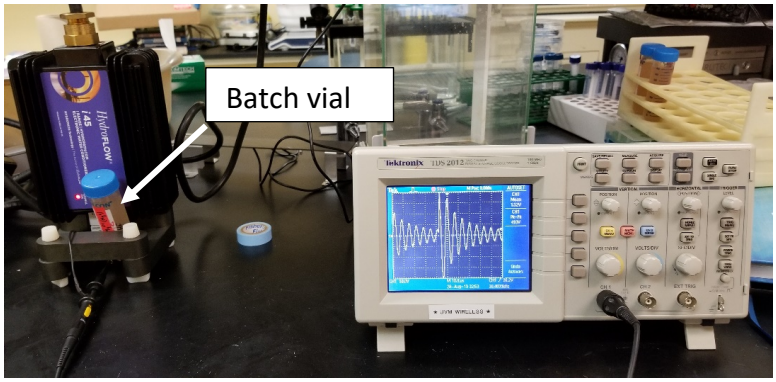


Figure 3. Batch experiments treating centrate with *Hydro*Flow.

A photograph of air dried solids on the membrane filter is shown in Figure 4. The solids that were exposed to 4 h of ±150 kHz *Hydro*Flow electric field signal (EMF) appeared to be dark brown, which is likely composed of a mixture of crystals and organics at a higher concentration (Figure 4b) compared to control sample (no *Hydro*Flow electric field signal) (Figure 4a).

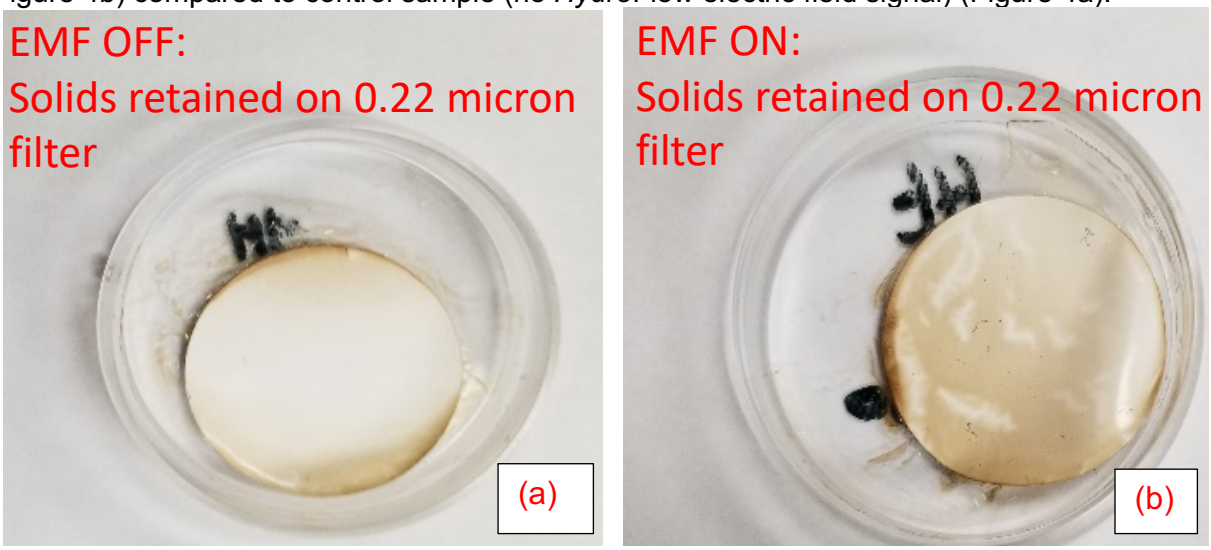


Figure 4. Control centrate solids (EMF OFF) (a), and *Hydro*Flow (EMF ON) treated solids (b). The exposure time was 4 h.

A high-resolution scanning electron microscopy analysis revealed crystals that resembled struvite morphology and energy dispersive X-ray spectroscopy confirmed the presence of phosphorus and magnesium in the crystals (Figure 5a and 5b), respectively. However, it appeared that the number of crystals per unit area were low while the crystal sizes were as large as 50 μm. These 50 μm-sized could be settled by gravity and recovered from the solution.

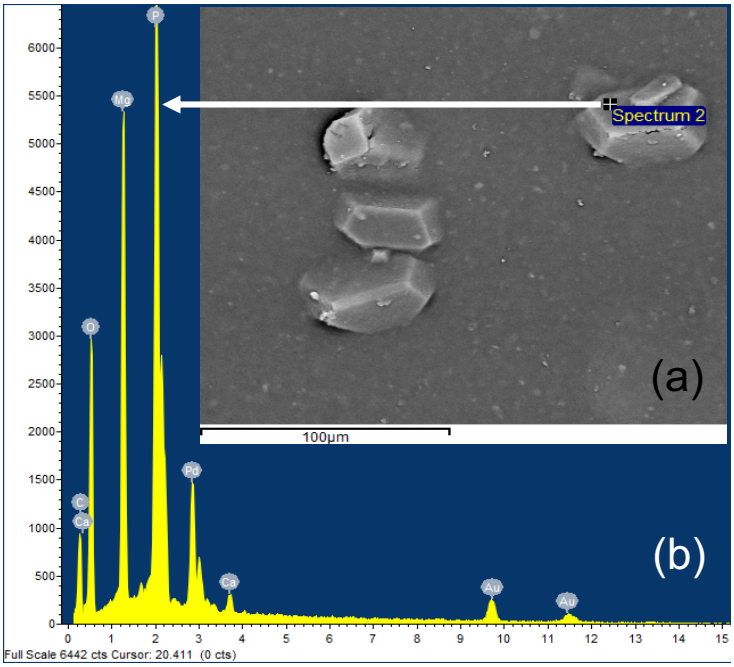


Figure 5. Scanning electron microscopy image of solids on the filter (a). The energy dispersive X-ray spectroscopy analysis of the solids (b). The exposure time was 4 h.

The centrate and settled solids from the control sample (no *Hydro*Flow) as well as the settled solids after treatment with ±150 kHz *Hydro*Flow were centrifuged and filtered using 0.22 μm polycarbonate filter. The solids were air-dried for X-ray fluorescence analysis. It was anticipated that the phosphorus-containing crystals will increase in the solids due to interactions with the *Hydro*Flow electric field. The elemental composition of the solids was analyzed using a semi-quantitative X-ray fluorescence technique. The results from X-ray fluorescence analysis are summarized in Table 3.

Table 3. X-ray fluorescence analysis of solids.

X-ray fluorescence (XRF) Analysis of settled and centrifuged

	%P	%S	%K	%Fe	%Cu	%Ca
Settled solids	8.14 ± 0.08	3.09 ± 0.04	13.36 ± 0.05	**3.36 ± 0.07**	0.03 ± 0.01	12.71 ± 0.05
Solids w/o EMF exp. (centrifuged)	9.23 ± 0.07	5.31 ± 0.05	**17.97 ± 0.06**	0.92 ± 0.05	0.03 ± 0.01	11.15 ± 0.05
Solids after EMF exp. (centrifuged)	**13.13 ± 0.07**	**12.16 ± 0.05**	11.84 ± 0.04	0.71 ± 0.03	**0.32 ± 0.01**	**12.34 ± 0.04**
EMF effect On Solids composition	**Increase**	**Increase**	Decrease	Decrease	**Increase**	Slight Increase

Based on the Table 3 results, the changes in the elemental composition of the settled solids exposed to ±150 kHz *Hydro*Flow for 4 h are as follows:

1) the percent **phosphorus** in the settled solids increased from 9% to **13%**
2) the percent sulfur in the settled solids increased from 5% to **12%**
3) the percent calcium in the settled solids slightly increased from 11% to **12%**
4) the percent copper in the settled solids increased from 0.03% to **0.32%**

Above results suggest that 4 h treatment with ±150 kHz *Hydro*flow electric signal was likely responsible for the observed increases shown in Table 3.

Furthermore, analysis of filter weights with retained solids on the control and *Hydro*flow treated indicated the following:

1) Control sample: weight of solids retained on the membrane surface was **0.1722 g**/80 mL filtered
2) *Hydro*Flow-treated sample: weight of solids retained on the membrane surface was **0.4576 g**/80 ml filtered

These results confirm that *Hydro*Flow treatment likely increased the concentration of settleable solids and possibly a fraction of them are phosphorus-containing struvite crystals. After the *Hydro*Flow treatment, **the total solids recovered on the filter were remarkably increased by 165% compared to the control samples**.

3.1.2 Test Condition 2. Batch mode treatment without and with *Hydro*Flow for time 1 h, 4 h, and 24 h.

The effect of exposure time on the formation and growth of crystalline solids and the phosphorus-containing crystals was investigated in the Test Condition 2. The samples were filtered and the solids were analyzed using scanning electron microscopy, and energy dispersive X-ray spectrometer. The results are shown in Figure 5 (1 h time) and Figure 6 (4 h time). The

compositional differences between 4 h and 24 h samples were insignificant so data corresponding to 24 h are not shown in Figures 5 and 6.

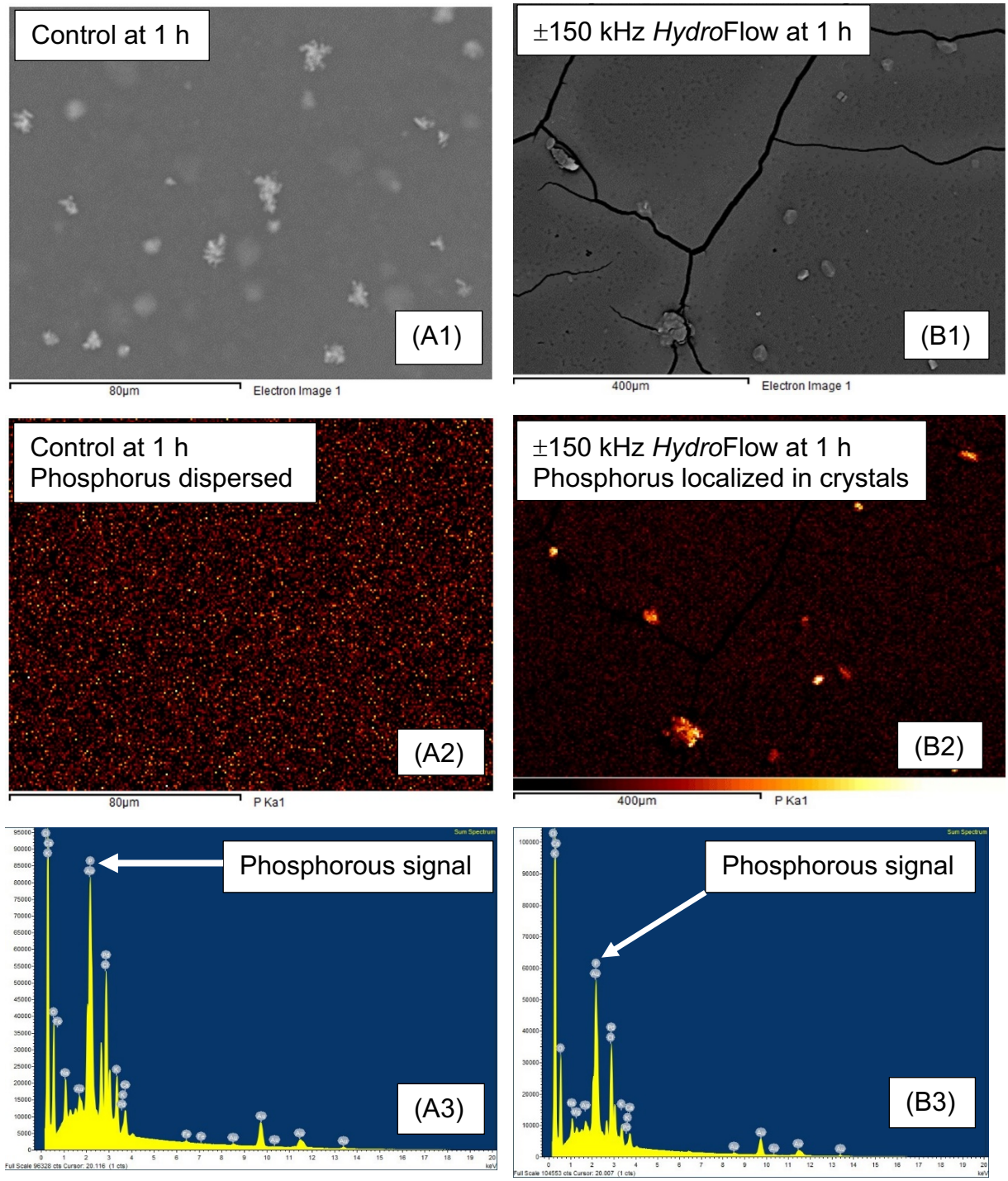


Figure 5. Scanning electron micrographs (A1 and B1), phosphorous elemental maps (A2 and B2), and energy dispersive X-ray spectra of control and ±150 kHz HydroFlow treated samples (A3 and B3). Time: 1h.

Phosphorous-containing solids appeared amorphous and dispersed across all solids retained on the membrane surface (Figure 5: A1 and A2 (1 h); Figure 6a (4 h)), as revealed by the scanning electron microscopy and energy dispersive X-ray spectrometer analysis. On the contrary, solids retained on the filter appeared crystalline and the phosphorus was remarkably localized in the crystalline solids just after 1 h as well as 4 h of treatment with ±150 kHz *Hydro*Flow treatment (Figure 5: B1 and B2, and Figure 6b and 6c).

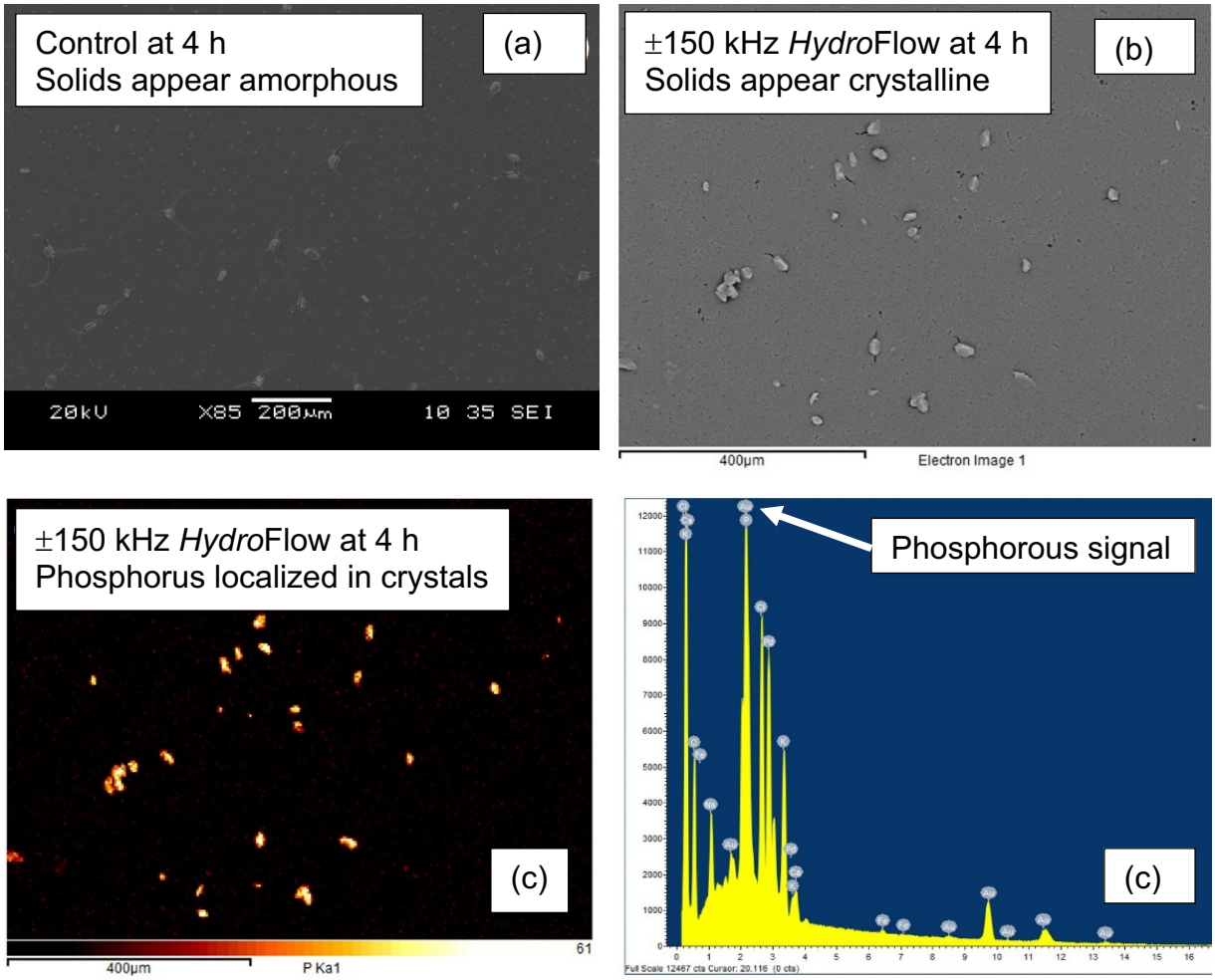


Figure 6. Scanning electron micrographs of the control (a) and ±150 kHz *Hydro*Flow solids (b), phosphorous elemental map of the *Hydro*Flow solids (c), and energy dispersive X-ray spectrum of the *Hydro*Flow solids (d). Time: 4h.

<u>3.1.3 Test Condition 3</u>. Batch treatment with *Hydro*Flow for 6 h followed by crossflow electric microfiltration.

The effect of magnesium ions (Mg^{2+}) as seed species and the *Hydro*Flow field on struvite formation was investigated. The hypothesis was that the Mg^{2+} ions can increase the struvite formation and ±150 kHz *Hydro*Flow treatment will decrease the nucleation time required for struvite formation. Furthermore, the struvite exposed to ±150 kHz *Hydro*Flow electric field will result in soft scale, which can be easily removed and recovered from the surfaces. The suspensions containing struvite crystals were captured and recovered using crossflow microfiltration in the presence and absence of electric fields across the membranes.

The centrate samples were treated for a maximum of 6 h, to mimic the residence time at Essex WRRF, and the struvite crystal formation was monitored and analyzed during that period. Two centrate samples, one obtained in March and the other in June, were exposed to Test Condition 3. The parameters including pH, conductivity, crystal nucleation time, and phosphorus concentration and recovery were measured. The phosphorus concentrations in the filtrate and concentrate from crossflow electric microfiltration were also measured.

Batch and Crossflow Treatment- Seeding with Mg^{2+} ions

Seeding solution: 0.3525 g of magnesium chloride ($MgCl_2$) was dissolved in 100 mL of ultrapure water by stirring at 400 rpm. The stock solution concentration of Mg^{2+} ions was 900 mg/L.

Procedure: 45 g of centrate water in 50 mL polypropylene vials were exposed to ±150 kHz *Hydro*Flow electric signal for 6 h. Another set of samples were set aside for 6 h but without exposure to the *Hydro*Flow field, which served as the controls. At the end of 6-h period the samples were filtered using 0.22 μm polysulfone membranes (Millipore) using crossflow microfiltration. The centrate samples were spiked with Mg^{2+} ions at 100 mg/L prior to activating the ±150 kHz *Hydro*Flow electric field. The controls were also spiked with Mg^{2+} ions at 100 mg/L. The two different centrate samples, which were obtained in March and June, were tested under these conditions.

After filtration the membrane was air dried overnight and analyzed using scanning electron microscopy and energy dispersive X-ray spectroscopy for crystal morphology and elemental composition, respectively. The raw centrate, filtrate, and concentrate samples were analyzed for phosphorus and other elemental concentrations using ICP-AES (Figure 7). All samples were measured in triplicate.

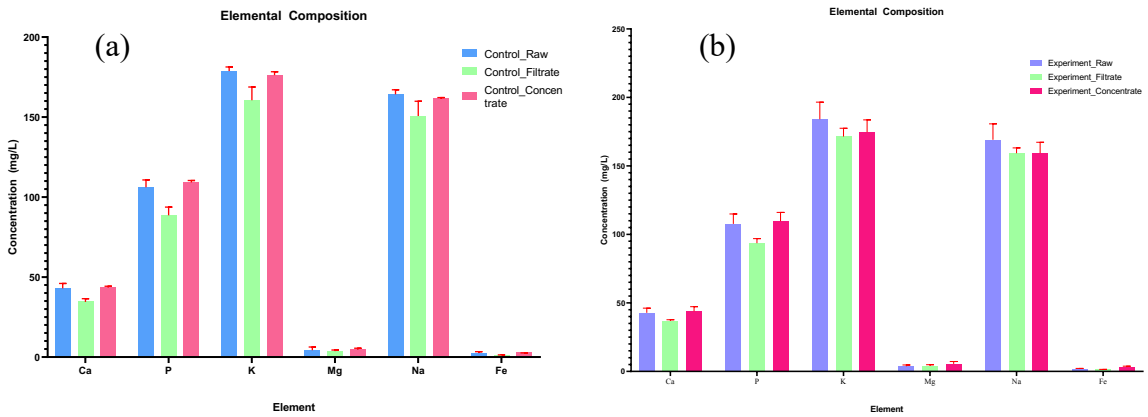


Figure 7. Elemental composition of centrate feedwater (raw), filtrate, and concentrate from microfiltration without (a) and with 6 h *Hydro*Flow electric signal (b). The differences in elemental composition in the presence and absence of *Hydro*Flow treatment were statistically insignificant ($p>0.05$).

In absence of additional Mg^{2+} ions (i.e., spike solution), and 6-h continuous crossflow microfiltration conditions the ±150 kHz *Hydro*Flow electric signal did not result in crystals that were large enough to be captured by 0.22 μm membrane, and therefore, the observed change in phosphorus concentration between the raw centrate and permeate (filtrate) was not that remarkable (Figure 7). On the contrary, the results from Test Conditions 1 and 2 suggest that although the number of struvite crystals per unit area of the membrane was small the crystal sizes

were as large as 50 µm after 4 h of *Hydro*Flow treatment. At these sizes the struvite crystals can readily settle to the bottom of the vial.

Centrate samples were thoroughly investigated with Mg^{2+} spike solutions and combination *Hydro*Flow and microfiltration. The most interesting results were obtained when both Mg^{2+} and ±150 kHz *Hydro*Flow electric field was applied simultaneously. A summary of the results from these experiments with spiked Mg^{2+} ions are shown in Table 4.

Table 4. *Hydro*Flow treatment and crossflow microfiltration

Sample	Visual Crystal Nucleation Time (h)	Phosphorus Recovery Efficiency (%)	pH
March 2019			
Centrate sample	n/a	n/a	8.23
Centrate sample treated **with** ±150 kHz *Hydro*Flow electric field signal	No visible crystal growth	9.53	8.19
Centrate sample treated **without** ±150 kHz *Hydro*Flow electric field signal	No visible crystal growth	4.73	8.36
Mg^{2+} spiked into Centrate sample and treated **with** ±150 kHz *Hydro*Flow electric field signal	2.5	84.63	8.15
Mg^{2+} spiked into Centrate sample and treated **without** ±150 kHz *Hydro*Flow electric field signal	4	88.07	7.78
June 2019			
Centrate sample	n/a	n/a	7.41
Centrate sample treated **with** ±150 kHz *Hydro*Flow electric field signal	No visible crystal growth	4.5	7.69
Centrate sample treated **without** ±150 kHz *Hydro*Flow electric field signal	No visible crystal growth	10.97	7.97
Mg^{2+} spiked into Centrate sample and treated **with** ±150 kHz *Hydro*Flow electric field signal	5.5	78.61	7.81
Mg^{2+} spiked into Centrate sample and treated **without** ±150 kHz *Hydro*Flow electric field signal	6.5	76.26	7.94

Key findings from Table 4 are as follows:

1. Mg^{2+} ions and ±150 kHz *Hydro*Flow electric field significantly decreased the struvite nucleation time from 4 h to 2.5 h.
2. Struvite crystals were formed more rapidly in the presence of both Mg^{2+} ions and *Hydro*Flow electric field compared to Mg^{2+} ions only.
3. **85% of dissolved phosphorous was recovered in the form of struvite within 2.5 h**.
4. Physical examination of struvite crystals revealed that **Struvite formed a soft scale (a loosely held together crystal clusters) on the surfaces**.
5. Struvite nucleation time and recovery appears to be sensitive to slight changes in pH.

Visual and Quantitative Observations of Struvite Crystals

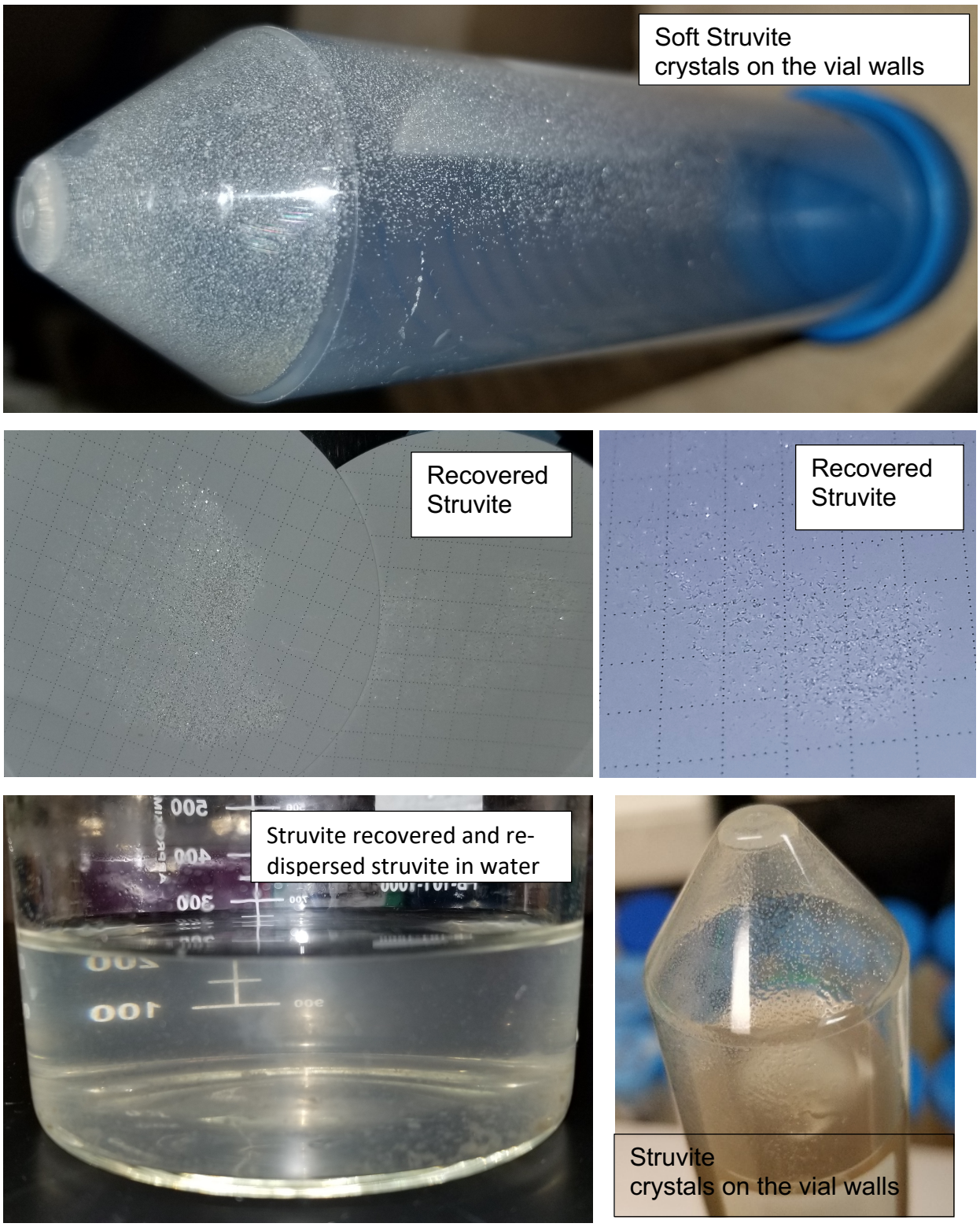
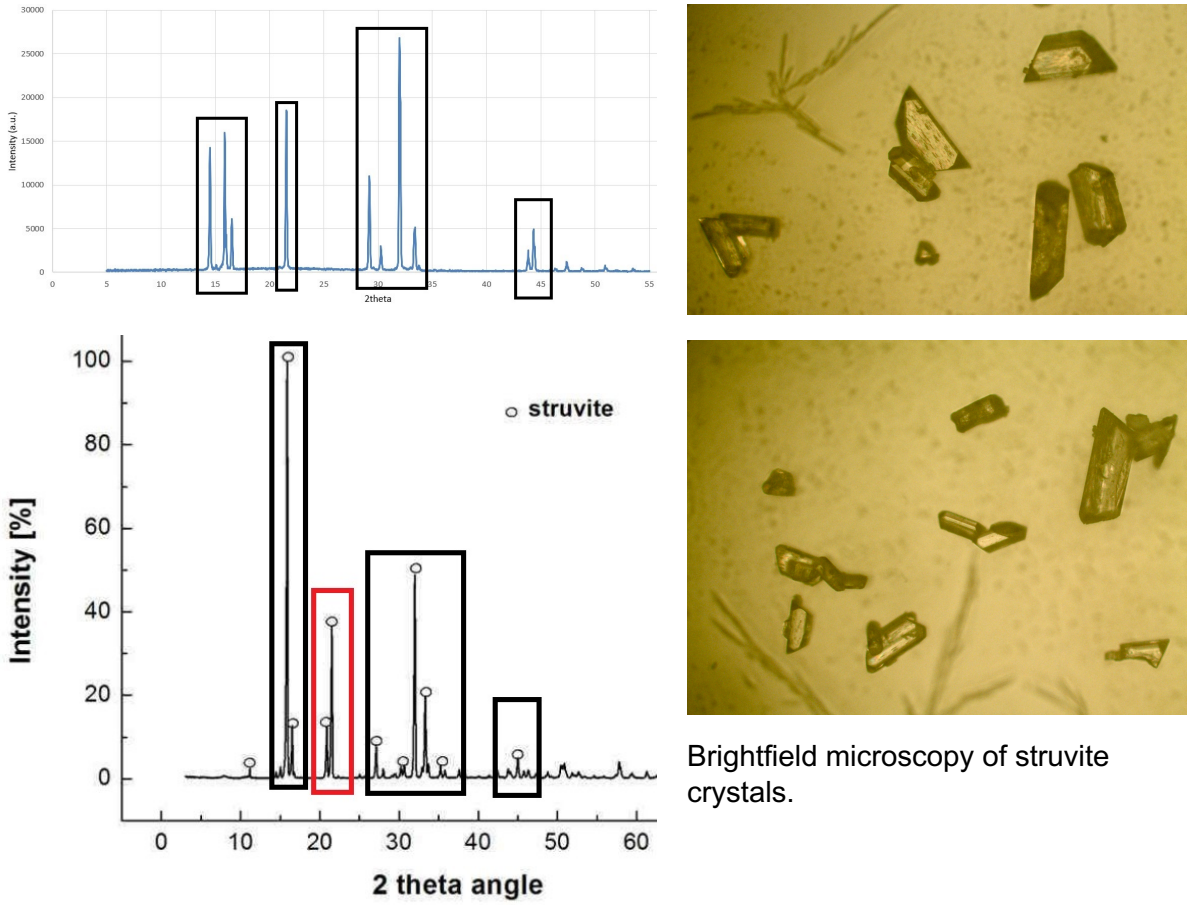


Figure 8. Struvite crystals formed by Mg^{2+} and ±150 kHz *Hydro*Flow electric field signal.

Struvite crystals were found to be a form of soft scale on vial surfaces and they were easily recovered by simple scraping or high intensity rinsing.

X-ray diffraction analysis confirmed that the crystals were struvite (Figure 9). The crystal structure of struvite is consistent with the struvite structure that was precipitated under similar wastewater conditions. However, the crystal structure was different from pure struvite. This change in structure was likely the result of treatment with ±150 kHz *Hydro*Flow and was probably responsible for the transformation of “hard scale” nature of struvite into “soft scale”. This “soft scale” nature of struvite is important because it would allow easy recovery with minimal energy from any technical surface including holding tanks, distribution pipes, membrane surfaces, and others.



Brightfield microscopy of struvite crystals.

Figure 9. XRD spectrum of struvite (current work) (A); XRD spectrum of struvite (Zhang, T. et al 2014, 21 (1) Ecol Chem Eng S) (B); Brightfield images of struvite crystals that were recovered from the vial (C-D).

The experimental set up for crossflow electric filtration is shown in Figure 10. The centrate with spiked Mg^{2+} was filtered using 0.22 μm polysulfone membrane at a transmembrane pressure of 5 psi. The oscillating electric field was applied at 100 kHz, 1 A, and 3 V peak-peak across the membrane. During the filtration the clear filtrate was collected. At the end of 6 h operation, the samples of raw centrate, filtrate, and concentrate were collected and sent to Endyne Lab for the phosphorus and other elemental analysis. We are still waiting on these results.

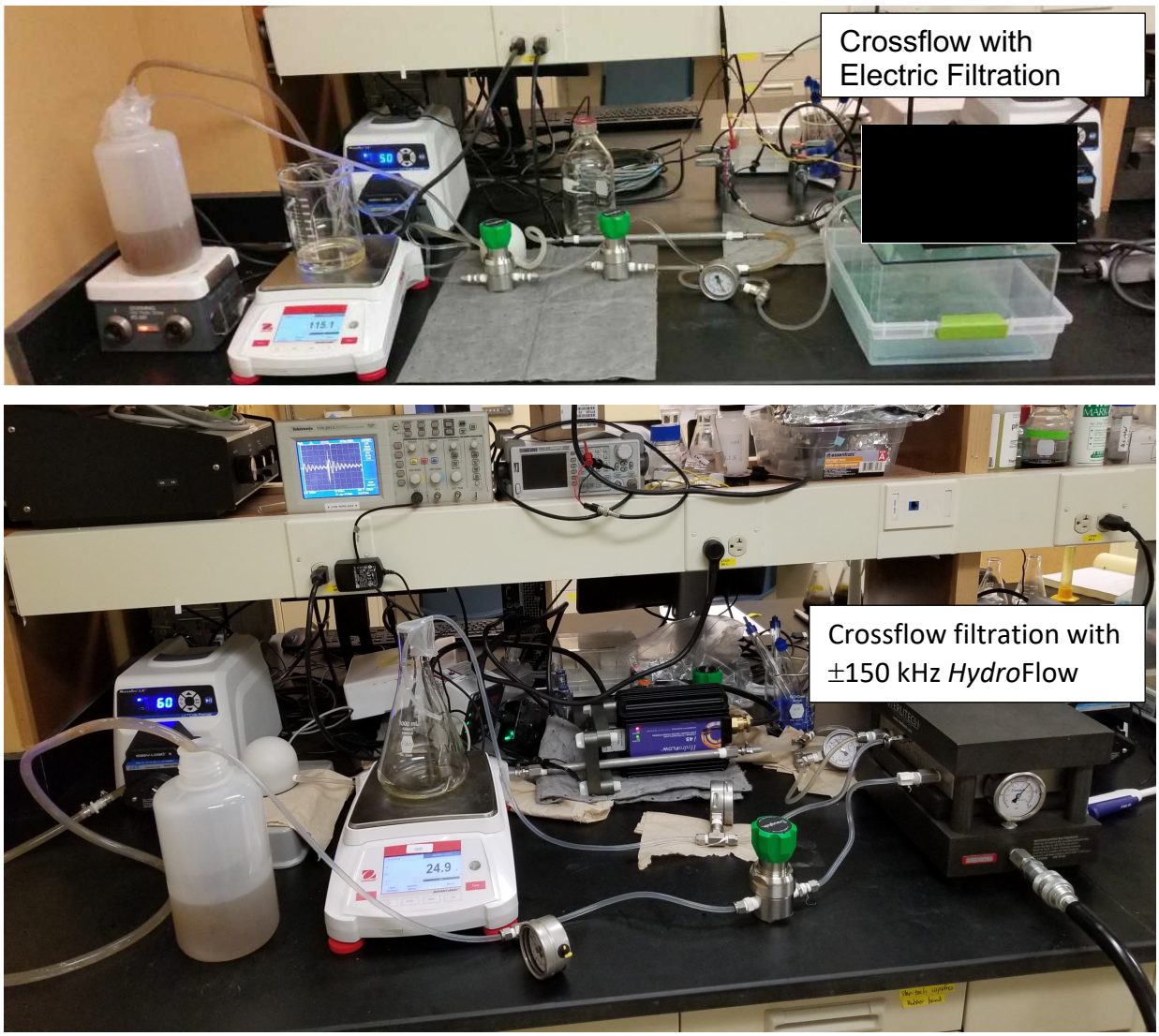


Figure 10. Test condition 3: Schematic of crossflow electric filtration without and with *Hydro*Flow systems.

4.0 CONCLUSIONS

- A combination of Mg^{2+} ions and ±150 kHz *Hydro*Flow electric field was found to be most effective at capturing phosphorus in the form of struvite. **The phosphorus recovery in the form of "soft scale" (i.e., loosely held together clusters) struvite was about 85% at pH 8.12**. The 7.0-8.5 pH is typical of dewatering centrates.
- Above treatment rapidly, about 38% less time, precipitated struvite in the form of "soft scale" compared to controls that were not treated with ±150 kHz *Hydro*Flow electric field. The nucleation time appears to be sensitive to slight changes in pH.
- It appears that higher pH will lead to greater and rapid precipitation. Further investigation is required to determine the effects of pH, Mg^{2+} dosage (concentration and contact time), operation conditions (batch vs continuous).
- In the absence of Mg^{2+}, ±150 kHz *Hydro*Flow electric field alone was able to agglomerate suspended solids to a level that was easily captured by filters. When compared with controls

(no *Hydro*Flow), **the percentage of solids retained by the filter increased to 165% due to ±150 kHz *Hydro*Flow electric field**.

- Based on the above findings, we suspect that at significantly lower nucleation time (< 2.5 h) the struvite crystal sizes may be in the range of few microns or sub-microns that can be easily retained by microfilter or ultrafilters depending on the treatment requirements.
- The X-ray diffraction analysis confirmed that struvite formed under *Hydro*Flow electric signal had an altered crystal structure that might have given the **"soft scale"** nature to the struvite. This characteristic allows easy recovery of struvite as well as easy cleaning of technical surfaces including holding tanks, distribution pipes, reactors, and membrane surfaces.