Separation of Ammonia and Phosphate Minerals from Wastewater using Gas-Permeable Membranes

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Florence, SC
Recent development at USDA of systems and methods to recover N, P and value-added materials from wastes

- 1. Improved ammonia recovery from liquid with gas-membranes
- 2. Simultaneous N and P recovery with membranes
- 3. Recovery of ammonia without chemicals
Escalating U.S. Fertilizer Costs

Why recover N?

Average Farm Price ($ ton⁻¹)

Year


Anhydrous Ammonia

Urea 44-46% Nitrogen

Energy and Agriculture

Fertilizers 28%

Diesel 27%

Electricity 21%

Gasoline 9%

Pesticides 6%

Natural Gas 4%

LP Gas 5%
Why recover phosphorus?

Cordell, D., et al., Chemosphere 84:747-758
North Carolina produces approximately 750 million chickens, 40 million turkeys, 3.5 billion table eggs, and 19 million hogs per year.

**Animal Manure – Surplus N & P, Ammonia emissions in areas of concentrated animal production**

**Surplus Phosphorus**

**Ammonia Emissions**

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**SURPLUS N**

Percent of Agronomic Crop and Forage Nitrogen Needs Supplied by Recoverable Plant Available Manure Nitrogen at the County Level in North Carolina

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Fig. 1. County scale NH₃ emission density for North Carolina along with measurement sites. Livestock activity data represent 2000 levels. All other activity data represent 1996 levels.

Walker et al., Atmos. Environ. 38:1235-1246
Value Chain without Solution

- Key Material
- Livestock
- Wastewater (Manure)
- Lagoons
  - Land Application
  - Hauling
The Technology

What do you do?

• Our technology simultaneously removes and recovers both nitrogen and phosphorus from manures and wastewaters.

Why do you do it?

• This creates value added products from wastes and helps society with a cleaner environment.
Value Chain with Solution

Key Material → Livestock

Key Material → Wastewater (Manure)

Key Material → Equipment

Key Material → Chemicals

Nitrogen Recovery Treatment

Phosphorus Recovery Treatment

Phosphorus Products

Nitrogen Products

Clean Water
Ecosystem Map With Solution

How your product interacts with the world once it is in the hands of the customer

Customers
- Swine
- Dairy
- Municipal Wastewater
- Aquaculture?

Nitrogen Product Manufacturer

Phosphorus Product Manufacturer

Service Providers

Suppliers
- Pumps
- Mixers
- Membrane modules

Equipment Manufacturers

Engineering Companies

Tourism Industry (fishing/recreation)

Clean Water

- Homeowner
- Farmers
- Greenhouse

Liquid N Fertilizer

Phosphorus Pellets

Animal Feed

Water Quality Nutrient Credits

Environmental Impact/Regulations
- Clean Water
- Reduced Emissions
New technology: Recovery of Ammonia from Manure

- Ammonia is separated using gas-permeable membranes
- Applications include liquid manures and air in livestock houses
- Product is liquid fertilizer with 50,000 to 100,000 ppm N
Recovery and Concentration of Ammonia

- Ammonia permeation through microporous, hydrophobic membranes
- Reduced ammonia emissions from livestock operations
- Product is ammonia solution with > 50,000 ppm N
Gas-permeable membranes

- **Medical uses:** Used in membrane oxygenators to imitate the function of the lungs in cardiopulmonary bypass, to add oxygen to, and to remove carbon dioxide from the blood (Gaylor, 1988).

- **Clothing & shoe industries:** Used to provide waterproof and breathable fabrics in sportswear and footwear (i.e. GORE-TEX® Products, 1968)
For this research we used gas-permeable membranes made of expanded polytetrafluoroethylene (ePTFE).

PTFE is stretched to form a strong, porous material.

Manufacture of Gas Permeable Membrane
Recovery of Ammonia from Liquid Manure with Gas-permeable Membranes

- Technology captures ammonia emissions
- Produces liquid fertilizer with > 50,000 ppm nitrogen

![Diagram of Anaerobic Digestion System]
WHAT IS INTENDED TO DO?

- Removal of ammonia gas from the liquid manures before it escapes into the air.

- Nitrogen is recovered from liquid manures in a concentrated, purified form.
Concept of Ammonia Capture from Wastewater using Gas Permeable Membrane

Dirty Liquid with Ammonia

Membrane Pores

Acidic Liquid

Tubular or Flat Membrane Manifold Submerged in the Wastewater

NH₃
H⁺ NH₄⁺
Gas-permeable membrane system:
The ammonia gas (NH₃) passes through

Liquid Manure

H⁺ + NH₃ → NH₃ + H⁺

Strip solution (Aqueous acid)

NH₄⁺

Gas-filled pore

Gas-permeable membrane system:
The ammonia gas (NH₃) passes through

Liquid Manure

H⁺ + NH₃ → NH₃ + H⁺

Strip solution (Aqueous acid)

NH₄⁺

Gas-filled pore

Polymer (e-PTFE)

Hydrophobic Polymer (e-PTFE)
Ammonia removal from animal waste using gas permeable membranes

Does it work?

**SWINE LAGOON**
302 mg NH₄-N/L, pH 8.3

Rate = 153 mg N/L/day

$R^2 = 0.998$
Retrofit of manure storage units to harvest the ammonia

Anaerobic Livestock Wastewater Lagoon with Ammonia Recovery System
Recovery and Concentration of Ammonia from Liquid Swine Manure using Gas Membranes (10 batches using same stripping solution)

Recovered NH$_4$-N was concentrated to 53,000 ppm
Microporous gas-permeable membrane: In tests, the soluble carbon did not pass through.

Synthetic Wastewater:
- Glucose (500 ppm COD)
- KHP (1000 ppm COD)

Strip solution (water):
- H$_2$O
- 0 ppm COD

Hydrophobic Polymer (e-PTFE)

Gas-filled pore
### Design Parameter: Effect of wastewater pH:

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Initial Source pH = 8.3</th>
<th>Initial Source pH = 10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass NH₄-N in Trap (mg)</td>
<td>NH₄-N Recovery from Source (%)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.86</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>2.44</td>
<td>2.7</td>
</tr>
<tr>
<td>3</td>
<td>3.72</td>
<td>4.1</td>
</tr>
<tr>
<td>4</td>
<td>4.77</td>
<td>5.3</td>
</tr>
<tr>
<td>5</td>
<td>5.39</td>
<td>6.0</td>
</tr>
</tbody>
</table>

N Recovery was ~ 1.2 % per hour at pH 8.3 and 13% per hour at pH 10 (increased 10 times)
Wastewater

\[ \text{H}_2\text{O} + \text{NH}_3 \]

\[ \text{NH}_4^+ + \text{OH}^- \]

Strip solution

(Aqueous acid)

\[ \text{NH}_3 + \text{H}^+ \]

\[ \text{NH}_4^+ \]

Gas-permeable membrane used for separation of free ammonia (\(\text{NH}_3\))

Hydrophobic Polymer (e-PTFE)

Gas-filled pore
## Design Parameter: Effect of waste strength

### Swine manure characteristics

<table>
<thead>
<tr>
<th>Manure strength</th>
<th>Swine Farm Type</th>
<th>pH</th>
<th>NH$_4$-N (mg/L)</th>
<th>TKN (mg/L)</th>
<th>EC (mS)</th>
<th>COD (mg/L)</th>
<th>TS (g/L)</th>
<th>VS (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>Piglet</td>
<td>8.64</td>
<td>1065</td>
<td>1345</td>
<td>8.470</td>
<td>4519</td>
<td>4.89</td>
<td>2.58</td>
</tr>
<tr>
<td>Medium</td>
<td>Farrow-finish w/ separation</td>
<td>7.57</td>
<td>1680</td>
<td>2743</td>
<td>14.080</td>
<td>24405</td>
<td>17.41</td>
<td>10.33</td>
</tr>
<tr>
<td>High</td>
<td>Finishing</td>
<td>7.52</td>
<td>2285</td>
<td>3699</td>
<td>16.980</td>
<td>34081</td>
<td>29.87</td>
<td>20.13</td>
</tr>
</tbody>
</table>
Ammonia recovery from livestock manure using gas-permeable membrane module and concentrator tank (Closed loop system).
Experimental device for ammonia capture from manure using gas-permeable membranes (closed loop).
Process pH adjusted with alkali (7.7 to 9)
Removal of ammonia in the manures and recovery in the acid tank

LOW STRENGTH

HIGH STRENGTH

MEDIUM STRENGTH
Ammonia recovery rate increases with manure strength

<table>
<thead>
<tr>
<th>Manure strength</th>
<th>Initial NH4 mg N/L</th>
<th>NH4 removed %</th>
<th>NH4 recovery %</th>
<th>NH4 recovery rate (mg/L/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>low</td>
<td>1385</td>
<td>94</td>
<td>87</td>
<td>74</td>
</tr>
<tr>
<td>medium</td>
<td>2184</td>
<td>90</td>
<td>90</td>
<td>92</td>
</tr>
<tr>
<td>high</td>
<td>2971</td>
<td>88</td>
<td>90</td>
<td>194</td>
</tr>
</tbody>
</table>

M.C. Garcia and M.B. Vanotti, Waste Management 2014 (in press)
Ammonia was removed but carbon (volatile solids) was not removed.

Technology can be combined with anaerobic digestion to recover both the ammonia and the energy from manure.
Ammonia Recovery System with Anaerobic Digestion

- Confined Livestock
  - Raw Waste
    - Ammonia Removal Unit with Membrane Manifold System before Anaerobic Digestion
    - Mixer
    - Membrane Manifold System
    - Stripping Acid Solution Tank / Reservoir
    - Recovered Ammonia
    - Raw Waste Stripped of Ammonia
  - Raw Waste
  - Anaerobic Digester without Inhibitory Ammonia
    - Biogas
    - Treated Effluent
The gas-permeable membrane method had very low energy demand

Energy consumption of ammonia recovery methods (manure) kWh/m³ feed

NF = nanofiltration
RO = reverse osmosis
GPM = gas permeable memb.
AS = air stripping
IE = ion exchange/ zeolites
CP = Chemical precipitation
The gas-permeable membrane method (MD) had high chemical demand (NaOH to increase pH)

Chemical cost ($/m^3 feed)

NF = nanofiltration
RO = reverse osmosis
GPM = gas permeable memb.
AS = air stripping
IE = ion exchange/zéolites
CP = Chemical precipitation

Two ways can be used to increase manure pH and N recovery efficiency by the gas-permeable membrane system:

1. Add alkali chemicals (OH⁻)

2. Low-rate aeration

\[
\text{HCO}_3^- + \text{air} \rightarrow \text{OH}^- + \text{CO}_2 \\
\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}
\]
Two ways can be used to increase manure pH and N recovery efficiency by the gas-permeable membrane system:

1. Add alkali chemicals (OH⁻)

2. Low-rate aeration

\[ \text{HCO}_3^- + \text{air} \rightarrow \text{OH}^- + \text{CO}_2 \]

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]

- Aeration increases manure pH about 1 unit
- The aeration rate must be low to inhibit nitrification
- Nitrification inhibitor can be used (< 10 ppm)

Vanotti and Szogi. US 9,005,333
Recovery of Ammonia from Liquid Manure with Gas-permeable Membranes

- Technology recovers ammonia from liquid manure
- Produces liquid fertilizer with > 50,000 ppm nitrogen
Experimental device for ammonia capture from manure using gas-permeable membranes (closed loop).
N recovery: Effect of low-rate aeration
Covered lagoon effluent, North Carolina

Liquid with 2,100 mg/L NH4-N
Ammonia (NH3) recovery gas-permeable membrane system

- Raw Manure
- Anaerobic Digester
- Digested Effluent
- Low Aeration

- Pump
- Concentrator Tank
- pH

- Gas-permeable Membrane Module
- Recovered Ammonia
Changes in ammonia concentration in manure and the N recovery tank

Covered anaerobic lagoon effluent, NC
### Mass Balances of the Recovery of Ammonia - anaerobic digester effluent

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Initial NH₄⁺ in Manure</th>
<th>Remaining NH₄⁺ in Manure</th>
<th>NH₄⁺ removed from Manure</th>
<th>NH₄⁺ recovered in acidic solution</th>
<th>NH₄⁺ removal efficiency</th>
<th>NH₄⁺ recovery efficiency</th>
<th>NH₄⁺ Volatilized in air</th>
</tr>
</thead>
<tbody>
<tr>
<td>(days)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerated</td>
<td>5</td>
<td>3133 (151)</td>
<td>96 (29)</td>
<td>3037</td>
<td>2979 (2)</td>
<td>97</td>
<td>98</td>
</tr>
<tr>
<td>Non Aerated</td>
<td>25</td>
<td>3157 (132)</td>
<td>71 (19)</td>
<td>3086</td>
<td>2936 (40)</td>
<td>98</td>
<td>95</td>
</tr>
</tbody>
</table>
Significant cost reductions can be achieved with new concepts and research.

Operational cost of NH$_3$ recovery using gas-permeable membranes ($/4000$ pigs/year)
Changes in pH and alkalinity of manure during N recovery process

Covered anaerobic lagoon effluent, NC

![Graph showing pH and alkalinity changes over time for different farms and aerated conditions.]

- **pH**
  - Farm 1 Aerated
  - Farm 1 Non Aerated
  - Farm 2 Aerated
  - Farm 2 Non Aerated

- **Alkalinity (mg CaCO₃/L)**
  - Farm 1 Aerated
  - Farm 1 Non Aerated
  - Farm 2 Aerated
  - Farm 2 Non Aerated
Key finding

• The process removes ammonia and alkalinity and increases pH.

• These are **ideal conditions** for phosphorus precipitation and recovery.
Recovery of ammonia and phosphorus from animal manure

Influent P concentration: 150-200 mg/L
Influent N concentration: 1500-2000 mg/L

For Mg phosphates, two potential forms that can precipitate in liquid systems that contain \( \text{Mg}^{2+} - \text{NH}_4^+ - \text{PO}_4^{3-} \) and a high Mg/Ca ratio are struvite and newberyite (Boistelle et al., 1983; Abbona et al., 1988; Muster et al., 2013).

**Struvite**
\[
\text{Mg}^{2+} + \text{H}_2\text{PO}_4^- + \text{NH}_3 \rightarrow \text{MgNH}_4\text{PO}_4 + \text{H}^+
\]

**Newberyite**
\[
\text{Mg}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{MgHPO}_4 + \text{H}^+
\]
Digester Effluent

\[ \text{MgCl}_2 \]

\[ \text{NH}_4^+ \rightarrow \text{NH}_3 \]

\[ \text{HCO}_3^- \rightarrow \text{OH}^- \]

\[ \text{Mg}^{2+} \]

\[ \text{PO}_4^{3-} \]

\[ \text{NH}_4^+ \]

Gas-permeable membrane

Hydrophobic polymer

Gas-filled pore

Strip Solution (H+)

\[ \text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+ \]

\[ \text{MgHPO}_4 \rightarrow \text{MgNH}_4\text{PO}_4 \]

Recovered phosphate solids

Low rate aeration

Recovered ammonium salts
Nitrogen and Phosphorus Recovery Configuration 2: MgCl2 added to N reactor (no alkali added)

Influent P = 446 mg/L
Influent pH = 8.4
pH after aeration = 9.5
N recovery = 91%
P recovery = 100%
## Configuration 2 with MgCl2 added (without NaOH)

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Concentrations</th>
<th>MASS BALANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Influent Concentration</td>
<td>Effluent Concentration</td>
</tr>
<tr>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td>N</td>
<td>2354</td>
<td>69.2</td>
</tr>
<tr>
<td>P</td>
<td>446</td>
<td>23.5</td>
</tr>
</tbody>
</table>
## Configuration 2 with MgCl2 added (without NaOH)

### Concentrations

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Influent Concentration</th>
<th>Effluent Concentration</th>
<th>Initial Manure</th>
<th>Recovered Solid</th>
<th>Recovered by Membrane</th>
<th>Effluent</th>
<th>Total Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2354</td>
<td>69.2</td>
<td>100%</td>
<td>7.7%</td>
<td>83.1%</td>
<td>2.9%</td>
<td>90.5%</td>
</tr>
<tr>
<td>P</td>
<td>446</td>
<td>23.5</td>
<td>100%</td>
<td>104.3%</td>
<td>0%</td>
<td>5.3%</td>
<td>104.3%</td>
</tr>
</tbody>
</table>

### Composition of Recovered Solid

<table>
<thead>
<tr>
<th>N</th>
<th>P₂O₅</th>
<th>Mg</th>
<th>Ca</th>
<th>K</th>
<th>Plant Available P (Citrate soluble)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentages, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>26.4</td>
<td>10.0</td>
<td>2.0</td>
<td>1.7</td>
<td>99.00</td>
</tr>
</tbody>
</table>

Struvite = 5.7 N : 29 P₂O₅ : 10 Mg
Configuration 2
16.45 mmol / L MgCl₂
Mg:P = 1.2:1
0 mmol / L NaOH

Influent
N = 2354 mg (100.0 %)
P = 446 mg (100.0 %)

Nutrient Recovery System

Recovered by Membrane
N = 1949 mg (82.8 %)
P = 0 mg (0.0 %)

Recovered Solid
N = 184 mg (7.8 %)
P = 472 mg (105.9 %)

Effluent
N = 69 mg (2.9 %)
P = 24 mg (5.4 %)
Nitrogen and Phosphorus Recovery Configuration 1: MgCl2 added after N removal (no alkali added)

Influent P = 446 mg/L
Influent pH = 8.4
pH effluent after N recovery = 9.3
P recovery = 93.2%

Recovered Phosphates (Configuration 1)

- P recovered as **High-Grade Magnesium Phosphate**
- 99.7% plant available (standard citrate test)

### Chemical Composition

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_2$O$_5$</td>
<td>46.4%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>17.1%</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.4 %</td>
</tr>
<tr>
<td>Potassium</td>
<td>1.7 %</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.8 %</td>
</tr>
</tbody>
</table>

Newberyite (MgHPO$_4$.3H$_2$O): 41% P$_2$O$_5$ and 14% Mg

**Triple superphosphate** = 46% P$_2$O$_5$; **Rock phosphate** = 27-36% P$_2$O$_5$
## Configuration 1 with Municipal Side Stream Wastewater (after AD of sludges)

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Influent Concentration</th>
<th>Effluent Concentration</th>
<th>Initial Manure</th>
<th>Recovered Solid</th>
<th>Recovered by Membrane</th>
<th>Effluent</th>
<th>Total Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>731 mg/L</td>
<td>123 mg/L</td>
<td>100%</td>
<td>2.4%</td>
<td>90.5%</td>
<td>16.7%</td>
<td>92.3%</td>
</tr>
<tr>
<td>P</td>
<td>147 mg/L</td>
<td>6 mg/L</td>
<td>100%</td>
<td>79.2%</td>
<td>0%</td>
<td>4.1%</td>
<td>79.2%</td>
</tr>
</tbody>
</table>
Results obtained were consistent using *swine* and municipal *side-stream* digester effluents.

Composition similar to rare bio-mineral NEWBERYITE that is found in guano deposits.

| Composition of Recovered Phosphate Minerals *(Swine Effluent)* |
|---------------|---|---|---|---|---|
| N | P$_2$O$_5$ | Mg | Ca | K | Plant Available P |
| 1.8 | 46.4 | 17.1 | 0.4 | 1.8 | 99.7 |

| Composition of Recovered Phosphate Minerals *(Municipal Centrate)* |
|---------------|---|---|---|---|---|
| N | P$_2$O$_5$ | Mg | Ca | K | Plant Available P |
| 2.8 | 44.1 | 13.6 | 0.9 | 0.7 | 98.5 |

**Triple superphosphate = 46% P$_2$O$_5$; Rock phosphate = 27-36% P2O5**

Struvite = 5.7 N : 29 P$_2$O$_5$ : 10 Mg  
Newberyite 41 P$_2$O$_5$ : 14 Mg
Municipal Contrate P precipitate

$\text{MgCl}_2 + \text{NaOH}$

without $\text{NH}_3$ | with $\text{NH}_3$
Ecosystem Cost Map

5200-head swine farm (finishing)

N and P removal technology

- Manure
- Power
- Equipment
- Chemical
- Treated Wastewater

Recovered N
Recovered P
N Nutrient Credits
P Nutrient Credits

Capital and Operational Costs

<table>
<thead>
<tr>
<th>Cost Item</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment, Chemical, Power</td>
<td>$57,168.47</td>
</tr>
</tbody>
</table>

Potential Revenue

<table>
<thead>
<tr>
<th>Revenue Item</th>
<th>Revenue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sale of fertilizer products (N &amp; P)</td>
<td>$58,538.63</td>
</tr>
<tr>
<td>Additional Revenue: Sale of Non-point Nutrient Credits (2:1 trading ratio)</td>
<td>$ 61,449.93</td>
</tr>
</tbody>
</table>
Conclusions

• Phosphorus recovery was combined with ammonia recovery using gas-permeable membranes

• Aeration destroyed carbonates, increased pH, and enhanced N capture

• The process provided approximately 100% phosphorus recovery efficiencies

• With substantial ammonia capture, the recovered P contained very-high phosphate grade (biomineral newberyite)