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

WRRI Water Sustainability Through Nanotechnology Symposium
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United States Department of Agriculture, ARS
Florence, SC

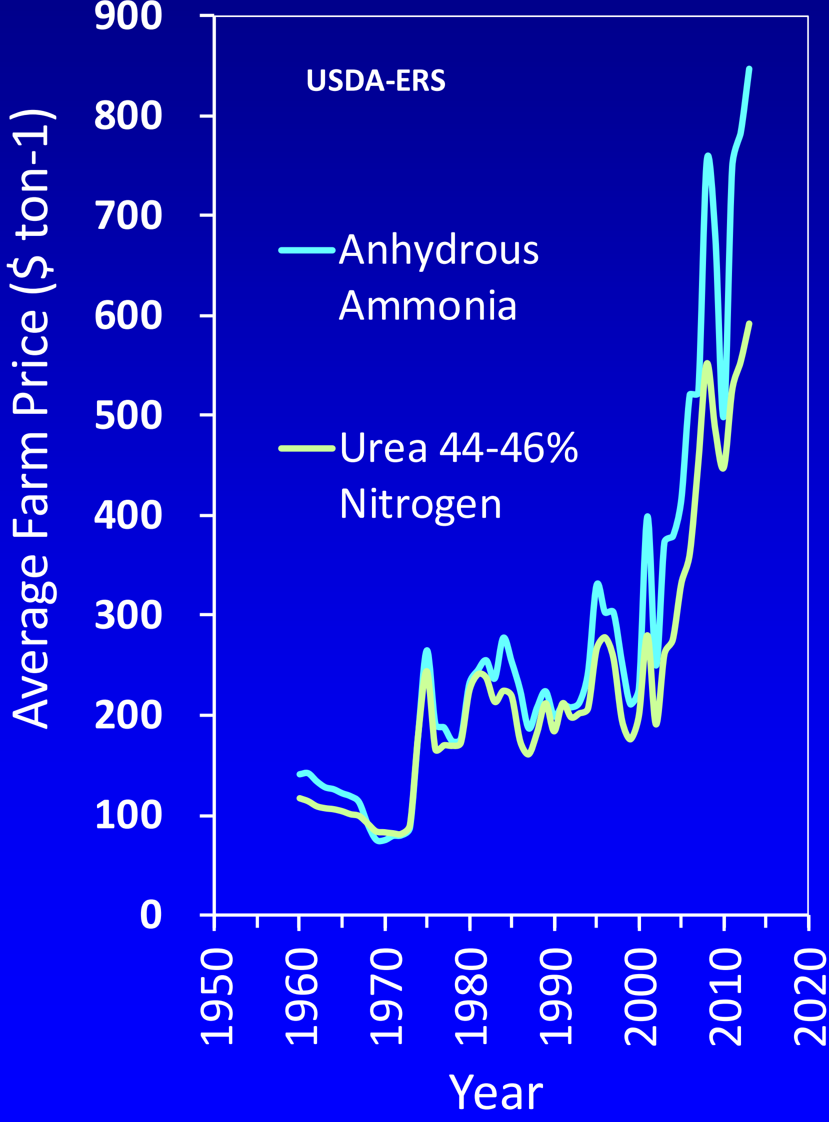
Presentation outline

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

Why recover N?

Escalating U.S. Fertilizer Costs



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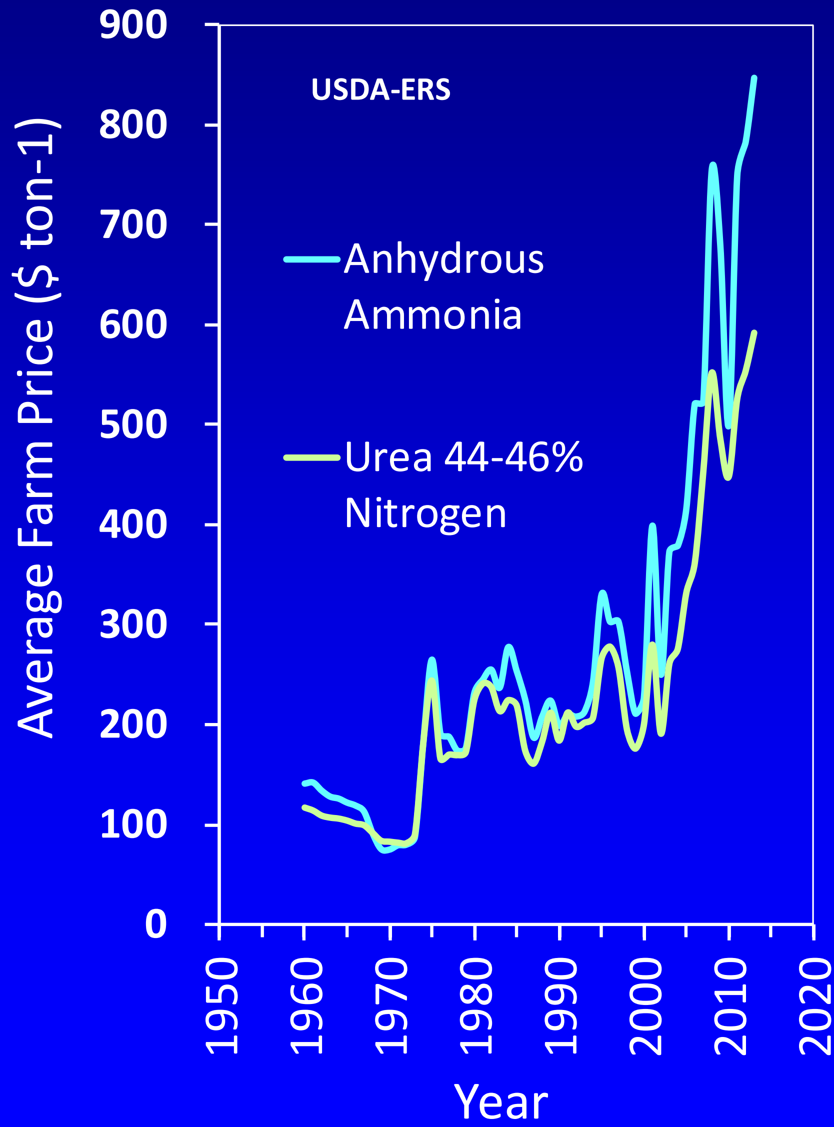
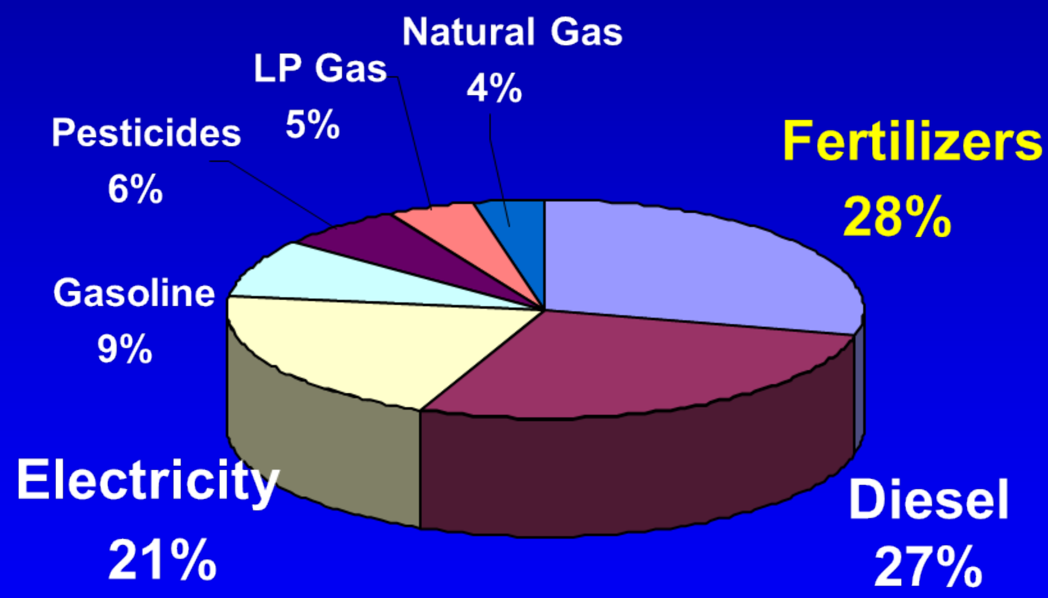
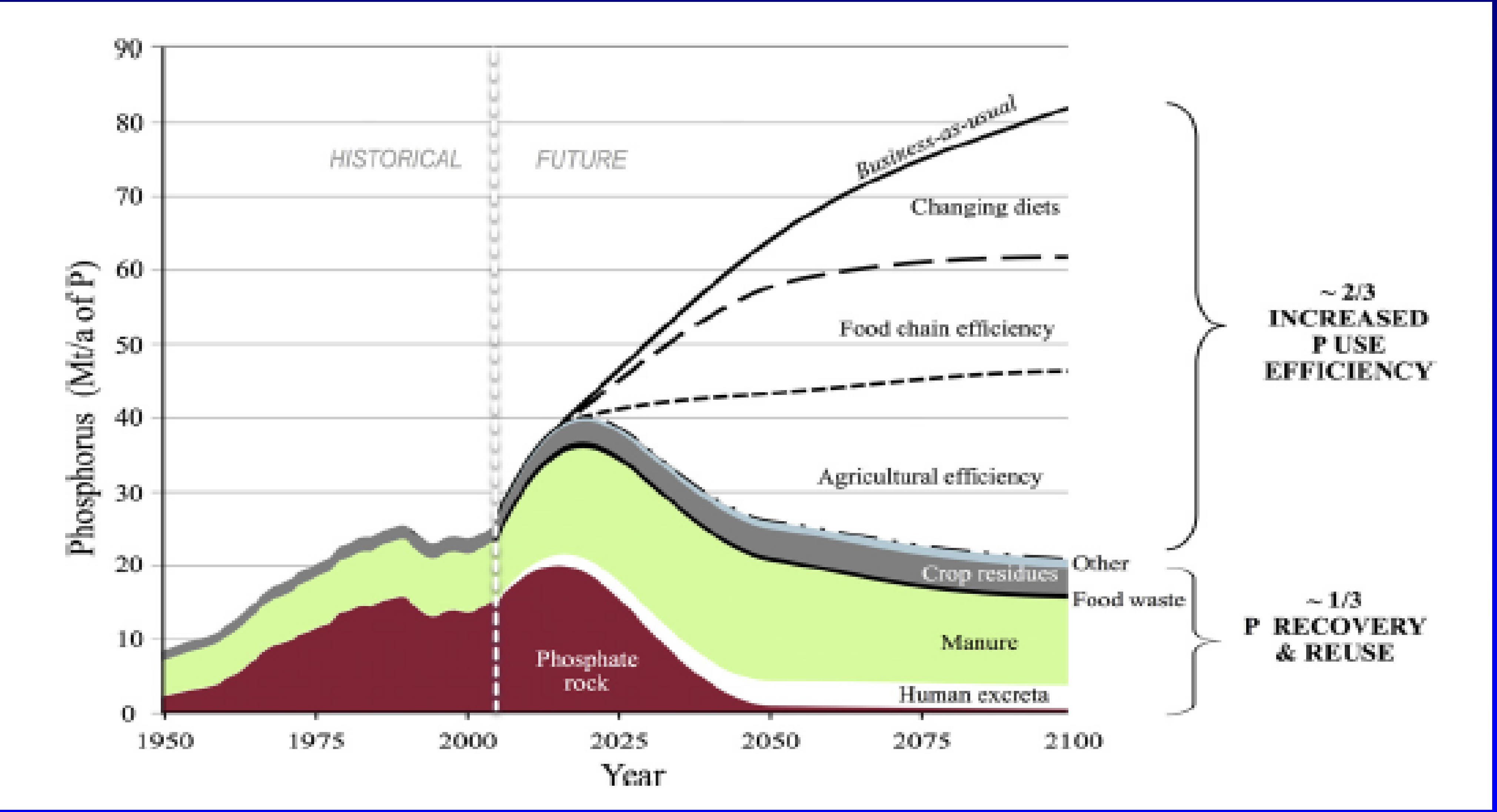


Energy and Agriculture

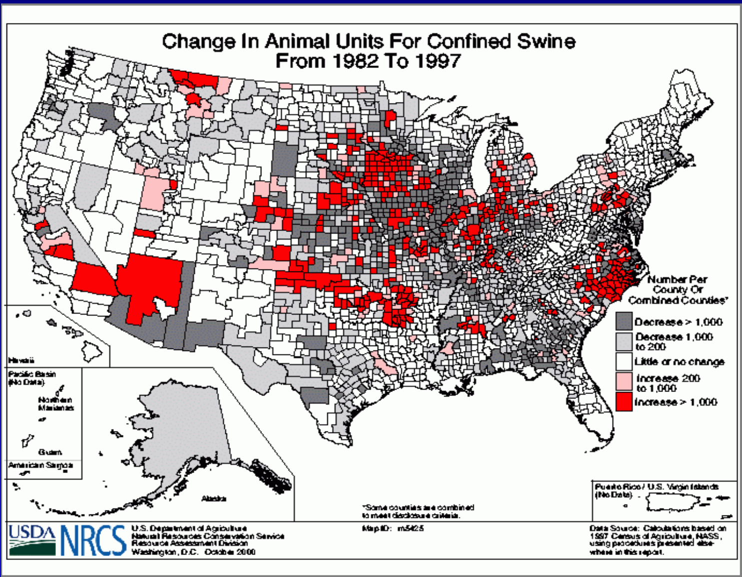


Why recover phosphorus?



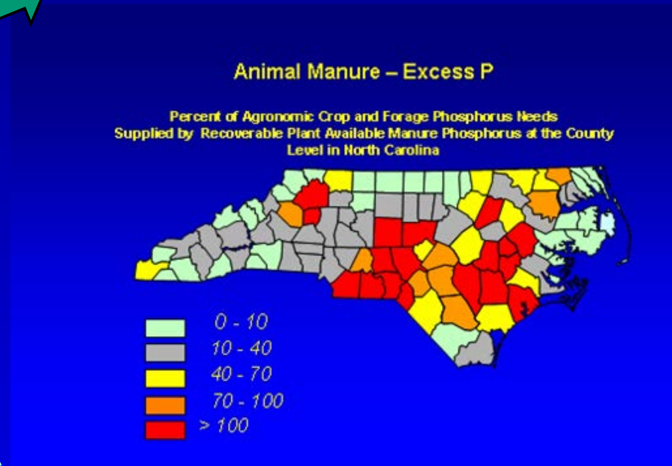
Cordell, D., et al., Chemosphere 84:747-758

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

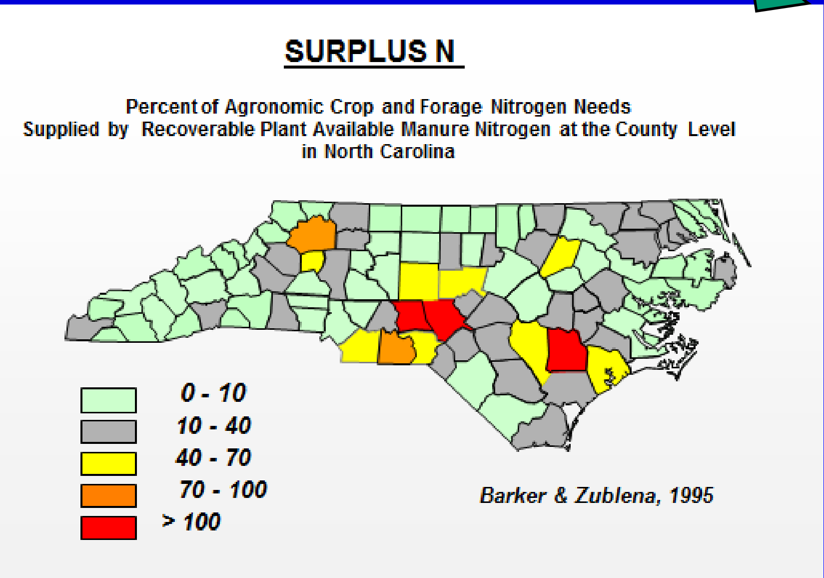


North Carolina produces approximately 750 million chickens, 40 million turkeys, 3.5 billion table eggs, and 19 million hogs per year.

Surplus Phosphorus



Ammonia Emissions



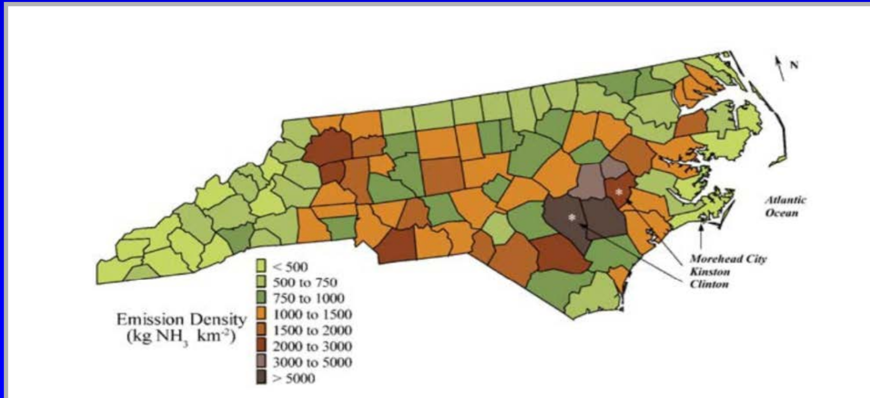
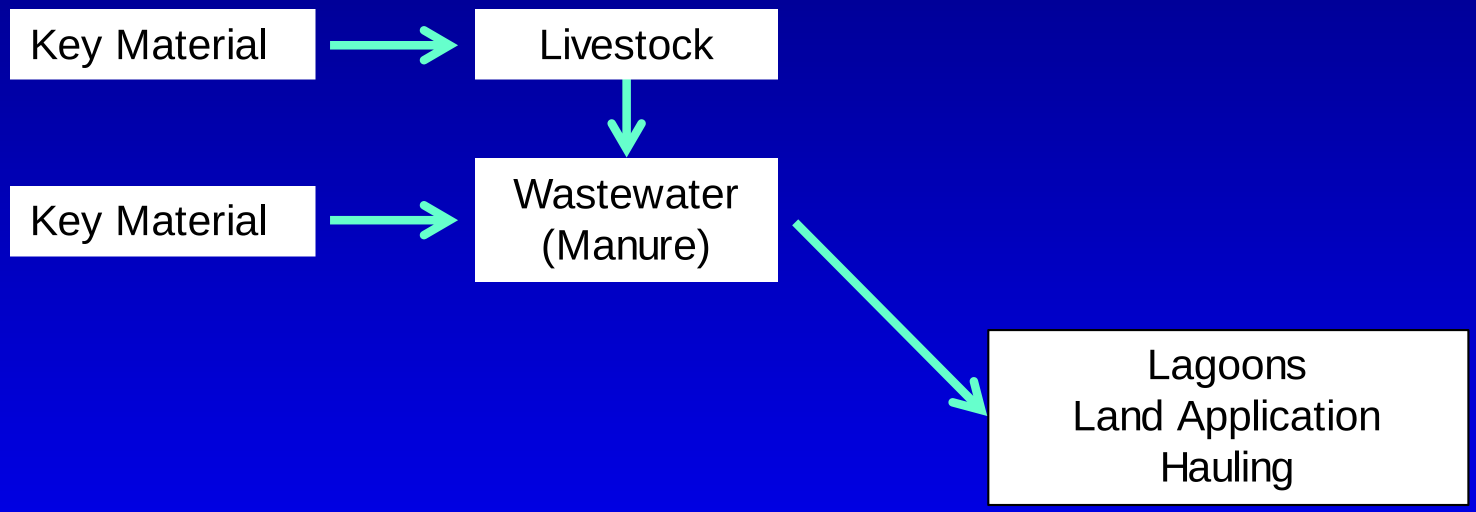


Fig. 1. County scale NH_3 emission density for North Carolina along with measurement sites. Livestock activity data represent 2000 levels. All other activity data represent 1996 levels.

Walker et al., Atmos. Environ. 38:1235-1246

Value Chain without Solution



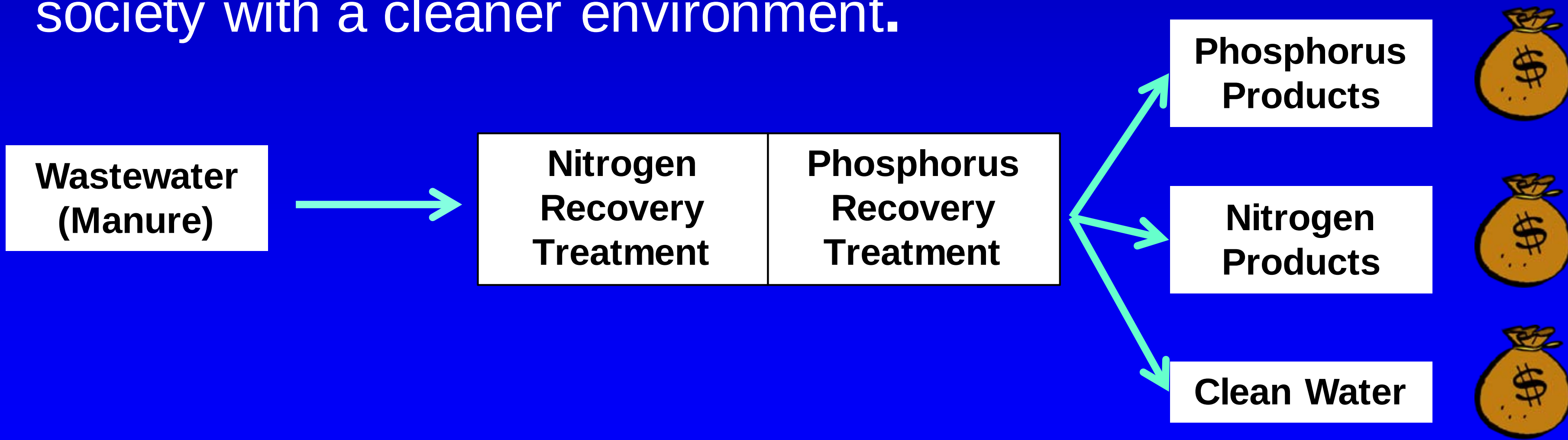
The Technology

What do you do?

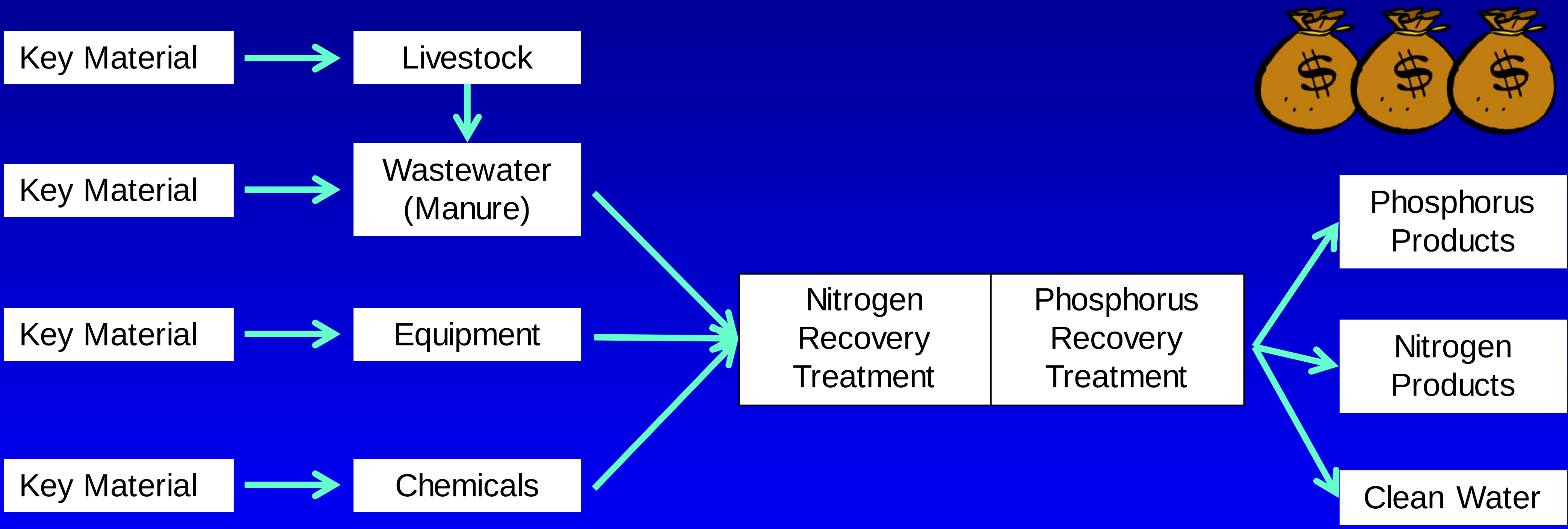
- Our technology simultaneously removes and recovers both nitrogen and phosphorus from manures and wastewaters.

Why do you do it?

- This creates value added products from wastes and helps society with a cleaner environment.

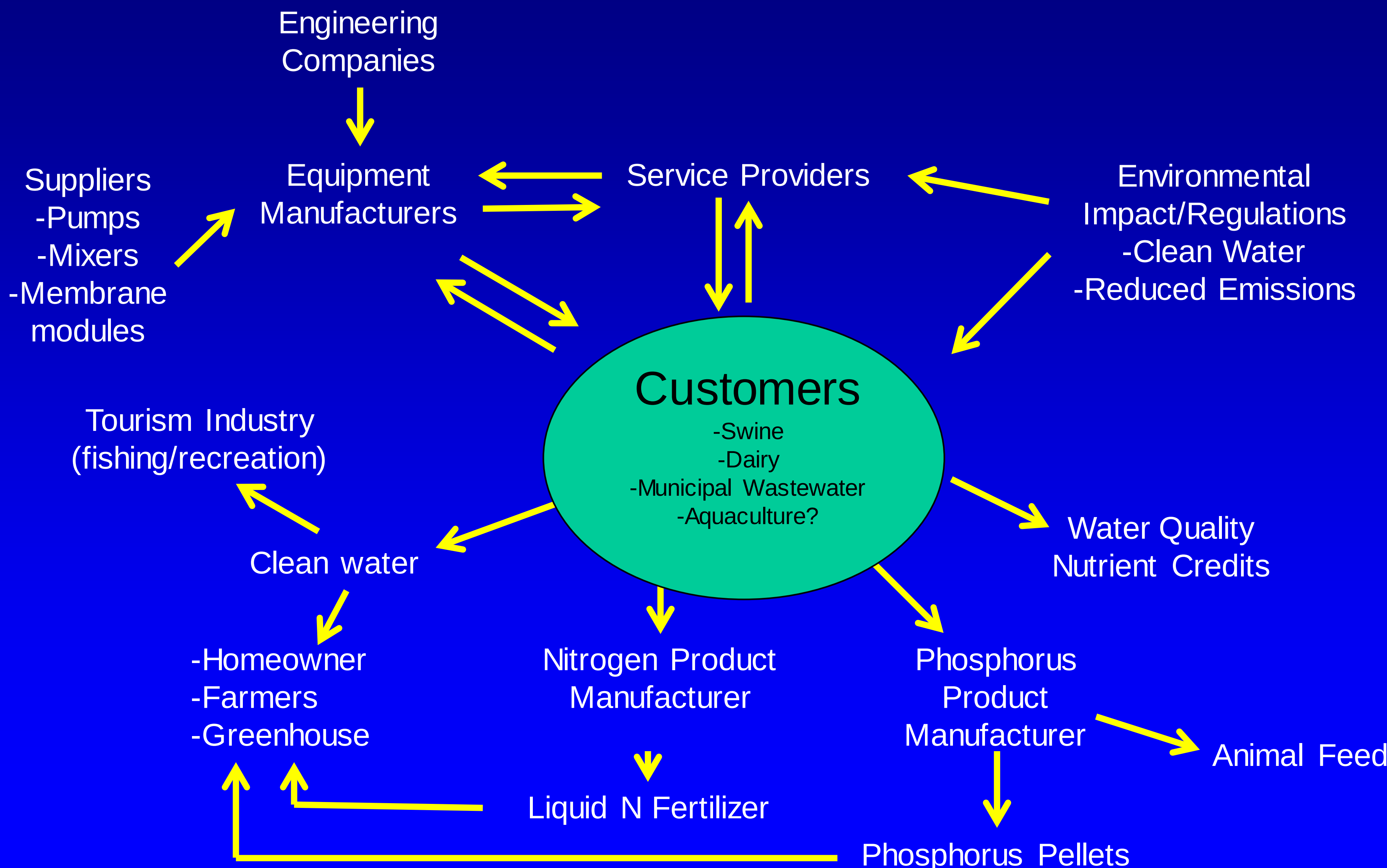


Value Chain with Solution

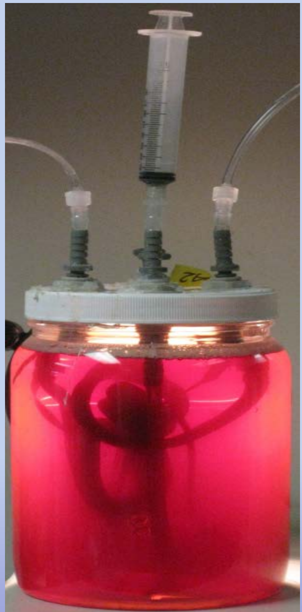


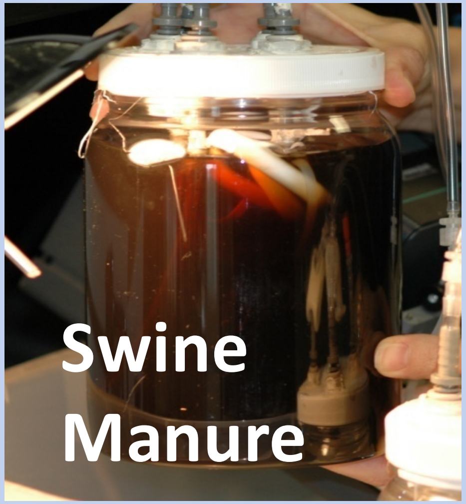
Ecosystem Map With Solution

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



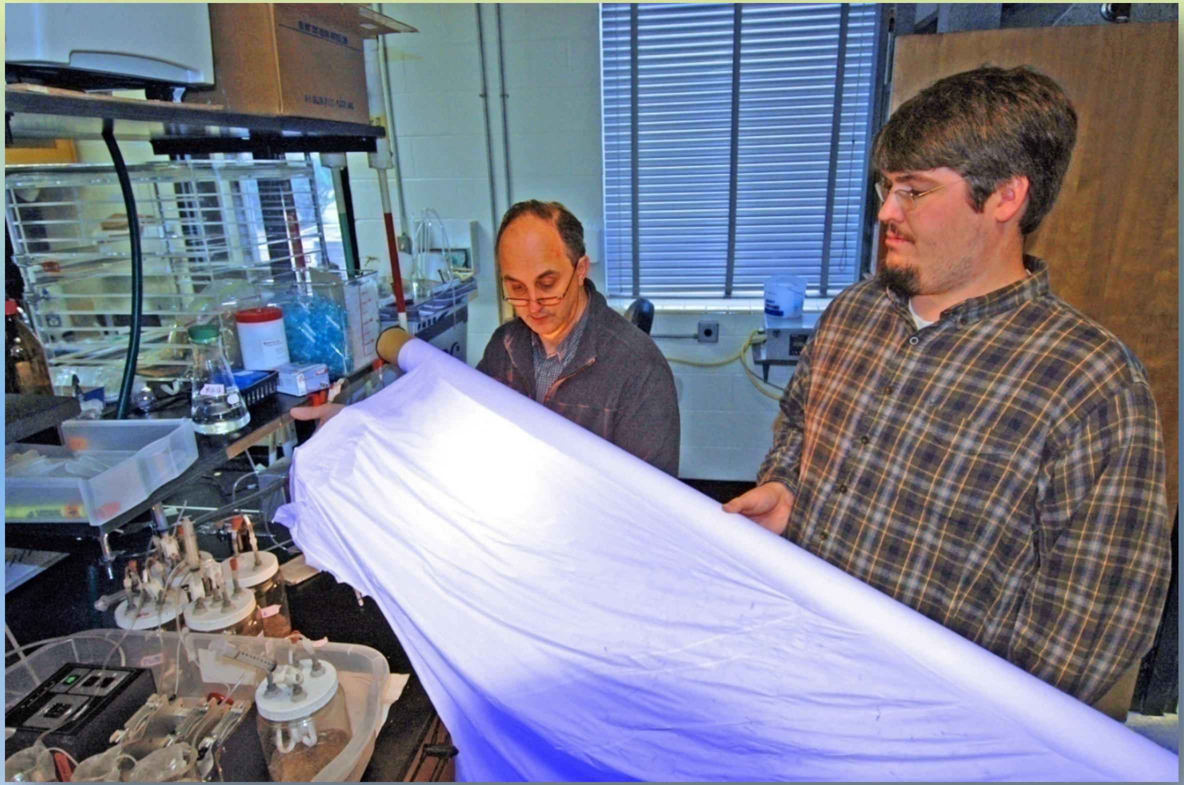
New technology: Recovery of Ammonia from Manure

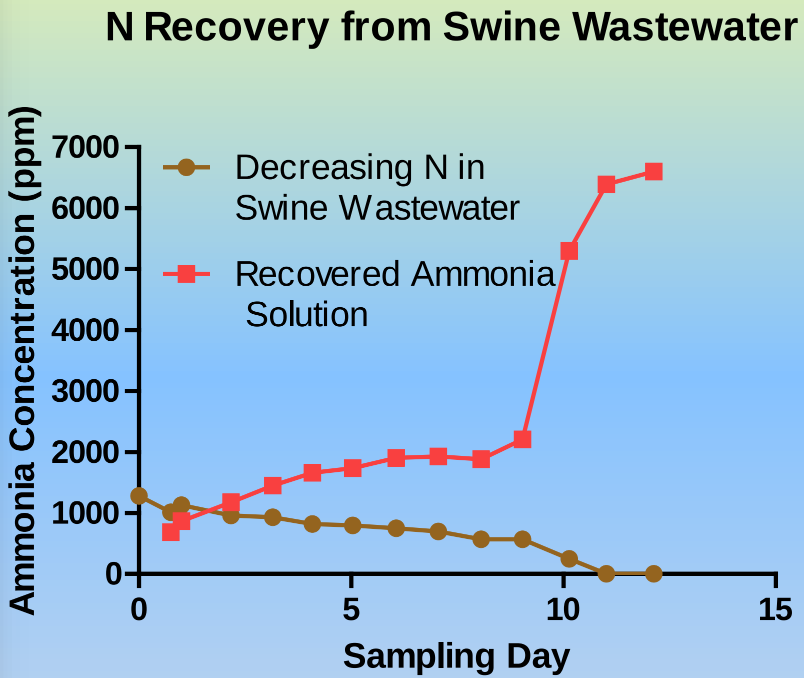




- ❑ Ammonia is separated using gas-permeable membranes
- ❑ Applications include <u>liquid</u> manures and <u>air</u> in livestock houses
- ❑ Product is liquid fertilizer with 50,000 to 100,000 ppm N

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

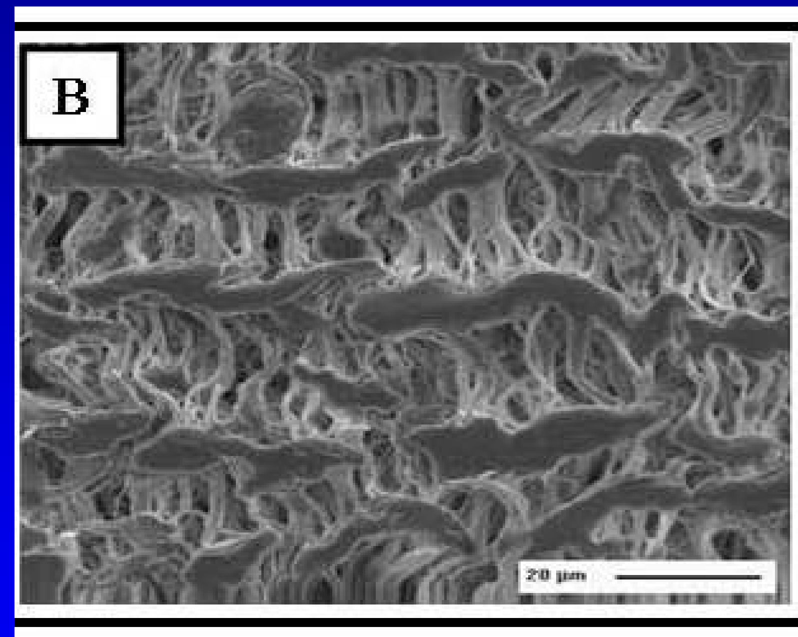
- **Medical uses:** Used in membrane oxygenators to imitate the function of the lungs in cardiopulmonary bypass, to add oxygen to, and to remove carbon dioxide from the blood (Gaylor, 1988).

- **Clothing & shoe industries:** Used to provide waterproof and breathable fabrics in sportswear and footware (i.e. *GORE-TEX® Products, 1968)*

For this research we used gas-permeable membranes made of <u>expanded</u> polytetrafluoroethylene (ePTFE)

PTFE is stretched to form a strong, porous material

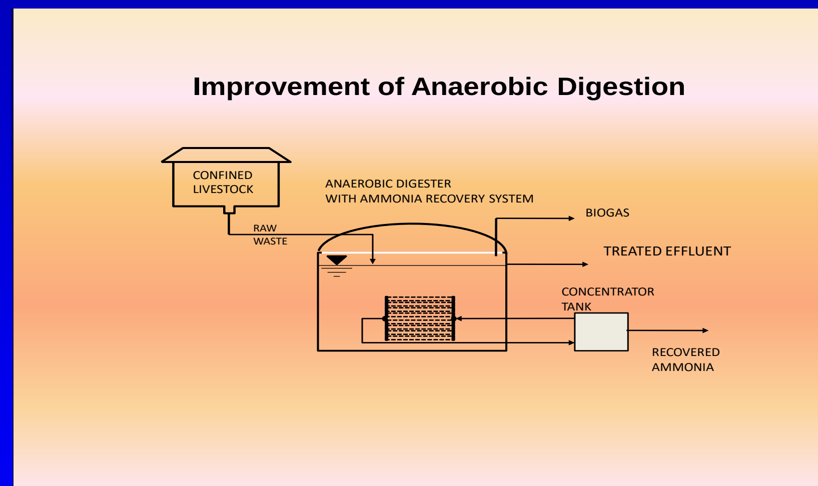
Manufacture of Gas Permeable Membrane

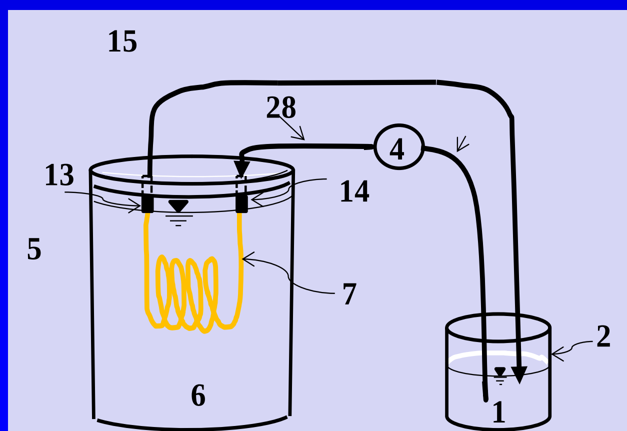


Gas Permeable Membrane
Microscopic structure (SEM)

Recovery of Ammonia from Liquid Manure with Gas-permeable Membranes

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

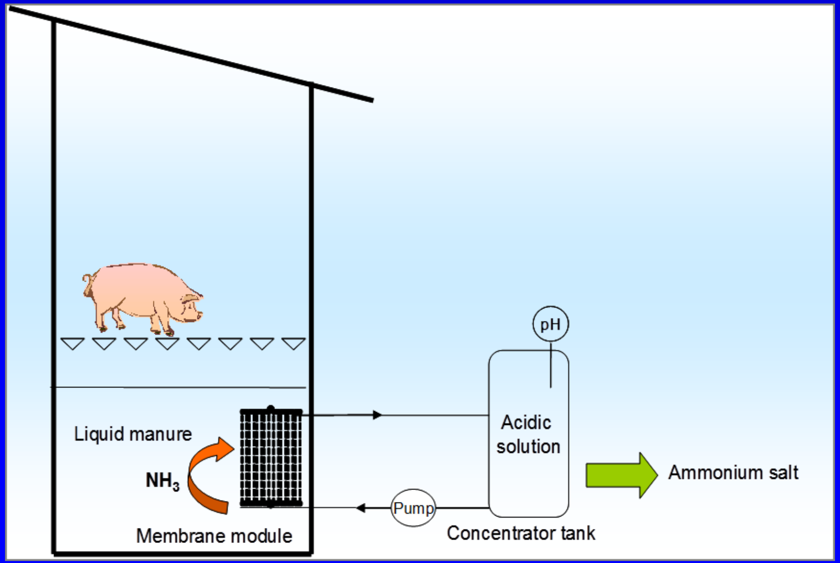




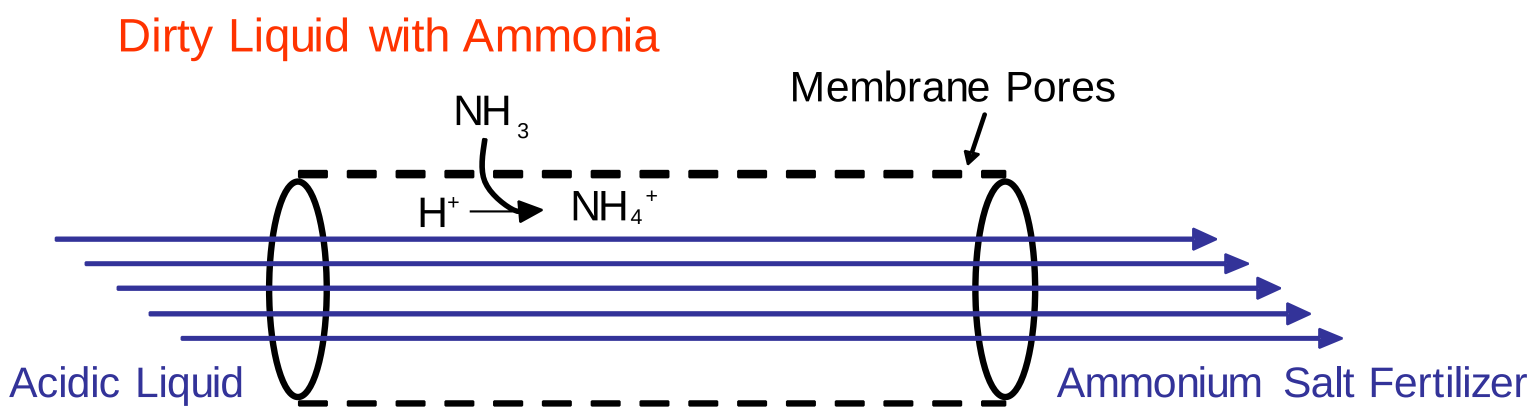
WHAT IS INTENDED TO DO?

- 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



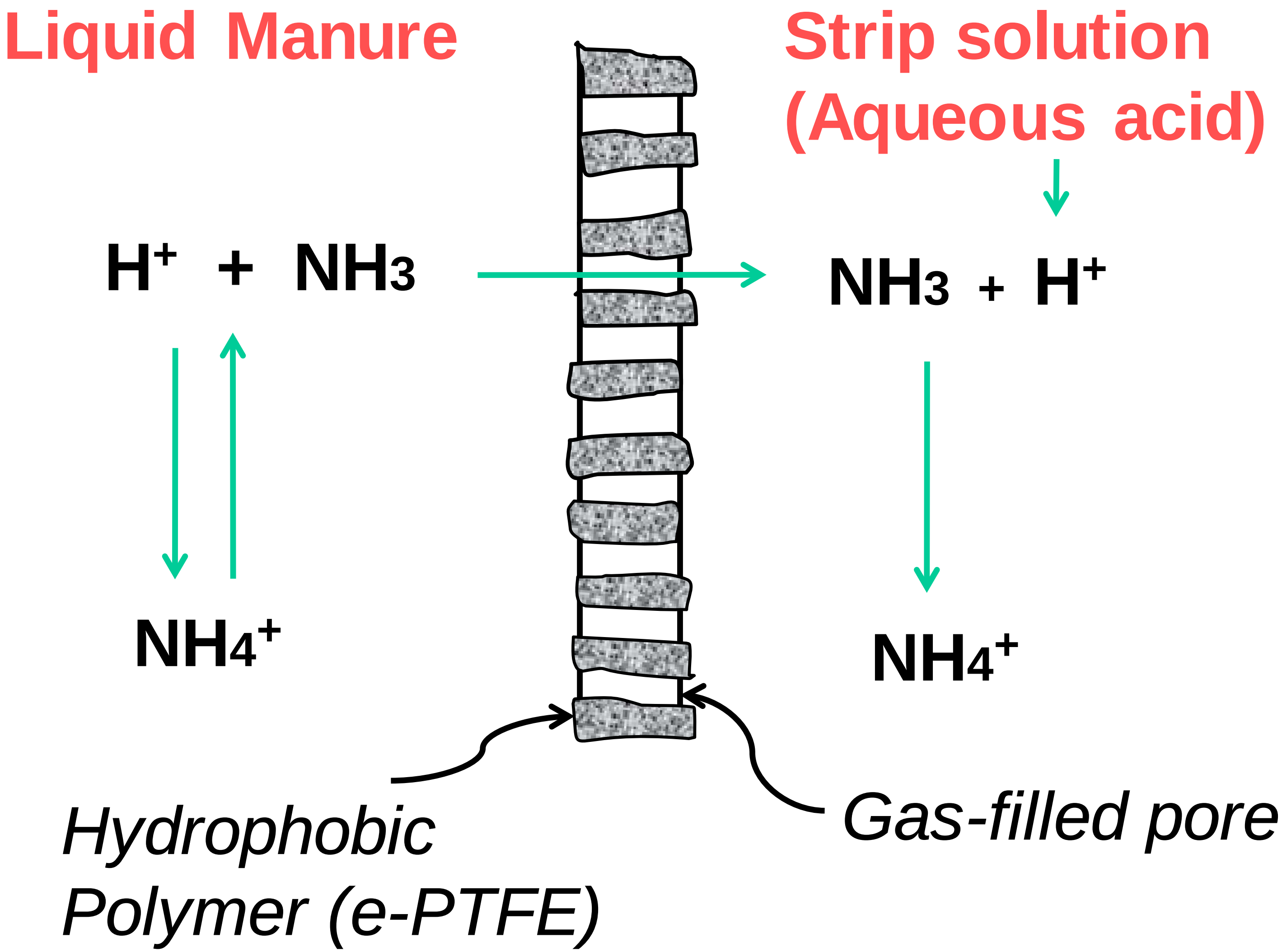
Concept of Ammonia Capture from Wastewater using Gas Permeable Membrane



Tubular or Flat Membrane Manifold Submerged in the Wastewater

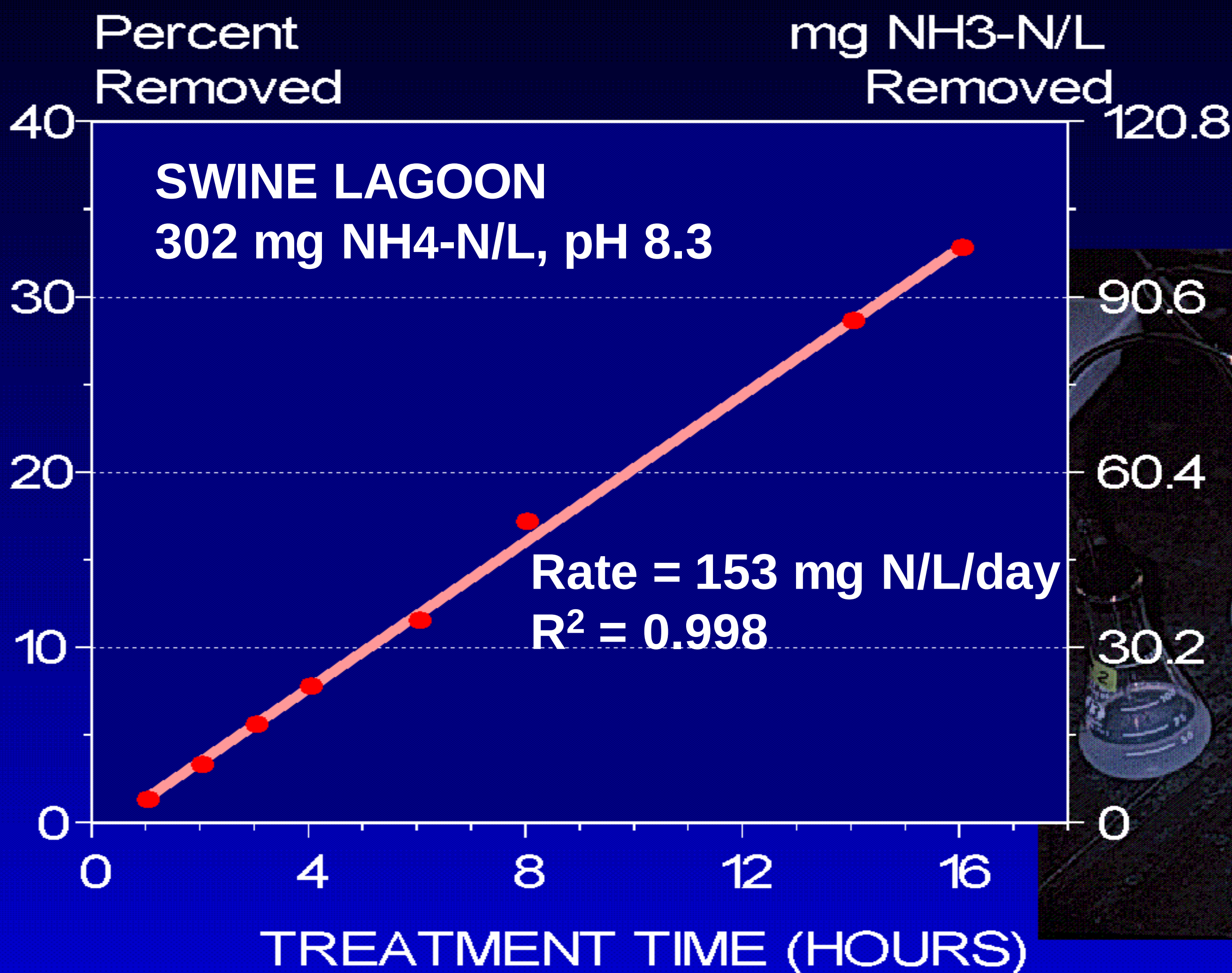
Gas-permeable membrane system:

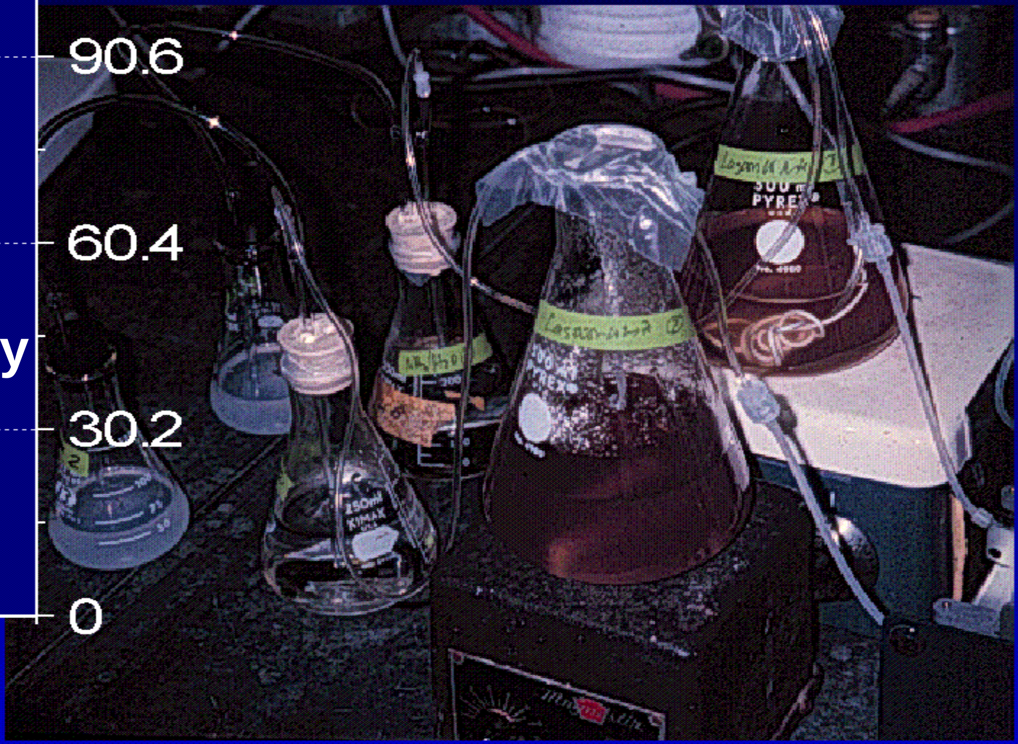
The ammonia gas (NH3) passes through



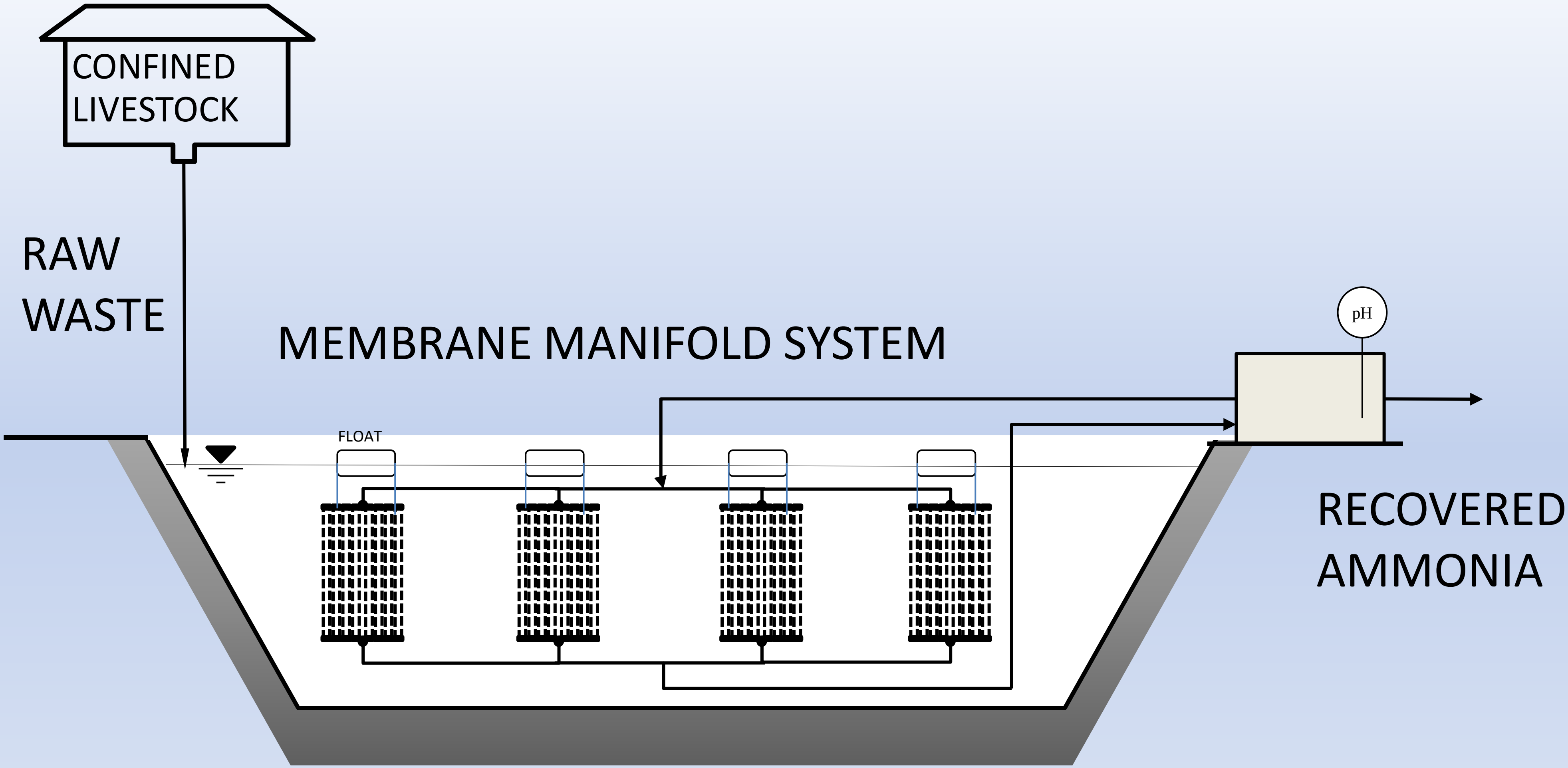
Does it work?

Ammonia removal from animal waste using gas permeable membranes



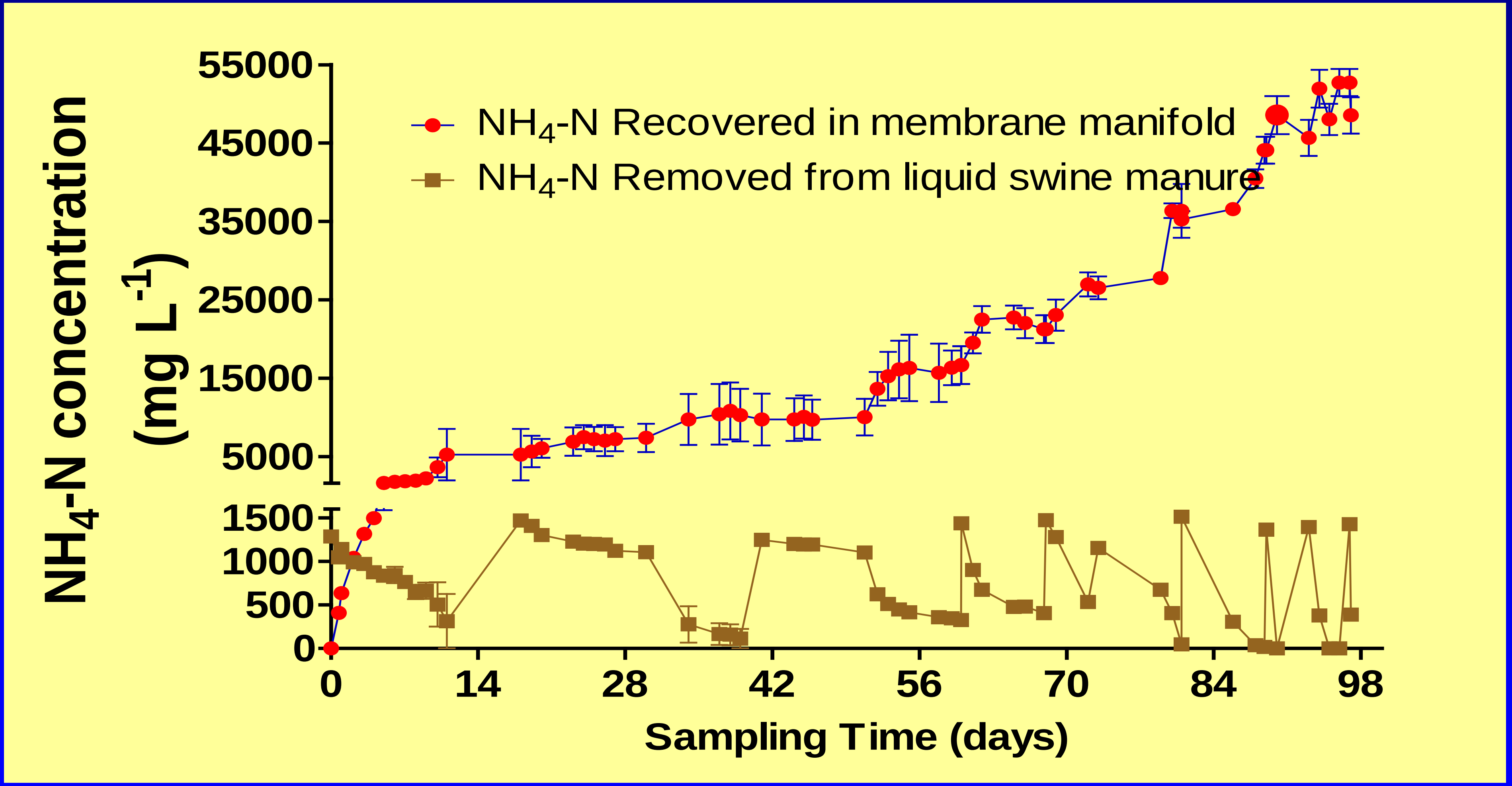


Retrofit of manure storage units to harvest the ammonia



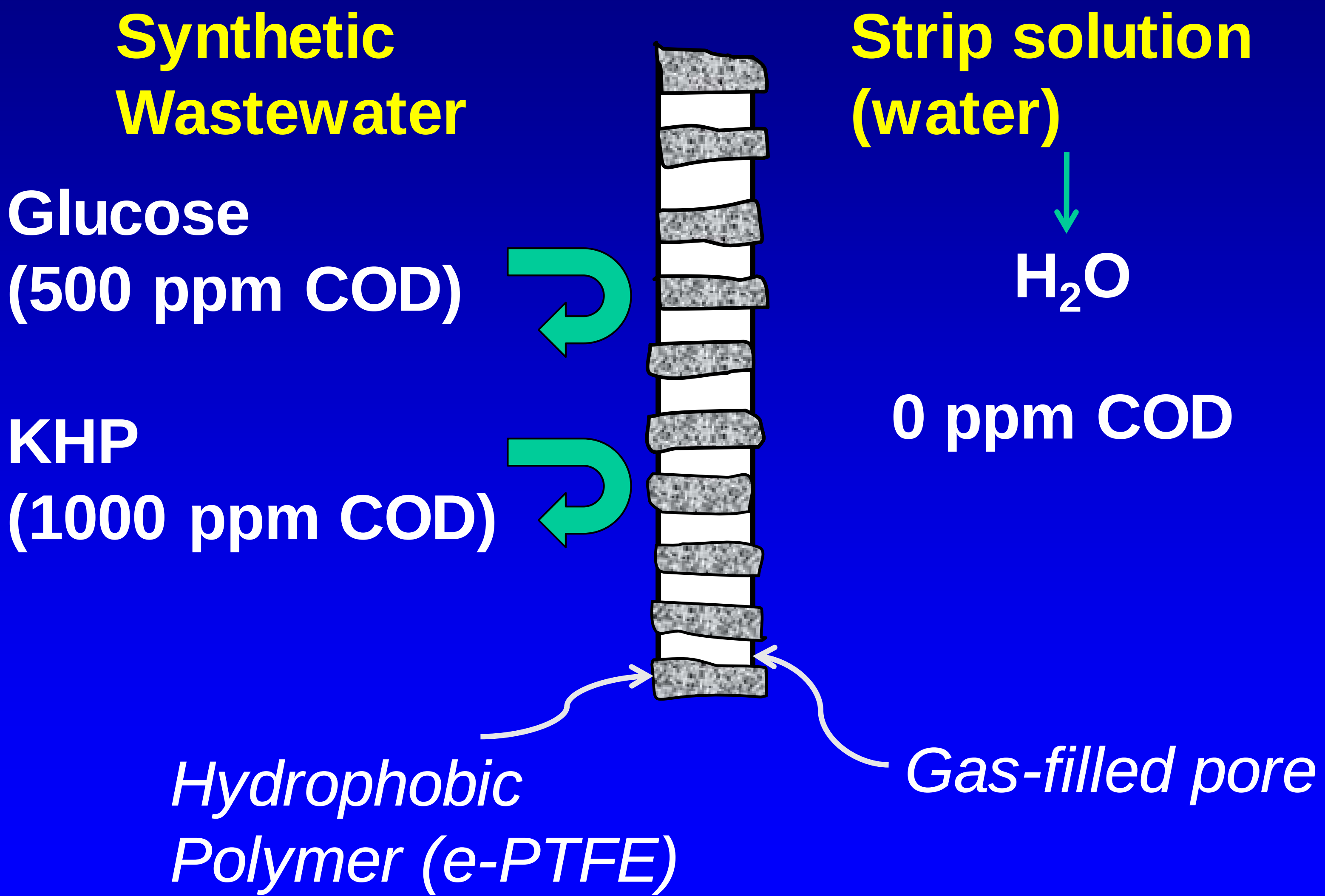
Anaerobic Livestock Wastewater Lagoon with Ammonia Recovery System

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

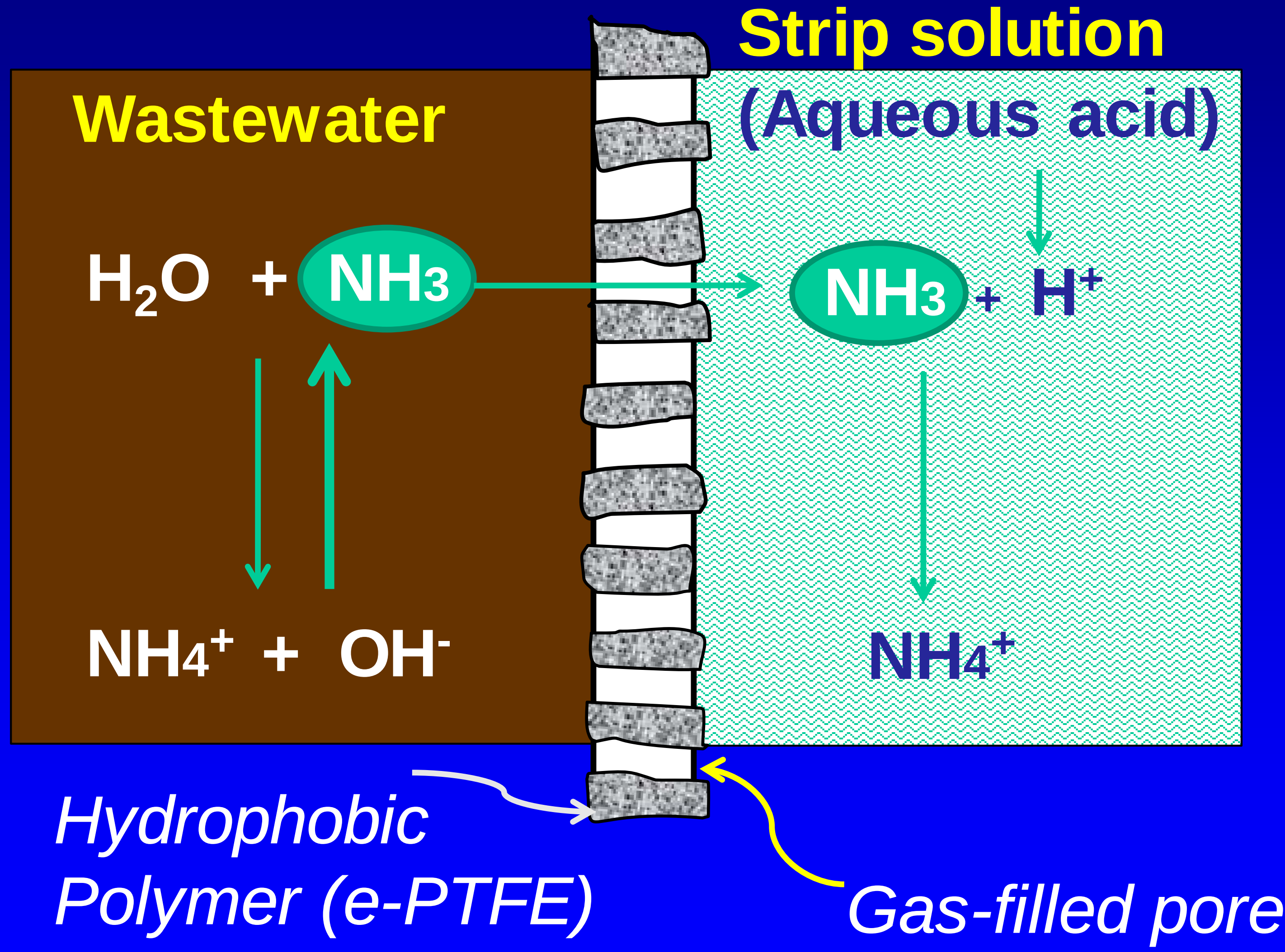


Design Parameter: Effect of wastewater pH:

Time (hours)	Initial Source pH = 8.3			Initial Source pH = 10.0		
	Mass NH_4-N in Trap (mg)	NH_4-N Recovery from Source (%)	pH of Trap	Mass NH_4-N in Trap (mg)	NH_4-N Recovery from Source (%)	pH of Trap
0	0	**0**	1.08	0	**0**	1.08
1	0.86	**1.0**	1.11	7.82	**8.7**	0.99
2	2.44	**2.7**	0.98	26.51	**29.4**	1.16
3	3.72	**4.1**	0.99	38.60	**42.9**	1.28
4	4.77	**5.3**	1.1	48.86	**54.3**	1.6
5	5.39	**6.0**	1.0	56.40	**62.7**	1.8

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

Gas-permeable membrane used for separation of free ammonia (NH_3)

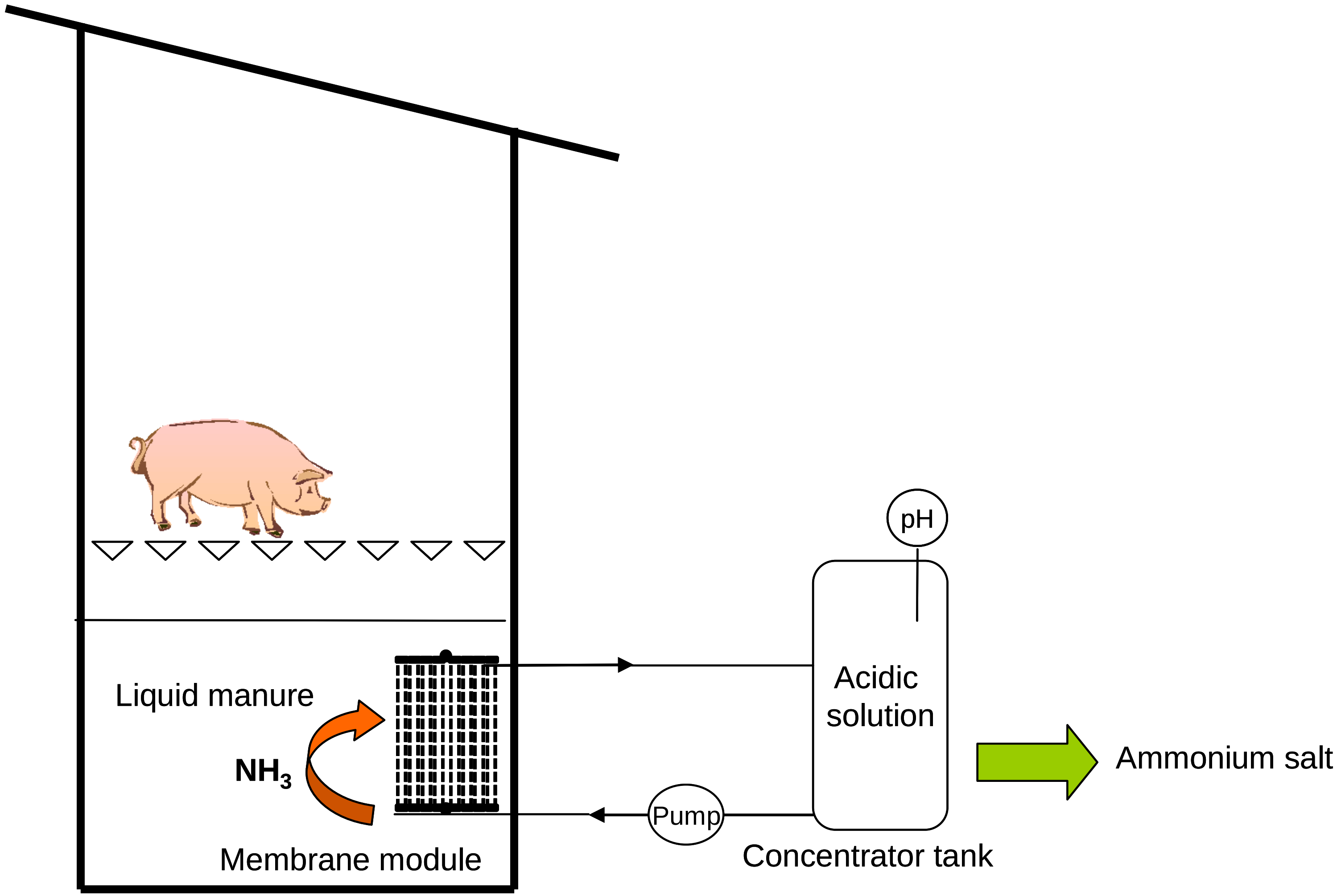


Design Parameter: Effect of waste strength

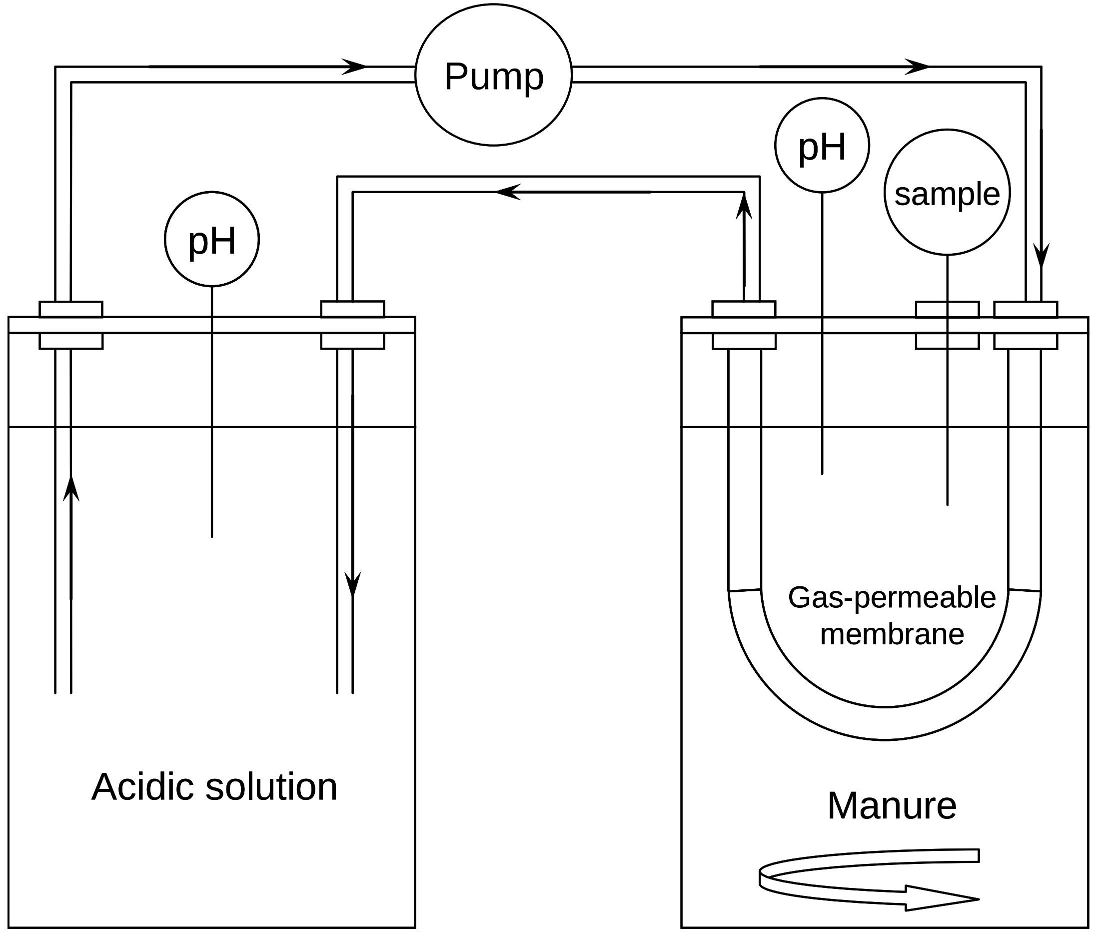
Swine manure characteristics

Manure strength	Swine Farm Type	pH	NH_4-N mg/l	TKN mg/L	EC (mS)	COD mg/L	TS g/L	VS g/L
Low	Piglet	8.64	1065	1345	8.470	4519	4.89	2.58
Medium	Farrow-finish w/ separation	7.57	1680	2743	14.080	24405	17.41	10.33
High	Finishing	7.52	2285	3699	16.980	34081	29.87	20.13

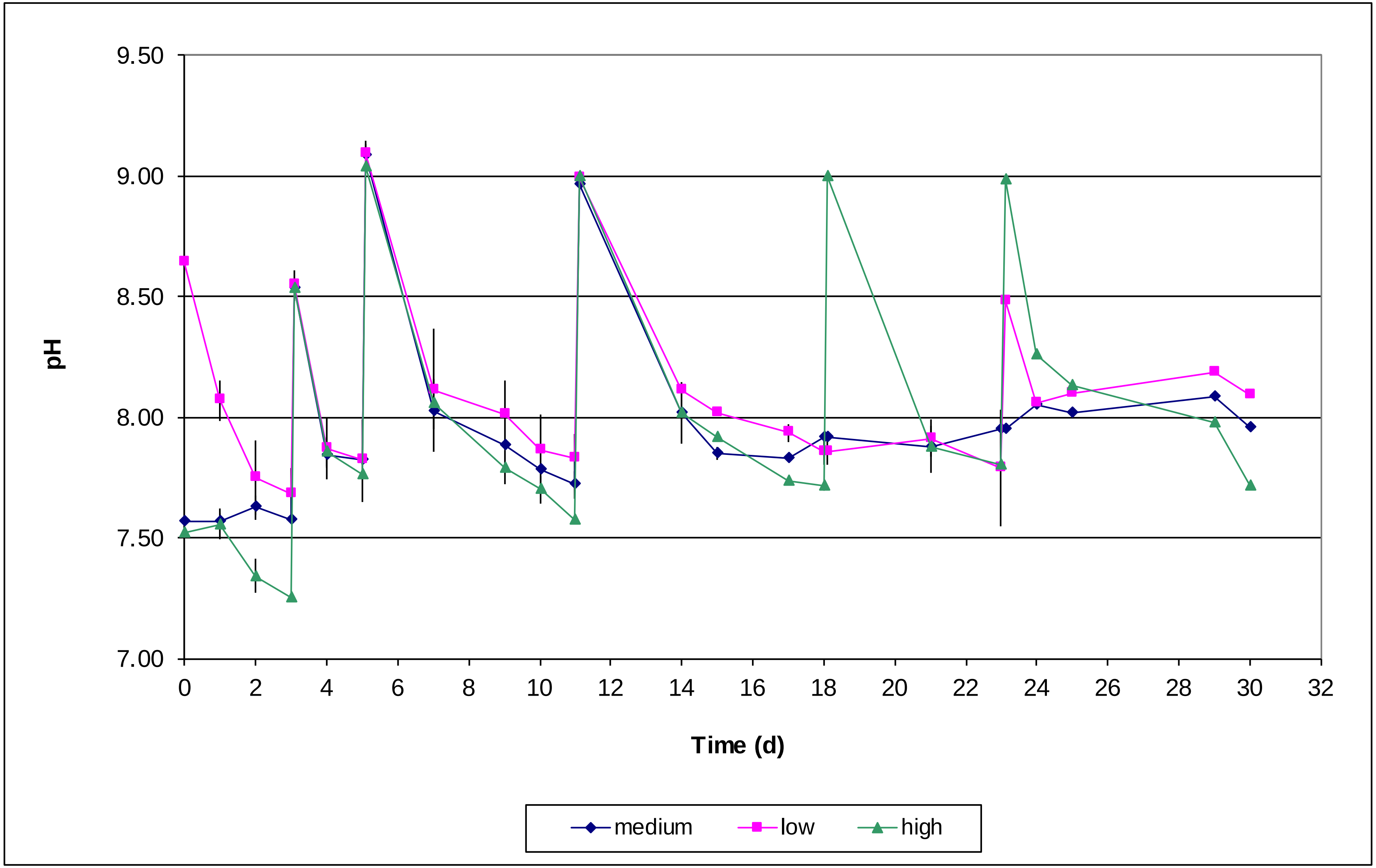
Ammonia recovery from livestock manure using gas-permeable membrane module and concentrator tank (Closed loop system).



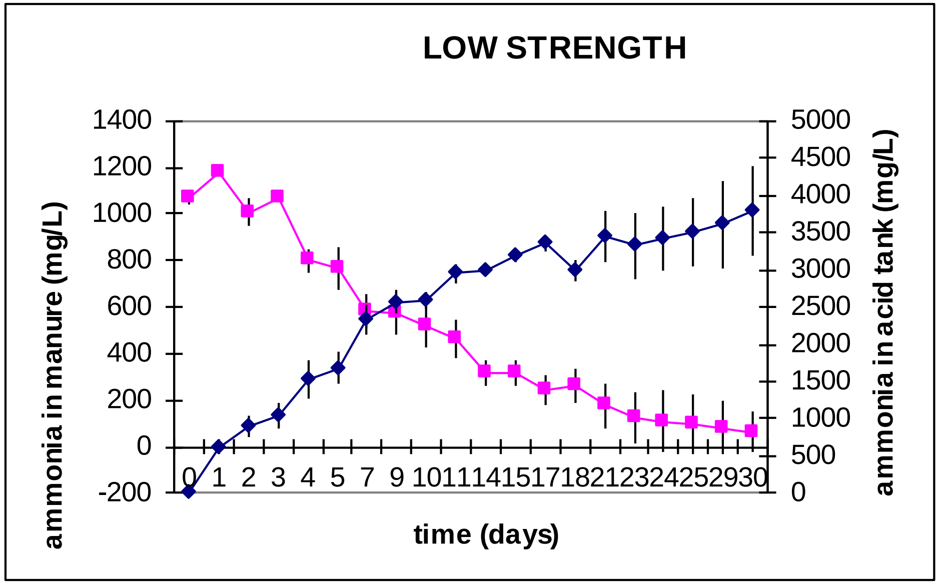
Experimental device for ammonia capture from manure using gas-permeable membranes (closed loop).

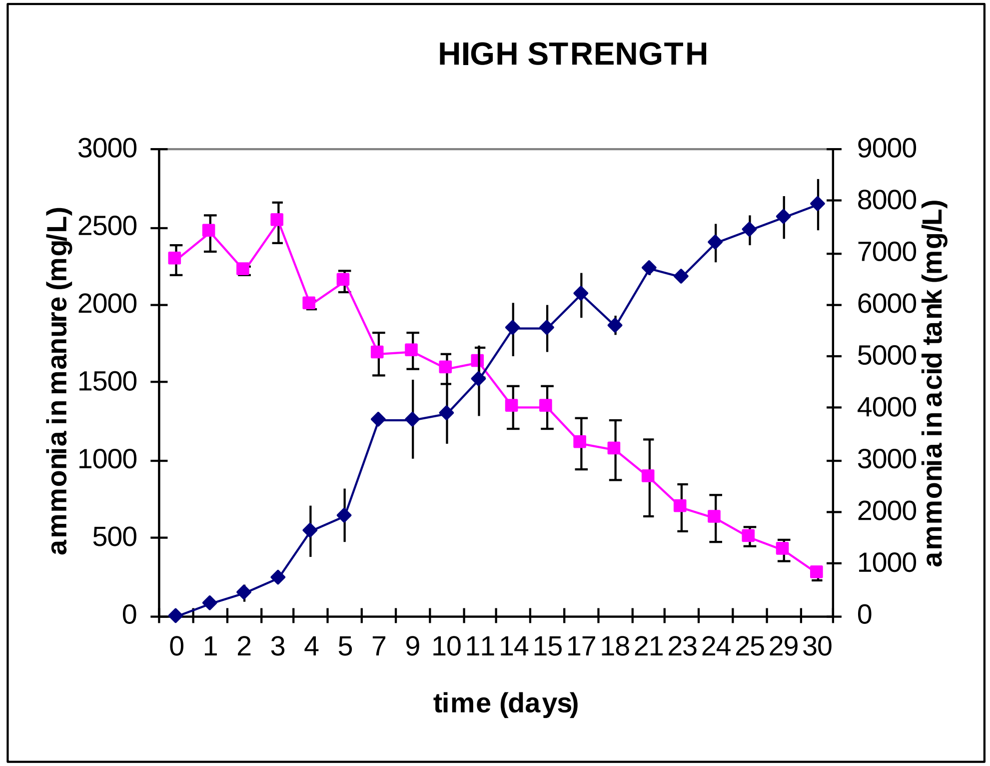


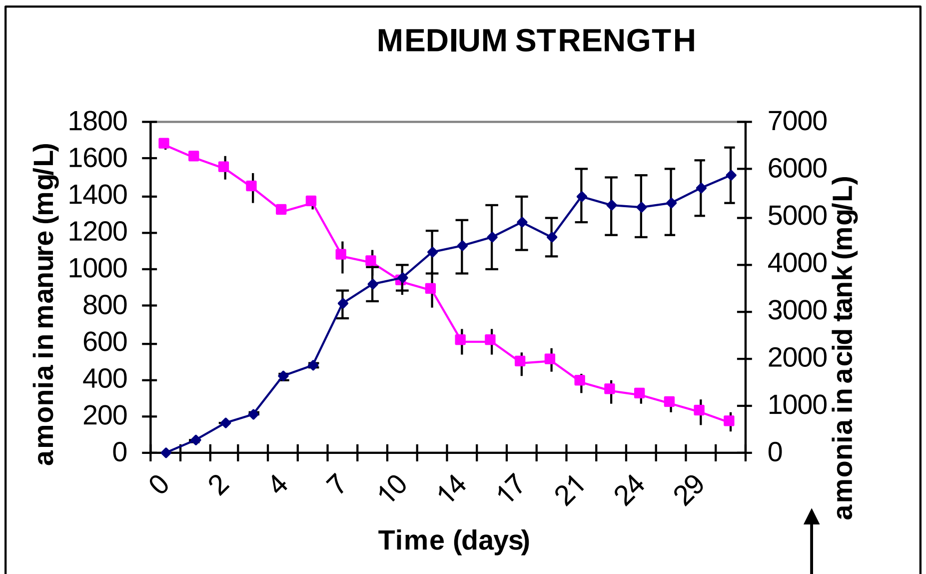
Process pH adjusted with alkali (7.7 to 9)



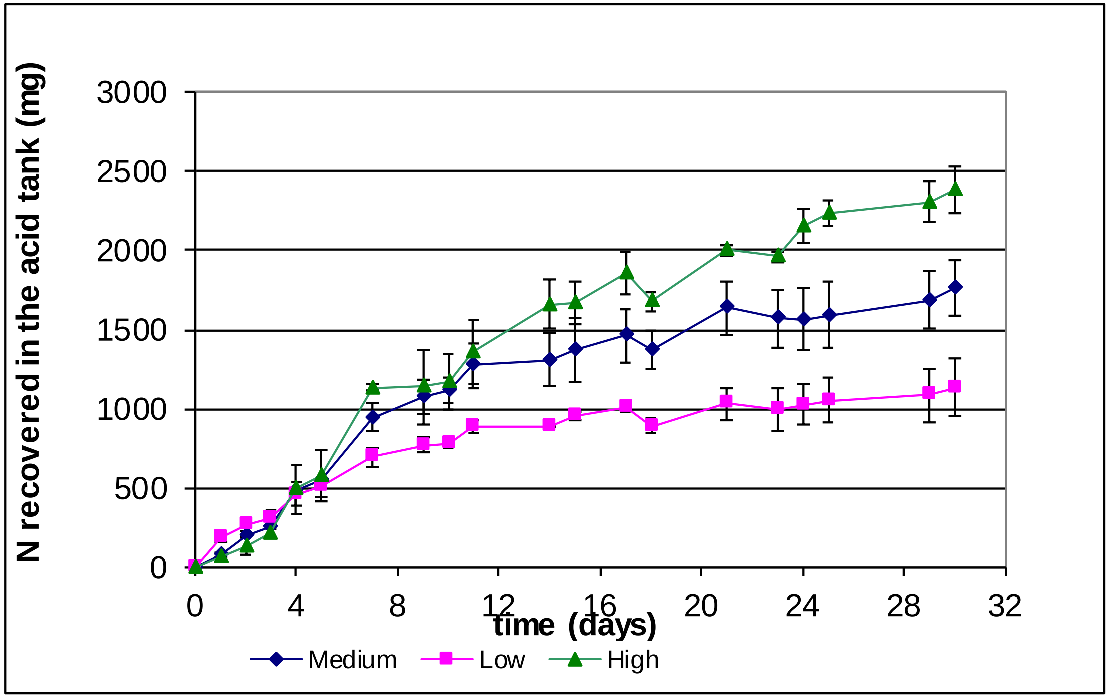
Removal of ammonia in the manures and recovery in the acid tank







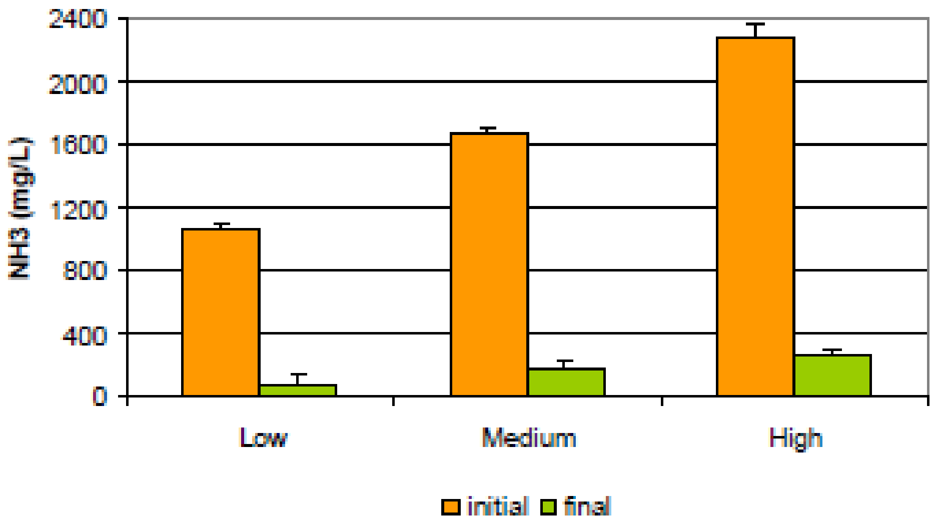
Ammonia recovery rate increases with manure strength



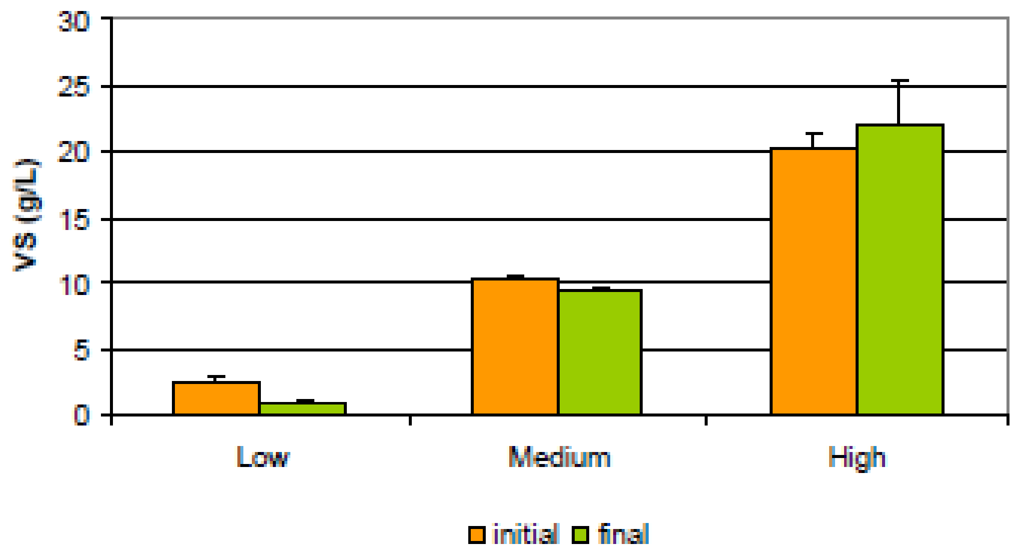
Manure strength	Initial NH4 mg N/L	NH4 removed %	NH4 recovery %	NH4 recovery rate (mg/L/d)
low	1385	94	87	74
medium	2184	90	90	92
high	2971	88	90	194

M.C. Garcia and M.B. Vanotti, Waste Management 2014 (in press)

Ammonia was removed

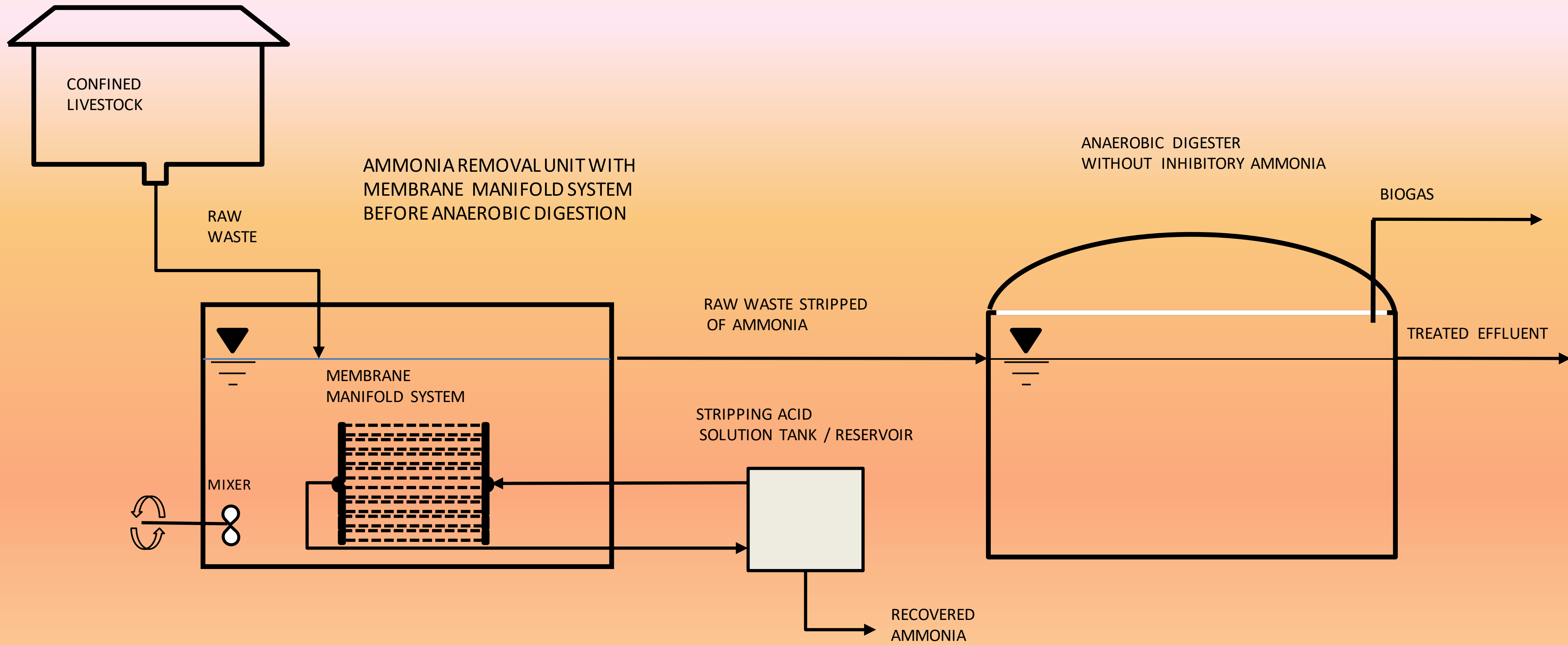


but carbon (volatile solids) was not removed



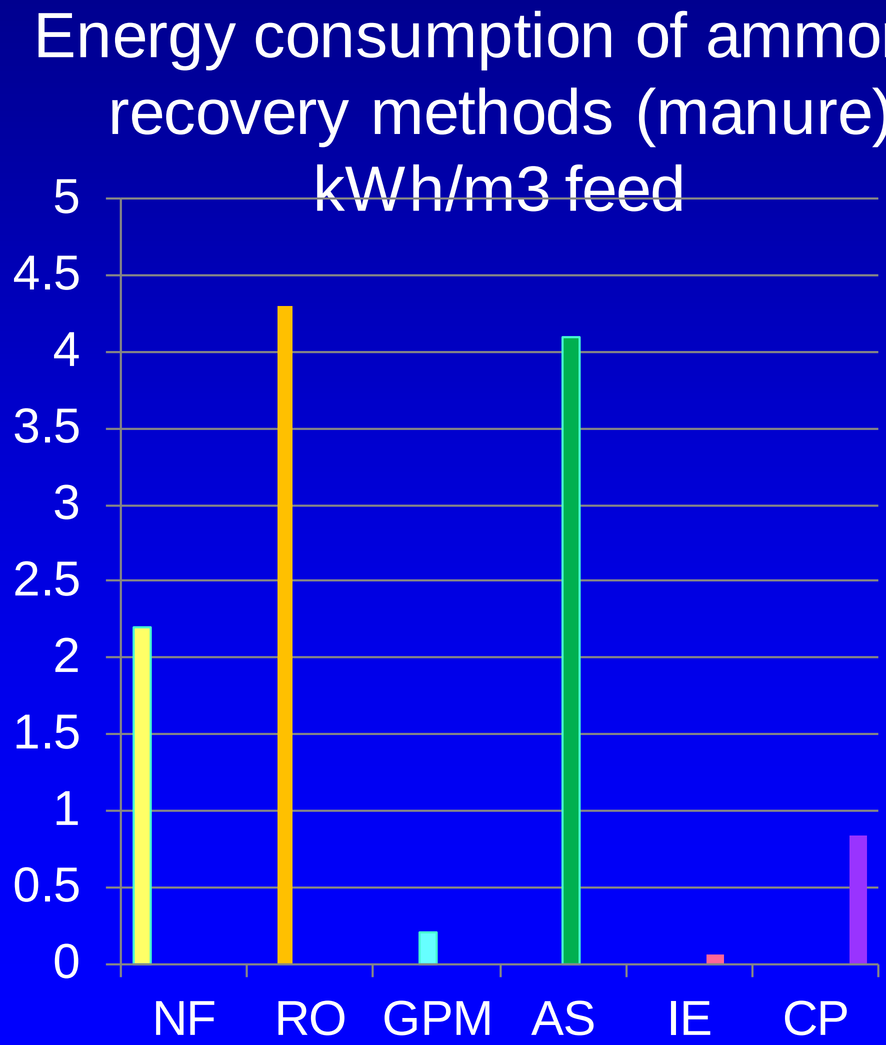
Technology can be combined with anaerobic digestion to recover both the ammonia and the energy from manure.

Ammonia Recovery System with Anaerobic Digestion



Zarebska et al. (2015) Ammonium fertilizers production from manure: A critical review.

The gas-permeable membrane method had very low energy demand



NF= nanofiltration

RO = reverse osmosis

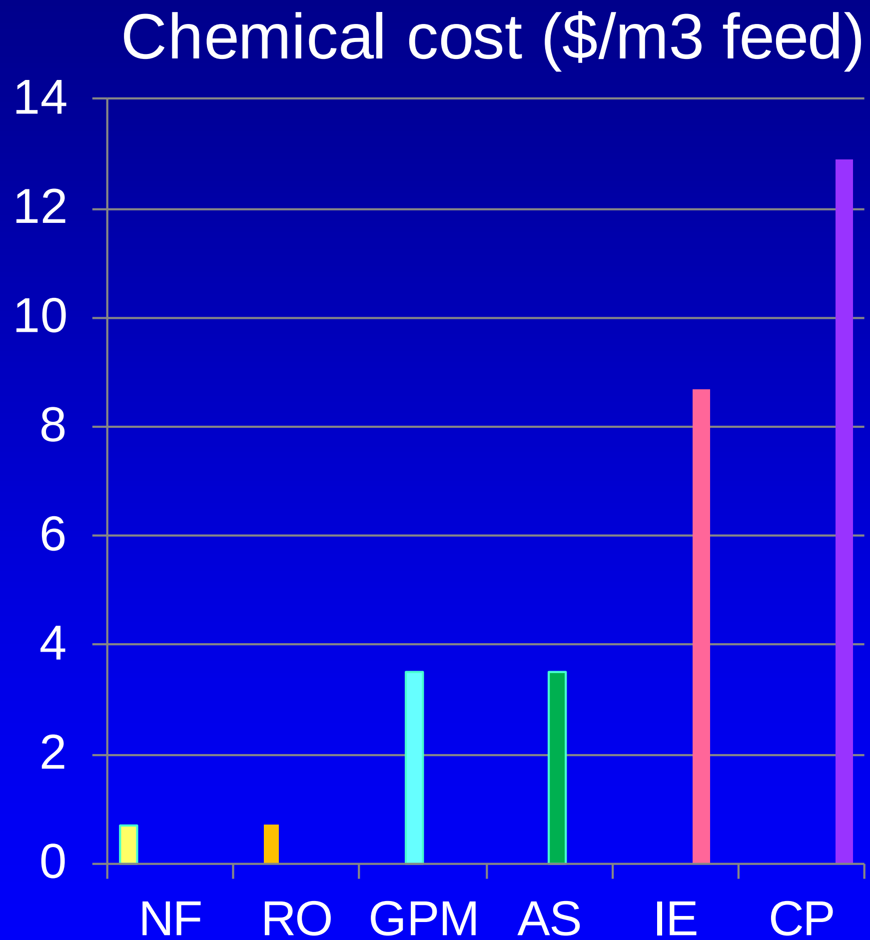
GPM = gas permeable memb.

AS = air stripping

IE = ion exchange/ zeolites

CP = Chemical precipitation

The gas-permeable membrane method (MD) had high chemical demand (NaOH to increase pH)



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Design Parameter: Effect of aeration

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**

$$HCO_3^- + air \rightarrow OH^- + CO_2$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

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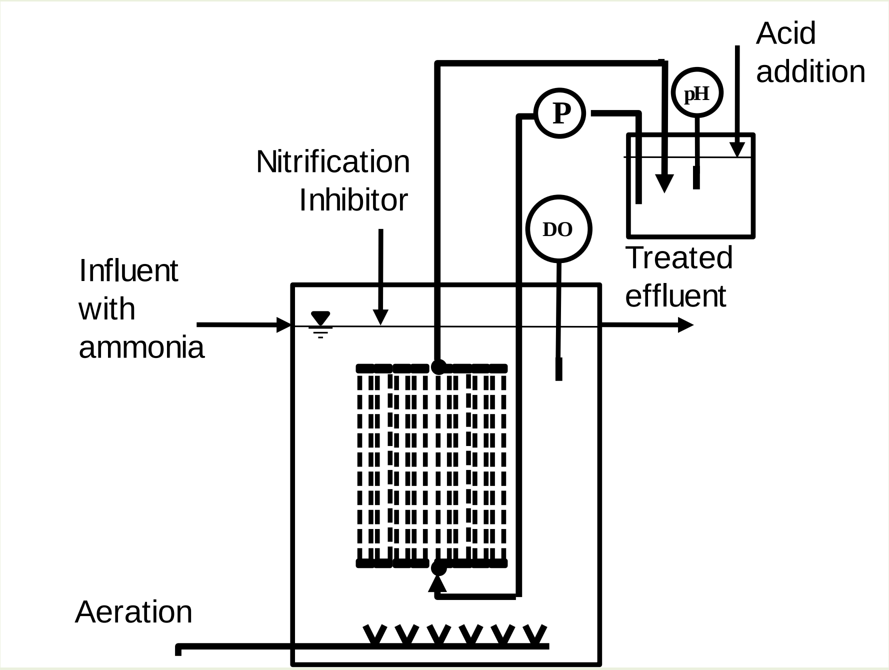
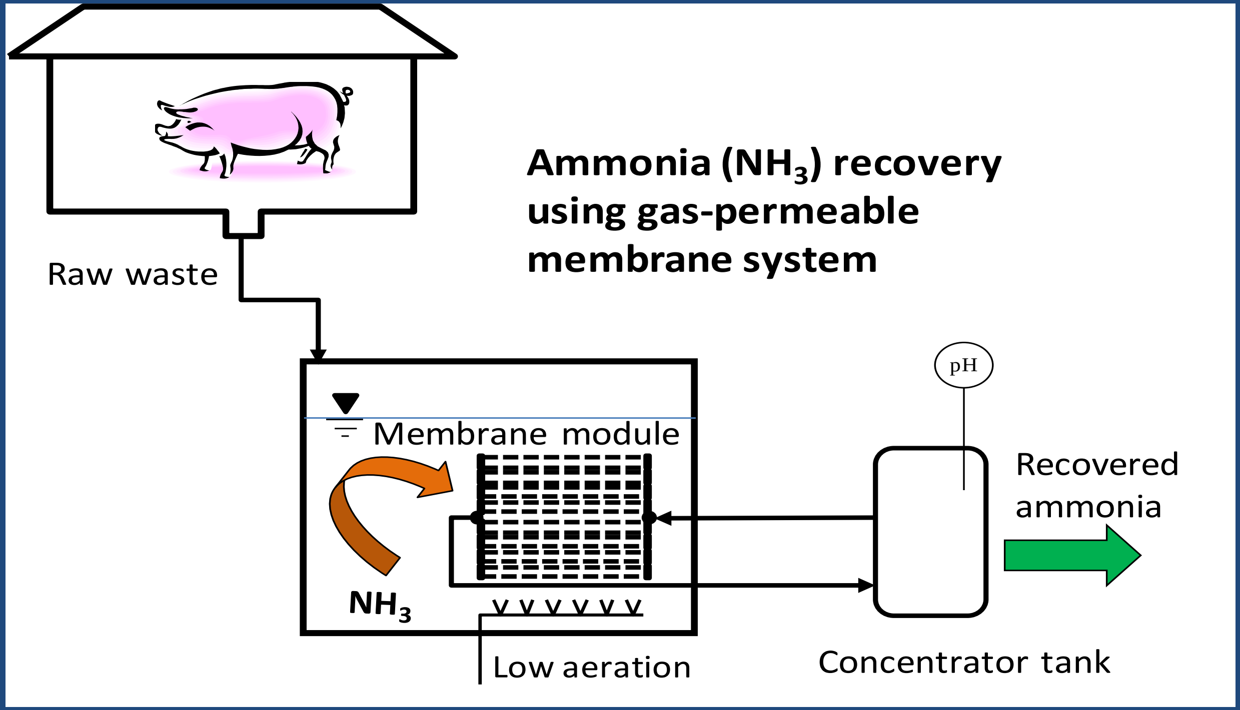


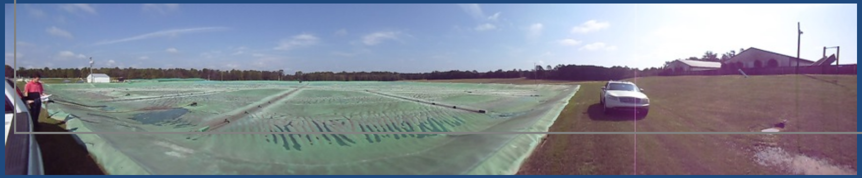
- **Aeration increases manure pH about 1 unit**
- **The aeration rate must be low to inhibit nitrification**
- **Nitrification inhibitor can be used (< 10 ppm)**

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
- US Patent in 2015: "Systems and Methods for Reducing Ammonia Emissions from Liquid Effluents and for Recovering the Ammonia" (US 9,005,333, Vanotti,M.B., and Szogi,A.A)





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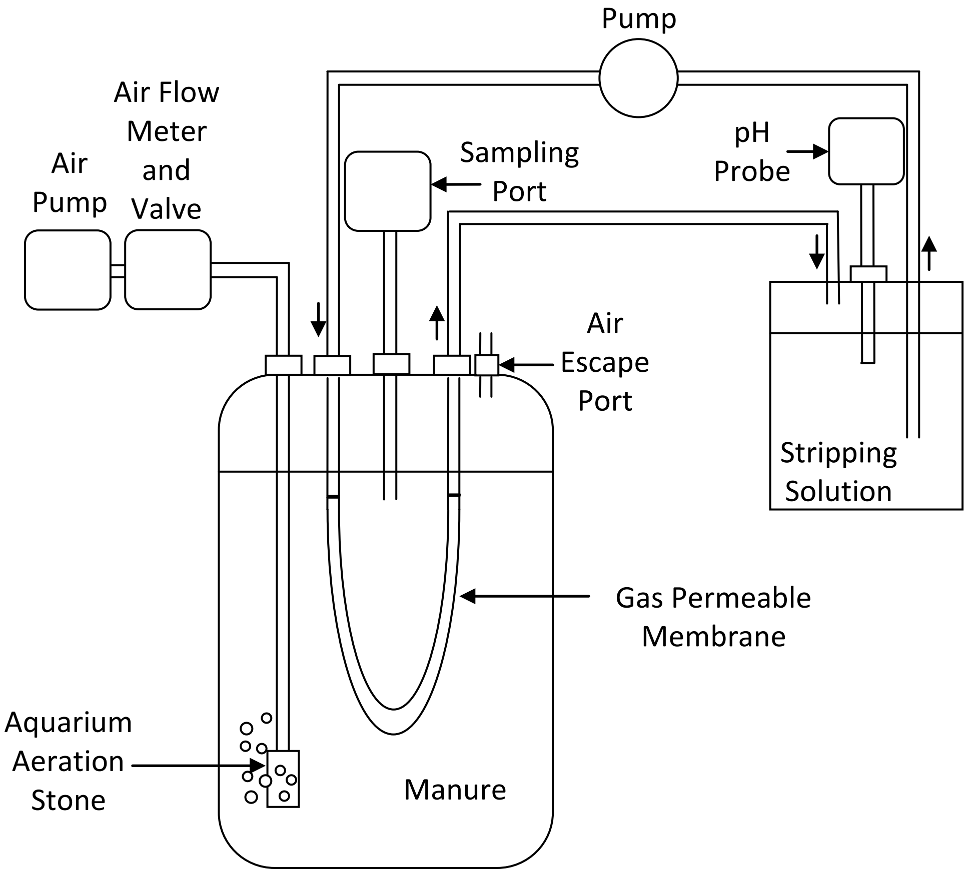
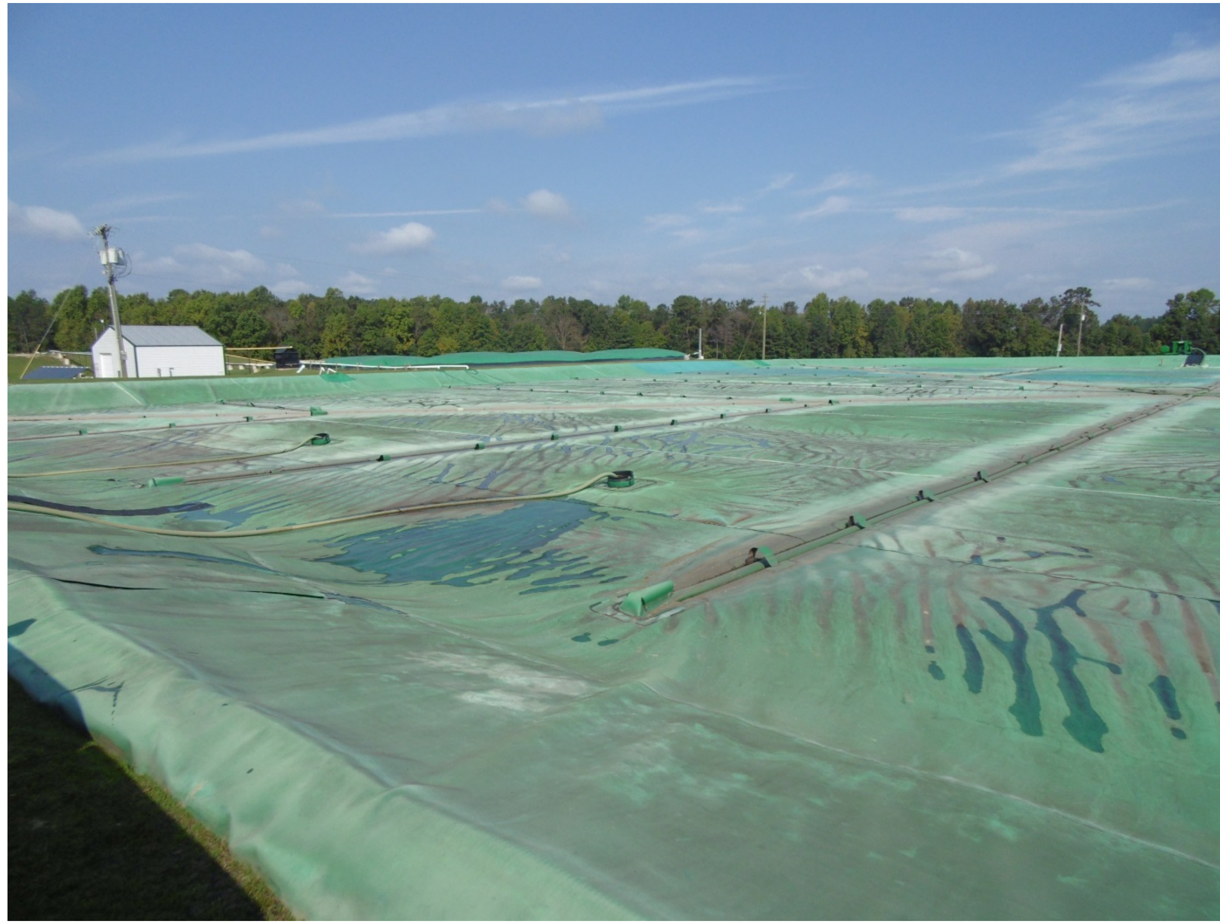
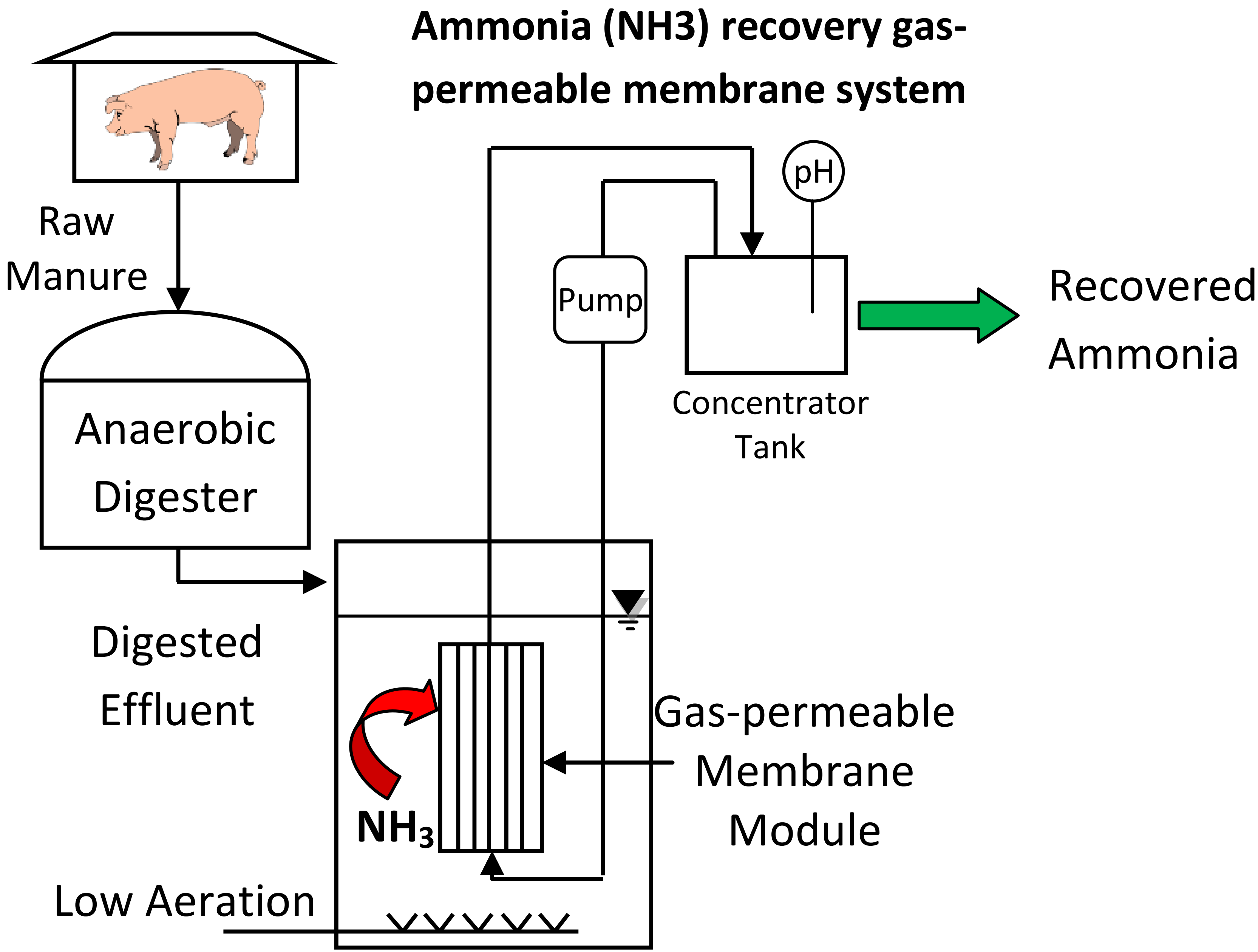


N recovery: Effect of low-rate aeration Covered lagoon effluent, North Carolina

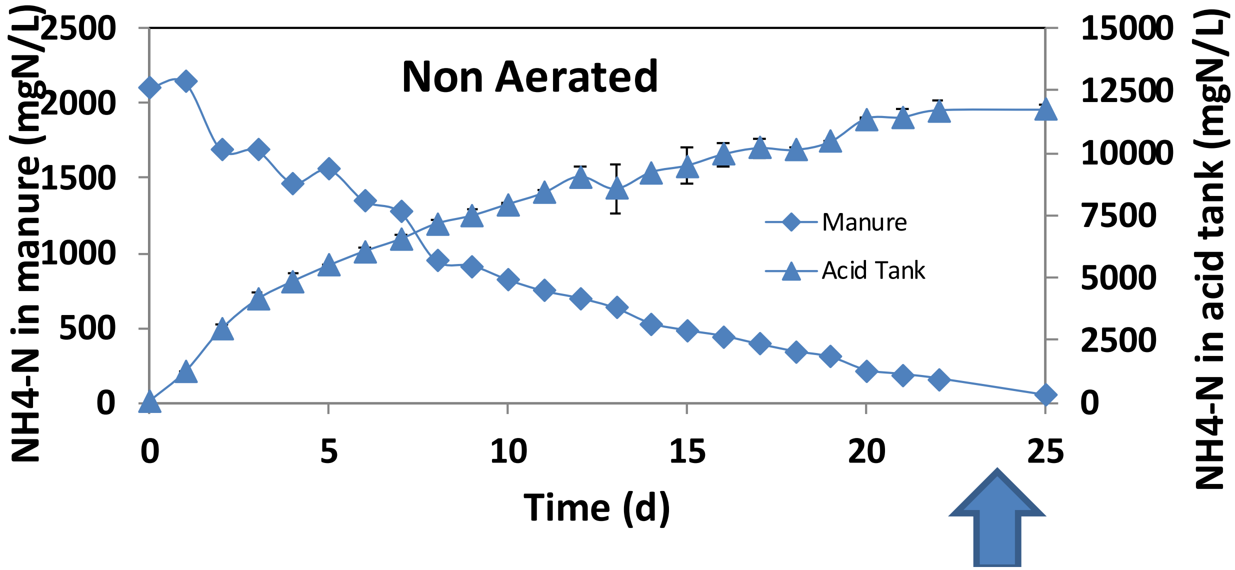


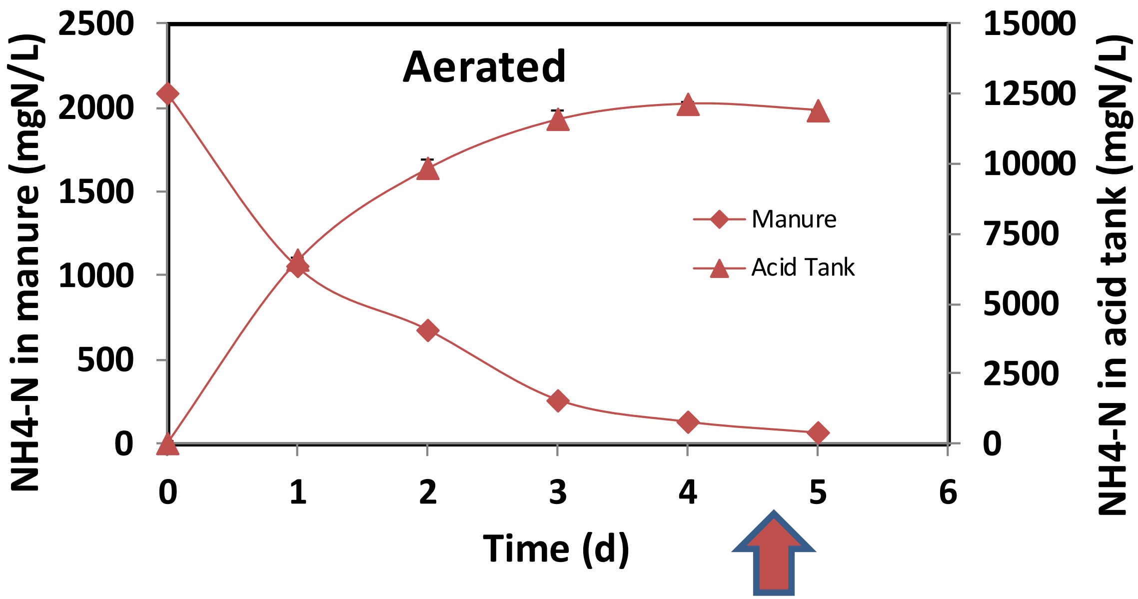
Liquid with 2,100 mg/L NH4-N


Ammonia (NH3) recovery gas-permeable membrane system
Raw Manure
Anaerobic Digester
Digested Effluent
Pump
pH
Concentrator Tank
Recovered Ammonia
NH_3
Gas-permeable Membrane Module
Low Aeration

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

	Treatment Time	Initial NH_4^+ in Manure	Remaining NH_4^+ in Manure	NH_4^+ removed from Manure	NH_4^+ recovered in acidic solution	NH_4^+ removal efficiency	NH_4^+ recovery efficiency	NH_4^+ Volatilized in air
	(days)	----------------------------mg N-----------------------				----------------%-----------------		
Aerated	5	3133 (151)	96 (29)	3037	2979 (2)	97	98	2
Non Aerated	25	3157 (132)	71 (19)	3086	2936 (40)	98	95	5

Contents lists available at ScienceDirect
Waste Management
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Enhancing recovery of ammonia from swine manure anaerobic digester effluent using gas-permeable membrane technology

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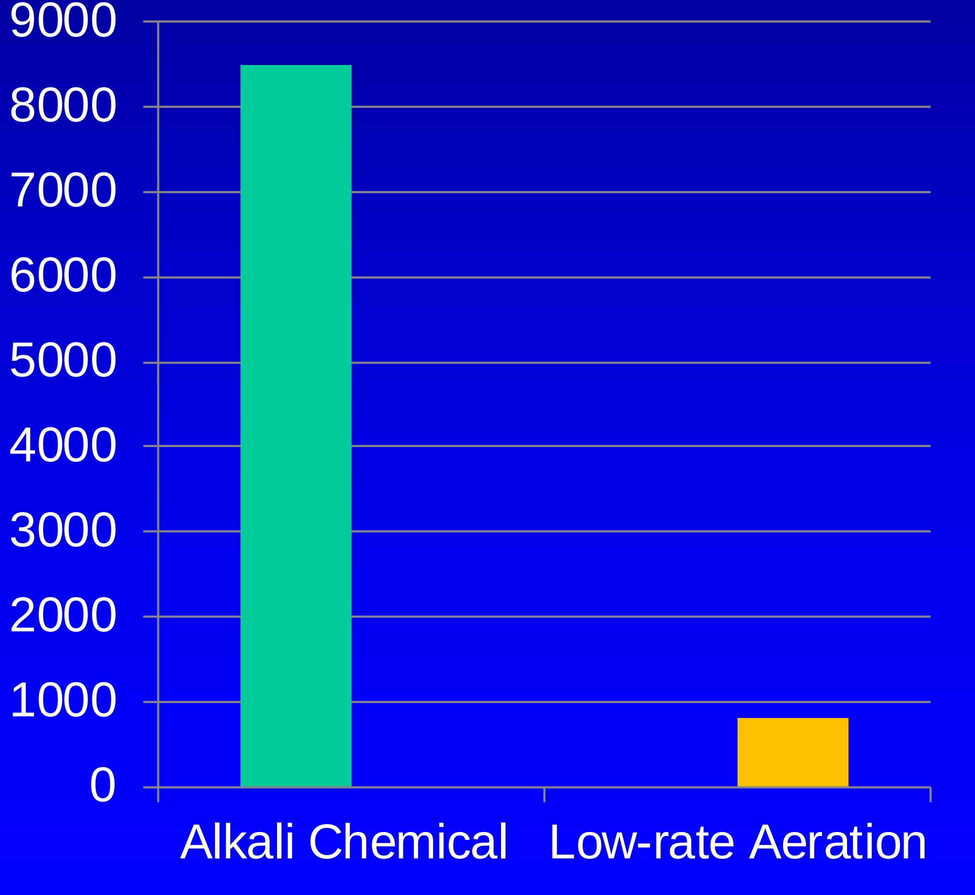
[a] United States Department of Agriculture, Agricultural Research Service, Coastal Plains Soil, Water and Plant Research Center, 2611 W. Lucas St, Florence, SC 29501, USA
[b] Agriculture Technological Institute of Castilla and Leon (ITACyL), Valladolid, Spain

ARTICLE INFO ABSTRACT

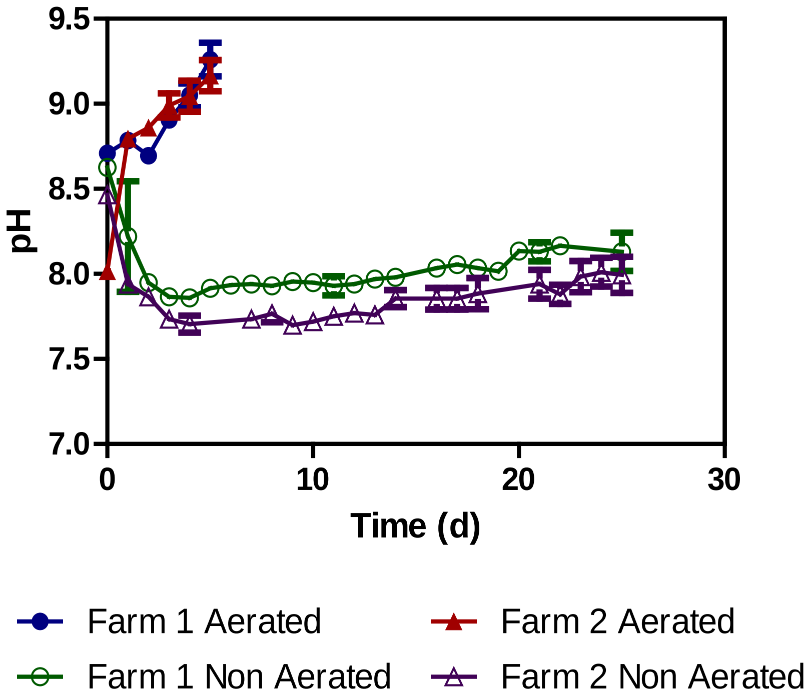
Significant cost reductions can be achieved with new concepts and research

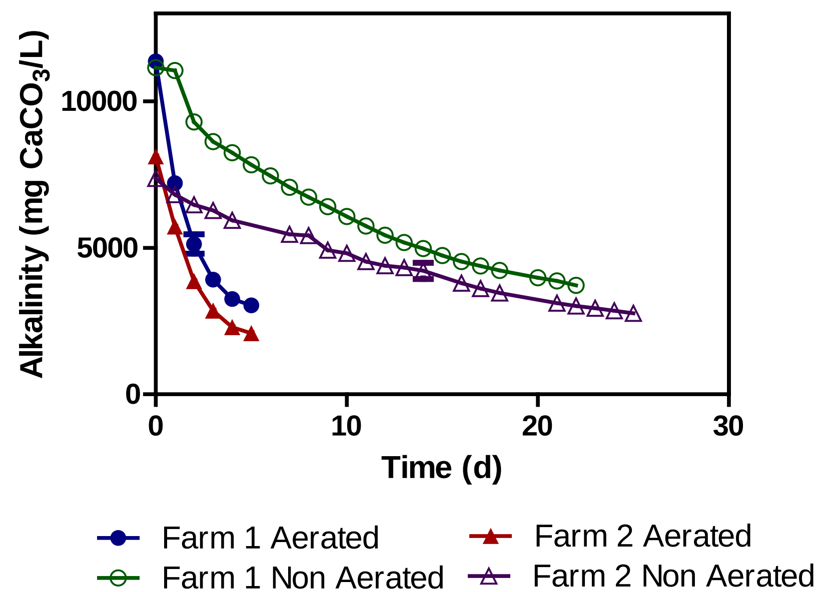
Operational cost of NH_3 recovery using gas-permeable membranes ($/4000 pigs/year)



Changes in pH and alkalinity of manure during N recovery process

Covered anaerobic lagoon effluent, NC





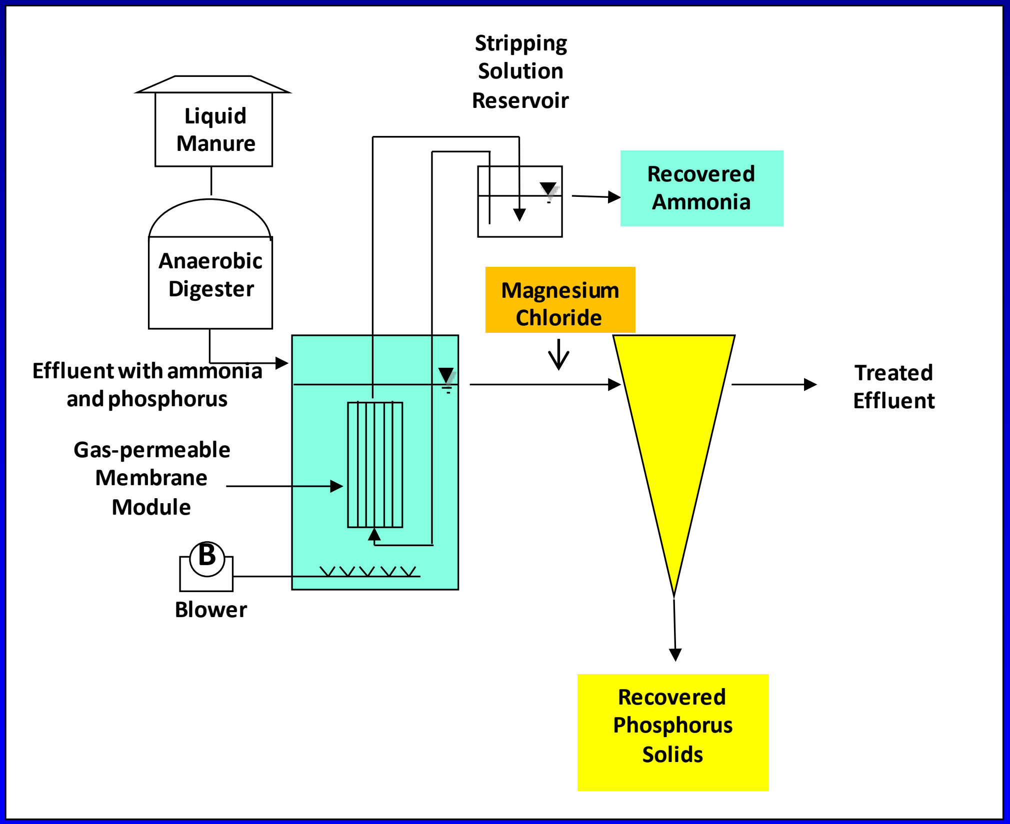
Key finding

- The process removes ammonia and alkalinity and increases pH.

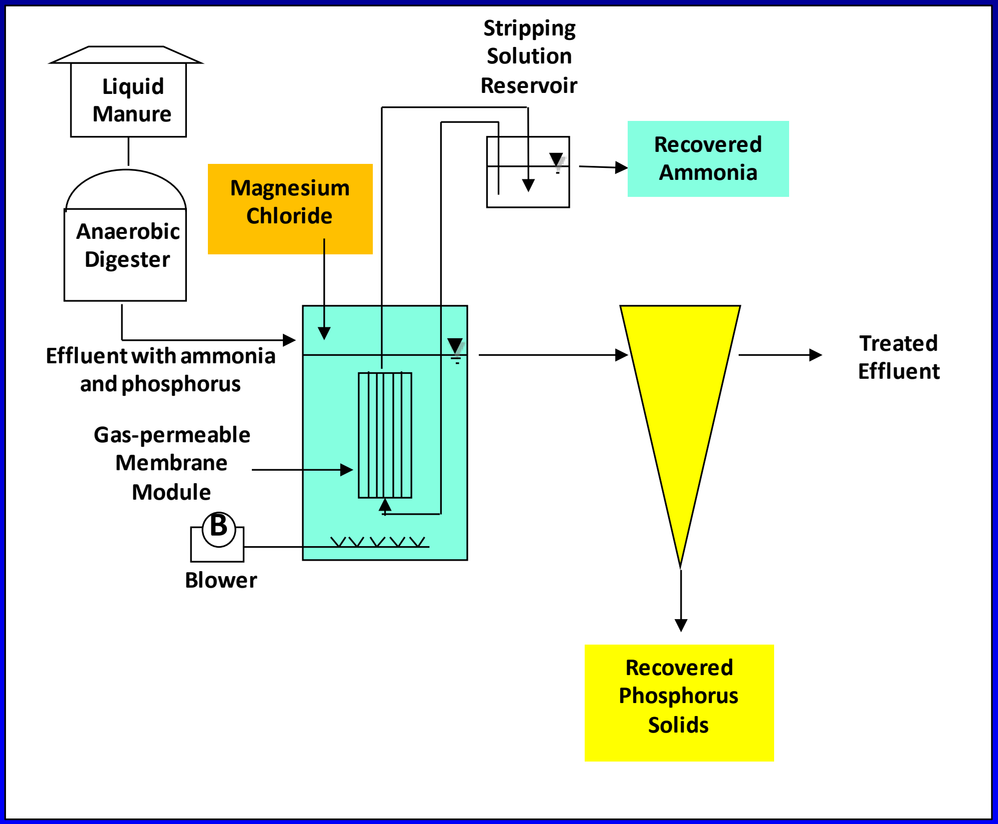
- These are ideal conditions for phosphorus precipitation and recovery

Recovery of ammonia and phosphorus from animal manure

Configuration 1



Configuration 2



Influent P concentration: 150-200 mg/L

Influent N concentration: 1500-2000 mg/L

US Pat. Appl. 62/169,387 (USDA 6/1/2015)

For Mg phosphates, two potential forms that can precipitate in liquid systems that contain $Mg^{2+}–NH_4^+–PO_4^{3-}$ and a high Mg/Ca ratio are struvite and newberyite

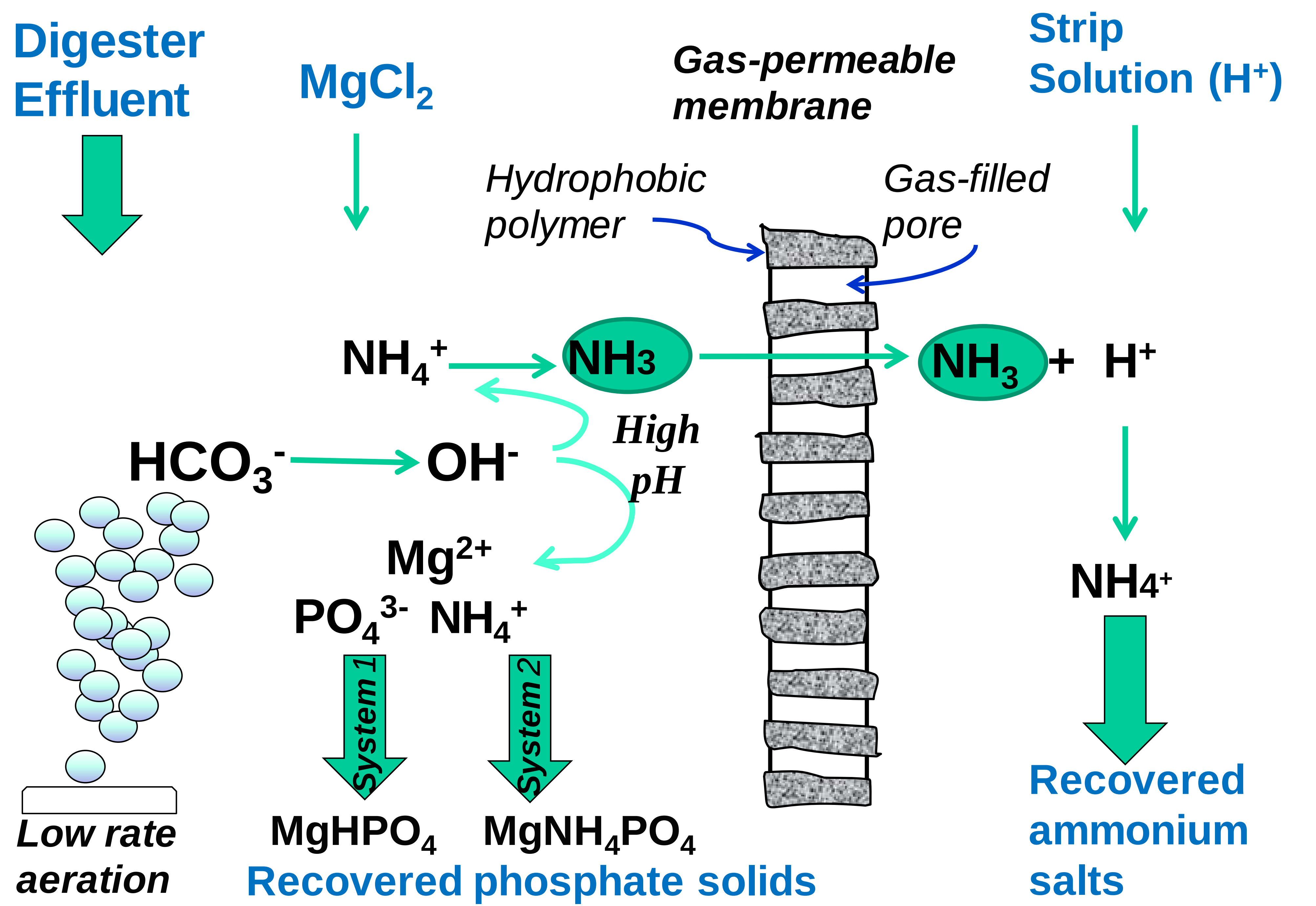
(Boistelle et al., 1983; Abbona et al., 1988; Muster et al., 2013).

Struvite

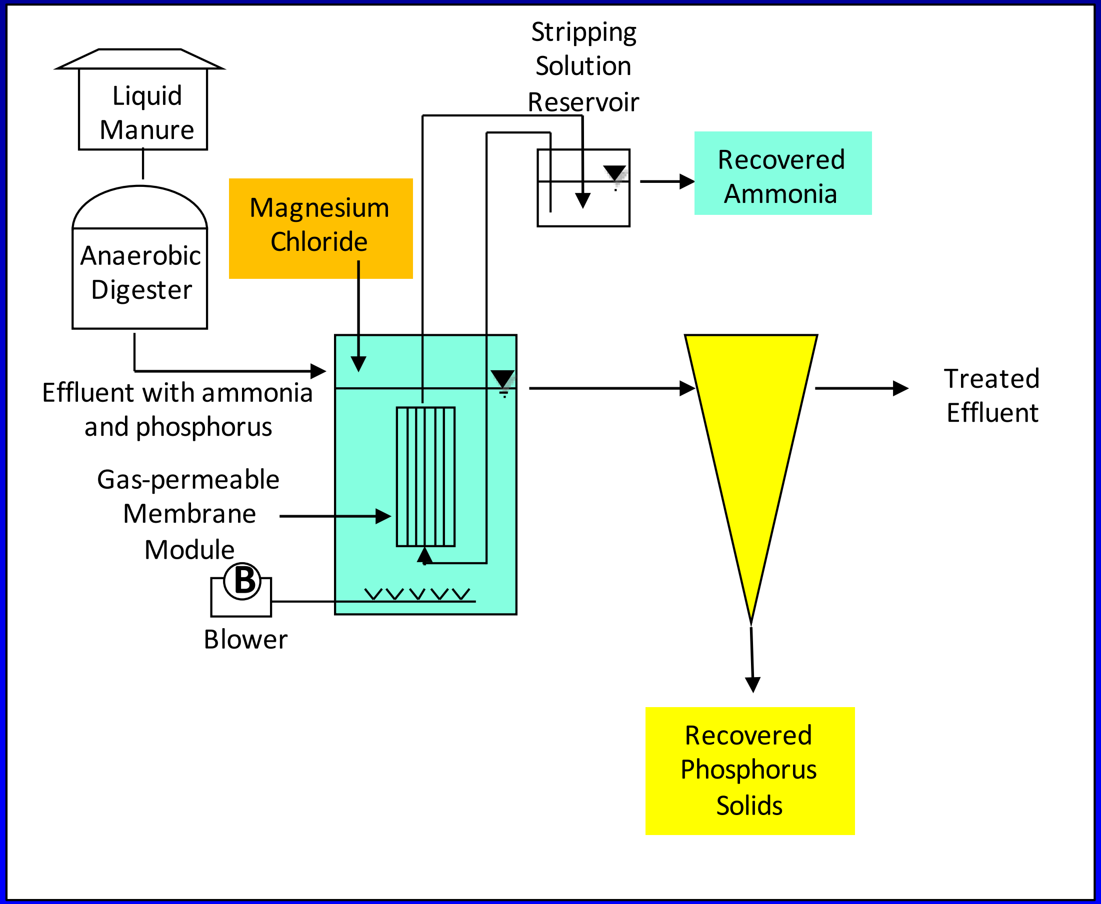
$Mg^{2+} + H_2PO_4^- + NH_3 \rightarrow \mathbf{MgNH_4PO_4} + H^+$

Newberyite

$Mg^{2+} + H_2PO_4^- \rightarrow \mathbf{MgHPO_4} + H^+$


Digester Effluent
MgCl2
Gas-permeable membrane
Strip Solution (H+)
Hydrophobic polymer
Gas-filled pore
NH4+
NH3
NH3 + H+
HCO3-
OH-
High pH
Mg2+
PO4 3- NH4+
NH4+
System 1
System 2
Low rate aeration
MgHPO4
MgNH4PO4
Recovered phosphate solids
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)

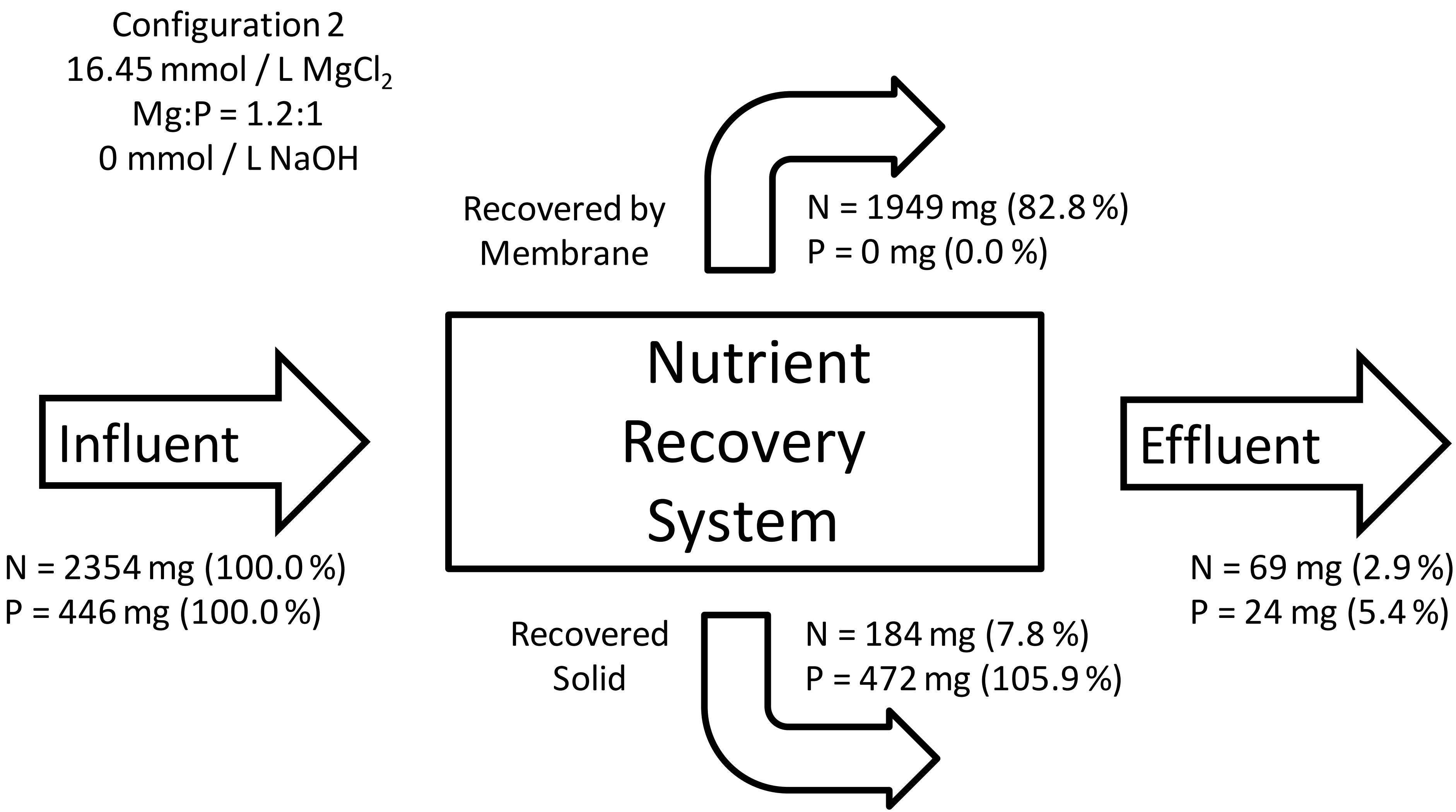
	Concentrations		MASS BALANCE				
Nutrient	**Influent Concentration**	**Effluent Concentration**	**Initial Manure**	**Recovered Solid**	**Recovered by Membrane**	**Effluent**	**Total Recovery**
	mg/L		**Percentages**				
N	2354	69.2	100%	7.7%	83.1%	2.9%	90.5%
P	446	23.5	100%	104.3%	0%	5.3%	104.3%

Configuration 2 with MgCl2 added (without NaOH)

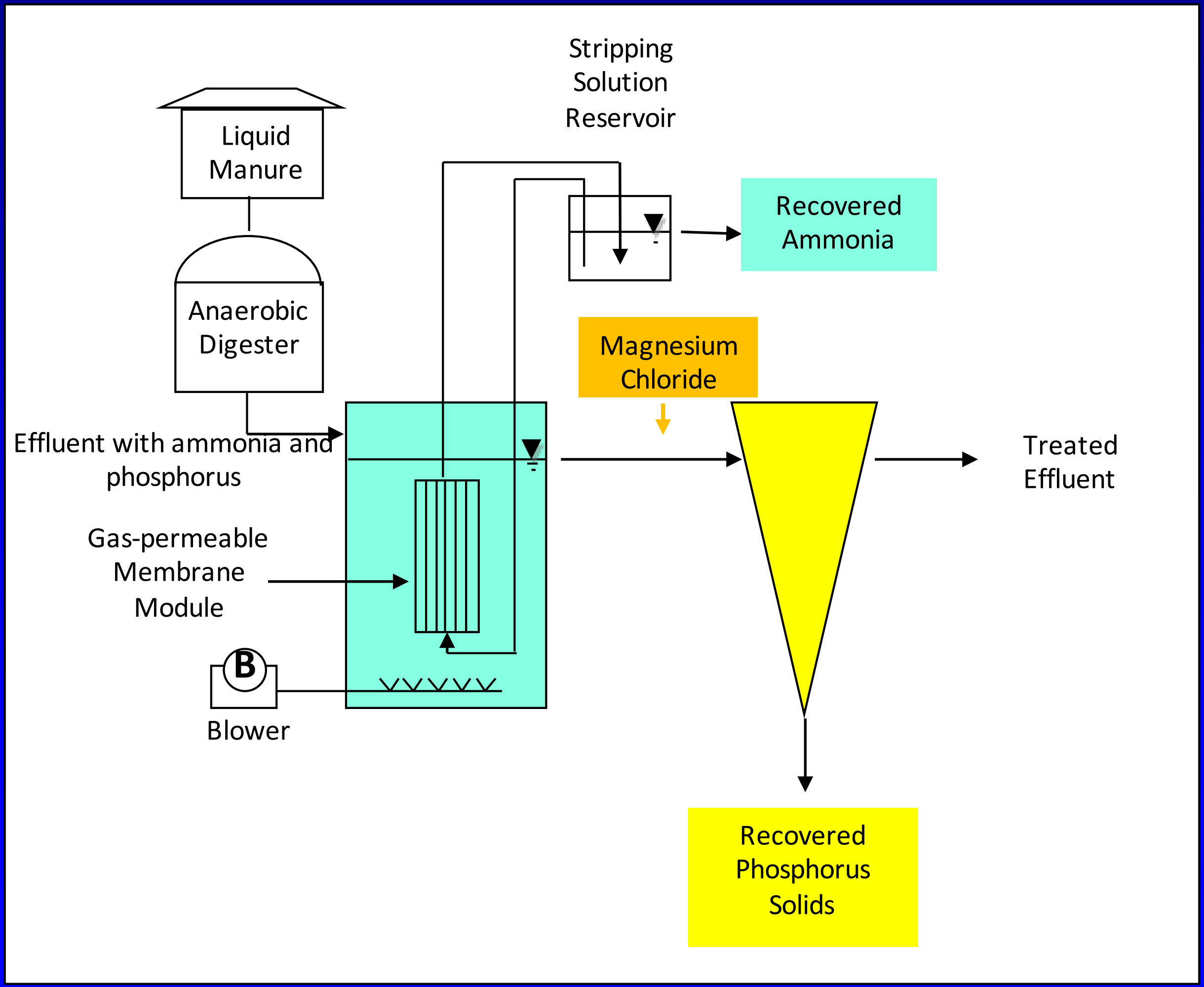
	Concentrations		MASS BALANCE				
Nutrient	Influent Concentration	Effluent Concentration	Initial Manure	Recovered Solid	Recovered by Membrane	Effluent	Total Recovery
	mg/L		Percentages				
N	2354	69.2	100%	7.7%	83.1%	2.9%	**90.5%**
P	446	23.5	100%	104.3%	0%	5.3%	**104.3%**

Composition of Recovered Solid					
N	P_2O_5	Mg	Ca	K	Plant Available P (Citrate soluble)
Percentages, %					
4.5	**26.4**	**10.0**	2.0	1.7	99.00

Struvite = 5.7 N : 29 P_2O_5 : 10 Mg


Configuration 2
16.45 mmol / L $MgCl_2$
Mg:P = 1.2:1
0 mmol / L NaOH
Recovered by Membrane
N = 1949 mg (82.8 %)
P = 0 mg (0.0 %)
Influent
Nutrient Recovery System
Effluent
N = 2354 mg (100.0 %)
P = 446 mg (100.0 %)
N = 69 mg (2.9 %)
P = 24 mg (5.4 %)
Recovered Solid
N = 184 mg (7.8 %)
P = 472 mg (105.9 %)

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%

US Pat. Appl. 62/169,387 (USDA 6/1/2015)

Recovered Phosphates (Configuration 1)

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

Chemical Composition

Constituent	Percentage
P_2O_5	46.4%
Magnesium	17.1%
Calcium	0.4 %
Potassium	1.7 %
Nitrogen	1.8 %

Newberyite (MgHPO4.3H2O)
41% P_2O_5 and 14% Mg

Triple superphosphate = 46% P_2O_5; Rock phosphate = 27-36% P2O5

Configuration 1 with Municipal Side Stream Wastewater (after AD of sludges)

	Concentrations		MASS BALANCE				
Nutrient	Influent Concentration	Effluent Concentration	Initial Manure	Recovered Solid	Recovered by Membrane	Effluent	Total Recovery
	mg/L		Percentages				
N	731	123	100%	2.4%	90.5%	16.7%	**92.3%**
P	147	6	100%	79.2%	0%	4.1%	**79.2%**

- 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_2O_5**	**Mg**	**Ca**	**K**	**Plant Available P**
Percentages, %					
1.8	**46.4**	**17.1**	0.4	1.8	**99.7**

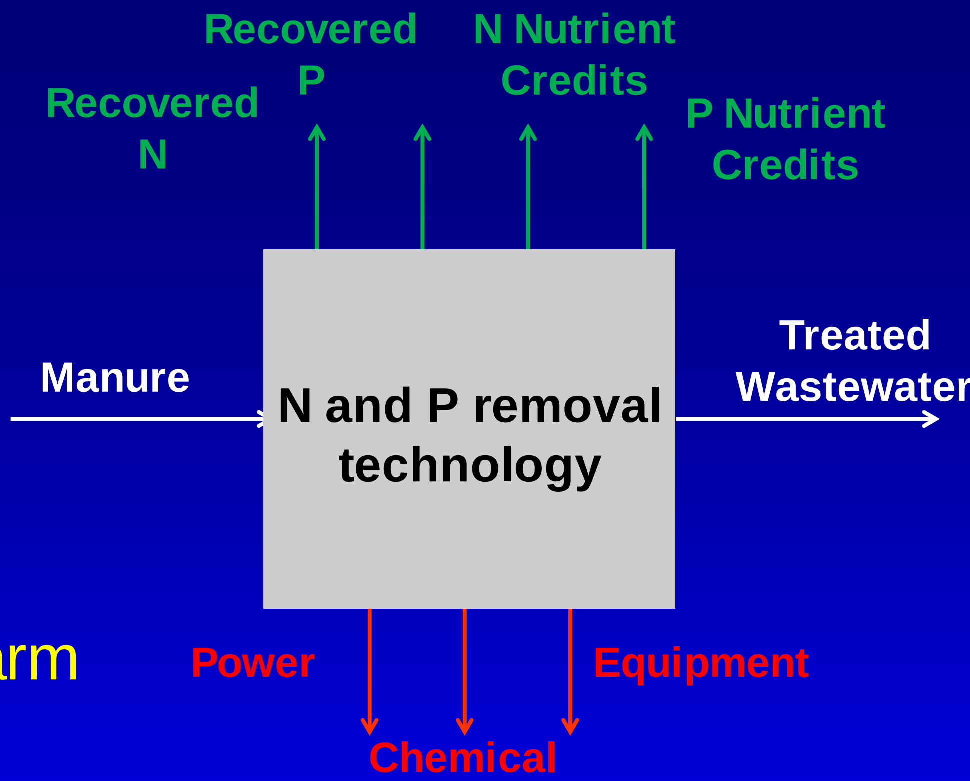
Composition of Recovered Phosphate Minerals (Municipal Centrate) James River WWTP, Virginia					
N	**P_2O_5**	**Mg**	**Ca**	**K**	**Plant Available P)**
Percentages, %					
2.8	**44.1**	**13.6**	0.9	0.7	**98.5**

Triple superphosphate = 46% P_2O_5; Rock phosphate = 27-36% P2O5

Struvite = 5.7 N : 29 P_2O_5 : 10 Mg **Newberyite 41 P_2O_5 : 14 Mg**


Municipal Centrate
P precipitate
MgCl2 + NaOH
without NH3
with NH3

Ecosystem Cost Map



5200-head swine farm (finishing)

Capital and Operational Costs	
Equipment, Chemical, Power	$57,168.47 / year
Potential Revenue	
Sale of fertilizer products (N & P)	$58,538.63 / year
Additional Revenue: Sale of Non-point Nutrient Credits (2:1 trading ratio)	$ 61,449.93 / year

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)

USDA Agricultural Research Service

https://www.ars.usda.gov/southeast-area/florence-sc/coastal-plain-soil-water-and-plant-conservation-research/