The Leading Edge of Phosphorus Recovery: A Brushite Recovery Pilot

Menachem Tabanpour
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Overview

- Part I
  - Water treatment around the world
  - Our vision for plants of the future
  - Stages of technology development

- Part II
  - Background
  - Technical objectives
  - Trials
  - Results

- Conclusions
Water Treatment Around the World

According to UN Water “2.5 billion people still lack improved sanitation. 1.1 billion people still practice open defecation, that’s 15% of the world population”

Apart from sociopolitical factors, cost is a major inhibitor to maintaining water quality.

Water Treatment Costs:
• Capital costs
• O&M
• Capacity building
Lake Amatitlán, Guatemala
Circular Economy

Concentration
- Mining
- Agriculture

Product Creation
- Manufacturing
- Harvesting

Dissipation
- Refuse
- Water

Product Use
- Lifestyle
- Food

Upcycling
- Waste as a resource
- Nutrient recovery

Nutrient Recovery & Upcycling LLC
Phosphate Ore

Waste

Manufacturing

Food System

Nutrient Recovery & Upcycling LLC
Filling the Gap

**Concentration**
- Primary sludge
- EBNR
  - WAS
  - Acid digest

**Capture**
- Brushite precipitation
- Struvite precipitation

**Product creation**
- Fertilizers
- Industrial precursors

**Product Use**
- Food production
- Manufactured goods

**Dissipation**
- Flushwater
- Runoff
Technology Readiness & Maturity Levels

Research & Development
- 1 – Basic Principles
- 2 – Technology Concept
- 3 – Proof of Concept

Technology Demonstration
- 4 – Lab validation
- 5 – Field validation
- 6 – Prototype

Production & Deployment
- 7 – Real environment prototype
- 8 – Qualified & tested
- 9 – Operation

Scale to Fit
- M1 – Pilot demonstrations
- M2 – Installations
- M3 – Fully standardized
Struvite and Brushite

Struvite forms ~pH 8

\[ \text{NH}_4^+ + \text{Mg}^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{NH}_4\text{MgPO}_4\cdot6\text{H}_2\text{O} + \text{H}^+ \]

Brushite forms ~pH 4.5 – 6.5

\[ \text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{CaHPO}_4\cdot2\text{H}_2\text{O} + \text{H}^+ \]
Struvite

- The Barak Lab at UW-Madison was crystallizing struvite using monomolecular membranes in 2002.
- Later found that struvite was a nuisance and potentially a way to recover phosphorus at WWTPs.

Struvite formed with Langmuir monolayer
Struvite on copper substrate with self-assembling monolayer
Woodridge, IL – Greene Valley (WGV) WWTP
Multi-phase Anaerobic Digestion

Primary Sludge (after settling and grit removal)

Waste Activated Sludge (after biological nutrient removal)

Organic Acid Digester

Thermophilic Digester

Mesophilic Digester

Methane

Biosolids (for land application)

Separator (Centrifuge, gravity belt thickener)

Centrate/filtrate (recycled to headworks)

Solids

Liquor

Spent Liquor

Brushite Crystallization Reactor

Calcium Hydroxide

Brushite Product

Proposed Phosphorus Recovery & Upcycling

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MMSD Soluble Ions During Anaerobic Digestion

Sample from 8 Aug 2007

ppm

Acid
Thermo
Meso
GBT Filtrate

P
Ca
Mg
MMSD Potential for Mineral Formation

Mineral Saturation

Log Saturation Ratio

Brushite
Struvite

GT Primary WAS Acid Digest Thermo Meso GBT
Chemical Modeling of Brushite Precipitation

P Precipitation from Acid Digest

Sample from 22 Mar 2016

<table>
<thead>
<tr>
<th>Description</th>
<th>pH</th>
<th>Solids</th>
<th>Soluble P in OAD</th>
<th>Soluble Ca in OAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>OAD</td>
<td>5.01</td>
<td>4.3%</td>
<td>100%</td>
<td>58%</td>
</tr>
</tbody>
</table>
Forming Brushite

- Increase of pH to 6.5 with calcium hydroxide after acid digester
- Small pH manipulation precipitates 90% of the soluble phosphorus
- Increasing the pH beyond 6.5 is unnecessary and makes it more difficult to recover the brushite
NRU Phosphorus Recovery Process

ACID PHASE VFA PRODUCTION & P-RELEASE → CENTRIFUGE → PHOSPHORUS RECOVERY REACTOR → BRUSHITE STORAGE

Calcium → Low-Phosphorus Cake → Low-Phosphorus Liquid Stream → DRYING AND PACKAGING
# MMSD Batch Trials

<table>
<thead>
<tr>
<th>Trials</th>
<th>Acid Digest Composition</th>
<th>pH</th>
<th>Temp °C</th>
<th>% Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-5</td>
<td>Primary/WAS</td>
<td>5.7</td>
<td>35.6</td>
<td>4.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trials</th>
<th>Soluble P (ppm)</th>
<th>Total P (ppm)</th>
<th>Soluble P as % of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-5</td>
<td>1200</td>
<td>1600</td>
<td>75%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trials</th>
<th>Soluble P Centrate Pre Precipitation (ppm)</th>
<th>Soluble P Centrate Post Precipitation (ppm)</th>
<th>P Reduction in Centrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-5</td>
<td>837</td>
<td>126</td>
<td>83%</td>
</tr>
</tbody>
</table>
Serves 200,000
12 MGD plant
WAS only
No BNR
Etc.

Woodridge, IL – Greene Valley WWTP
<table>
<thead>
<tr>
<th>Date</th>
<th>Event Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sep 2014</td>
<td>Project initiation</td>
</tr>
<tr>
<td>Apr 2015</td>
<td>Finalized process design</td>
</tr>
<tr>
<td>Aug 2015</td>
<td>Finished construction and implementation</td>
</tr>
<tr>
<td>Sep 2015</td>
<td>Hosted WEFTEC 2015 Tour</td>
</tr>
<tr>
<td>Oct 2015</td>
<td>Sampled and optimized pilot</td>
</tr>
<tr>
<td>Nov 2015</td>
<td>Sampled pilot and hosted tours</td>
</tr>
<tr>
<td>Dec-Mar 2015</td>
<td>Winter storage and data analysis</td>
</tr>
<tr>
<td>Apr 2016</td>
<td>Pilot reassembly and optimization</td>
</tr>
</tbody>
</table>
NRU Phosphorus Recovery Process
# WGV Pilot Acid Digest Properties

<table>
<thead>
<tr>
<th>Trial</th>
<th>Soluble P Digest [ppm]</th>
<th>Soluble P as % of Total P</th>
<th>Reduction in Centrate Soluble P</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>451</td>
<td>33%</td>
<td>95%</td>
</tr>
<tr>
<td>3</td>
<td>424</td>
<td>35%</td>
<td>88%</td>
</tr>
<tr>
<td>4</td>
<td>414</td>
<td>30%</td>
<td>90%</td>
</tr>
<tr>
<td>5</td>
<td>467</td>
<td>31%</td>
<td>91%</td>
</tr>
<tr>
<td>6</td>
<td>525</td>
<td>34%</td>
<td>89%</td>
</tr>
<tr>
<td>8</td>
<td>403</td>
<td>43%</td>
<td>88%</td>
</tr>
<tr>
<td>9</td>
<td>485</td>
<td>44%</td>
<td>81%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trials</th>
<th>P</th>
<th>Ca</th>
<th>Mg</th>
<th>Ca:P Molar Ratio</th>
<th>Brushite</th>
<th>Struvite</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>16.7%</td>
<td>27.0%</td>
<td>0.20%</td>
<td>1.26</td>
<td>97.1%</td>
<td>1.6%</td>
<td>1.3%</td>
</tr>
</tbody>
</table>
P Recovery as Brushite Efficiency/Potential

- Operating efficiency during stage blue
- Percent of soluble P recovered during stage in white
- Total soluble P recovered in green

Acid Digest 100% Soluble P

Centrate 80/80%

Precipitation 90/72%

Supernatant 15%

Brushite Recovered 90/65%

Return 35%

Methane Digester
Key Advantages

- Acid digesters are effective tool for P-release
- P recovery from an optimized acid digester will lead to a higher percentage of the total P recovered
- The precipitation is more easily controlled
- The NRU P Recovery Process footprint is roughly two-thirds smaller than other processes
- We produce a high-grade fertilizer
Greenhouse Pot Study

Brushite was compared to MAP, DAP, TSP, Rock Phosphate, and Struvite

- Various application rates to a P-deficient soil
- Corn yield and P in above ground dry matter were measured
Fertilizer Comparison Statistical Analysis

Dry matter yield (g per pot)

- Control
- Struvite
- Brushite
- MAP
- DAP
- TSP

Treatments: A > AB > BC > B > C > D
Concentration
- WAS
- Acid digestion

Capture
- Brushite

Dissipation
- Food system

Product Use
- Agriculture

Product Creation
- Fertilizer

Upcycled P Economy
Acknowledgements

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