THERMAL PROCESS SYSTEMS

Targeted Phosphorus Recovery

Patent-Pending Technology

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THERMAL PROCESS SYSTEMS

Phosphorus in Wastewater AnAer Pilot Targeted Phosphorus Recovery

Questions





An exceptionally dense bloom in lower Chesapeake Bay on 8/17/2015. Source: W. Vogelbein/VIMS.

BACKGROUND

Phosphorus in Wastewater Treatment

- Nutrient imbalances in soil a result of land applied biosolids
- Leaching to waterways has resulted in harmful effects
- Current regulations limit the amount of phosphorus in effluent streams
- Common practice is shifting phosphorus from liquid waste to solid waste e.g. ferric or alum precipitation
- Does not remove the potential of phosphorus to contaminate waterways later in its lifecycle

EBNR Nitrogen Removal



Source: www.wateronline.com/doc/biological-nutrient-0001

- Aerobic Nitrification
- Anoxic Denitrification
- \blacktriangleright N is emitted from the system as N₂ gas
- Process recycle streams



Source: Pugh, 2015

EBNR Phosphorus Removal



Source: www.wateronline.com/doc/biological-nutrient-0001

- Anaerobic growth of Phosphorus Accumulating Organisms (PAOs)
- Aerobic uptake of phosphate (PO_4^{3-})

EBNR Phosphorus Accumulating Organisms

Anaerobic

Aerobic



A BIG ISSUE HIDING IN PLAIN SIGHT

EBNR is very effective at removing P from wastewater

BUT...

It concentrates all that P into the solids that enter the digestion process

Cell lysis and bacterial decay rupture cell membranes and release contents

Phosphate precipitates have become a big operational concern

PAOs are rich in all the ingredients

Easy for plants to recycle large amounts of P causing a "cycle up" Need to maintain removal of influent P, even at lower levels



Aerobic Digester P levels at a BNR facility

BIOSOLIDS DEWATERING The Effects of Phosphorus

- Increase in P corresponds with decline in dewatering performance EBNR facilities especially susceptible
 Example Denver R Hite WWTP
- Several compounding factors
 - Availability of ortho-P
 - ► Mono- to Divalent ratio (M/D)
 - Extracellular Polymeric Substances (EPS)



BIOSOLIDS DEWATERING Phosphorus Availability and M/D

- ► High concentrations of ortho-P increase the chances of precipitates forming Struvite: $K_{sp} = -\log([Mg^{2+}][NH_4^+][PO_4^{3-}])$ Brushite: $K_{sp} = -\log([Ca^{2+}][HPO_4^{2-}])$
- Increase in M/D results in poorer dewatering

$$\frac{M}{D} = \frac{Na^{+} + K^{+}}{Mg^{2+} + Ca^{2+}}$$

Source: Kara, 2007

M/D increases when Na⁺ or K⁺ increase, Mg²⁺ or Ca²⁺ decrease Divalent P precipitates have negative effects on dewatering



BIOSOLIDS DEWATERING Extracellular Polymeric Substances

- EPS is a combination of macromolecules excreted by bacteria Negatively affects dewatering because of high stored water content
 Primary macromolecules are polysaccharides and proteins
- Ortho-P adheres to proteins Unfolds proteins; used in food processing to stabilize emulsions
 Expands EPS
 Allow more space for water storage -> poor dewatering



Sources: Selling; Rus, 2016

MANAGING P IN DIGESTION

P recovery technologies target struvite and brushite formation
e.g. Ostara®, Struvia[™], AirPrex[™], NuReSys[™], CalPrex[™], etc.
Often done as an intermediary or pretreatment step
Many plants remove P during dewatering via metal salt coagulants
e.g. Fe₂(SO₄)₃ & Al₂(SO₄)₃
Forms a precipitate (FePO₄ & AlPO₄) that drops into the cake
P not precipitated returns to head of the plant in the filtrate, centrate, etc.

MANAGING P IN DIGESTION

Continuously recycling P can cause a plant to "cycle up" Coagulant dosing optimized for dewatering may not capture all PO_4^{3-} Excess recycled P may be minimal at first, but builds up to critical levels over time PAOs reach a saturation point where effluent P limits cannot be met Metal salt addition during dewatering is constrained Amount of metal salt required to precipitate all incoming P becomes very large Lowers pH that brings corrosion concerns to dewatering equipment Chemicals are expensive

ANAER PILOT STUDY

Overall Goals

- Effectively combine anaerobic and aerobic digestion
- Create optimal environments for each of the different bacterial cultures
- Implement process control parameters to balance VFA production and conversion in the AD
- Decrease the overall HRT for the anaerobic digestion process with improved solids destruction and biogas production

ANAER PROCESS OVERVIEW

Flow Schematic



LAB RESULTS

Steady-State VS Destruction				
AD	SNDR	Total		
57.7%	15.3%	64.3%		

- Continued operation of the AD came with an increase in VS destruction
- Recycle maintained VFA/ALK under 0.3
- No spikes in VFA concentration or foaming events
- Low NH_3 and H_2S in biogas
- Biogas production is in upper end of literature values

AD VFAs and Alkalinity			
VFAs (mg/L)	938		
ALK (mg/L)	3372		
VFA/ALK	0.28		
VFA Conversion	57%		

AD Biogas Averages			
Hydrogen Sulfide (ppm)	21.0		
Ammonia (ppm)	6.06		
Carbon Dioxide (%)	38.1%		
Methane (%)	61.9%		
Biogas produced (ft^3/lb VS)	13.47		

DEWATERING RESULTS

Sample	Total Solids	Coagulant	Flocculant	Cake Solids	Coagulant	Flocculant
	(%)	(mL Ferric Sulfate)	(mL Polymer)	(%)	(active lb/dry ton)	(active lb/dry ton)
Pilot SNDR	1.90	0	5	28.7	0	10

- Fully mesophilic system yielded superior dewatering results
- Eliminated coagulant demand and significantly reduced polymer requirement
- High TS reduction and high cake solids lower amount of material to haul considerably
- AnAer system provides major benefits to dewatering operations

CURRENT OPERATION

Increased SNDR recycle from 60% to 200% of daily feed

- Consistent VS destruction & biogas production
- ► H_2S in biogas has lowered to <1ppm
- Ammonia decreased from 1500 mg/L to 500 mg/L
- ► Maintaining lower NH₃ keeps pH slightly lower; 7.2 \rightarrow 6.7
- Lower ammonia and pH both decrease struvite potential

TARGETED PHOSPHORUS RECOVERY A NEW APPROACH TO P MANAGEMENT Researching new methods for biosolids dewatering Begins with digestion – "solids conditioning" Address multiple issues negatively affecting dewatering Reduce chemical costs Form a product



SNDR ~2.25 TS

1. Conditioning



SOLIDS CONDITIONING

Storage Nitrification/Denitrification Reactor (SNDR)

- Developed to remove ammonia during digestion
- Also efficient at removing soluble COD, VFAs, proteins, and carbohydrates

Breaking up proteins and carbohydrates (polysaccharides) disrupts the production of EPS that negatively affects dewatering

- Reduces alkalinity through nit/denit cycles
- Effective when following ATAD or anaerobic digester

SNDR following anaerobic digestion

- Pilot research shows elimination of coagulant requirement
- ▶ Low polymer dose \rightarrow ~10 active lbs/dry ton

SNDR following ATAD

- Cell lysis in the ATAD creates strong emulsion
- Coagulant is needed to break the emulsion
- ► 10-20% reduction in polymer demand



Replacement of coagulant with strong acid

- Acid acts as a coagulant through charge neutralization e.g., H₂SO₄ vs Fe₂(SO₄)₃ & Al₂(SO₄)₃
- Acid hydrolysis ruptures cells, releasing stored P
- ► Lowers pH which prevents precipitates from forming Mg²⁺ and Ca²⁺ remain soluble → lower M/D
- Lower alkalinity = less acid required \rightarrow SNDR is key

- Ensure pH is at safe level for dewatering equipment
- Smaller H⁺ ions coagulate solids without forming large precipitates that add to cake weight
- \blacktriangleright Less material to bind \rightarrow less polymer
- Balances cake N/P ratio
- Lab testing shows >30% decrease in cake weight
- Centrifuge dewatering achieved >35% cake solids



Filtrate

- Liquid-solid separation results in P rich filtrate, centrate, etc.
- Minimal alkalinity and biological activity remaining
- Absence of solids removes "contaminants" that lower P recovery efficiency



Phosphorus rich filtrate

PHOSPHORUS RECOVERY

- **Chemical Precipitation**
- High P liquid stream with little pH buffer
- Target either brushite or struvite formation
- Precipitate readily forms at right conditions
- Soluble Ca²⁺ and Mg²⁺ already present reduce chemical demand



Struvite Solubility Curve Source: Kim, 2016

PHOSPHORUS RECOVERY Chemical Precipitation



TARGETED PHOSPHORUS RECOVERY

Lab Testing Results

	Low	High	Average
Total Phosphorus Solubilized	74%	96%	83%
Soluble Phosphorus Precipitated	91%	93%	92%
Total Phosphorus Removed	72%	89%	79%



PHOSPHORUS RECOVERY

Ion Exchange

- Liquid centrate can be passed through an ion exchange column
- Hybrid Ion Exchange Nano-Absorptive Media (HIX-Nano) Utilizes iron or zirconium oxides for ortho-P affinity
- More effective at lower pH



Phosphate sorption and release Source: Weinberg, 2017

PHOSPHORUS RECOVERY

Ion Exchange

- HIX(Fe)-Nano captures ortho-P and releases a concentrated solution to storage tank
- Ortho-P selectivity removes contaminants from effluent
- Concentrated P solution is ideal for making valuable products
 - Hydroponic fertilizers
 - Fluidized catalytic cracking catalysts
 - Lithium-ion battery cathode material



Source: Weinberg, 2017

IDEAL TPR SYSTEMS



IDEAL TPR SYSTEMS

SNDR after Anaerobic Digester

- SNDR recycle helps prevent formation of EPS in AD
- Biosolids don't require coagulant to dewater
- Lowering P return to headworks begins to "cycle down" plant
- Combines with lower NH₃ and pH in AD to significantly reduce precipitation potential

SNDR after ATAD

- SNDR greatly improves dewatering of ATAD material
- Lowering P return to headworks begins to "cycle down" plant

SUMMARY

Phosphorus in Wastewater

- ► EBNR moves P from water effluent to bacteria
- ▶ P and micronutrients are released during digestion
- Increases in P result in decline in dewatering performance

AnAer Pilot Study

- Implements effect process control for anaerobic digestion
- Demonstrated significant reduction in material hauling
- Reduces precipitation potential

Targeted Phosphorus Recovery

- Conditioning material is critical to providing a "cleaner chemistry"
- "Target" P to remain soluble through dewatering
- Removes expensive standard coagulants
- Improves dewaterability of biosolids
- Multiple routes for recovering P after dewatering

WHAT'S NEXT?

AnAer

- Complete steady-state operation
- ► Install & operate on-site pilot
- Continue patent-approval process

Targeted Phosphorus Recovery

- Continue lab research to optimize current process
- ► Install & operate on-site pilot at ThermAer[™] facility
- Continue patent-approval process



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Thank you!

Questions/Comments?

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