SYSTEMIC Living Lab conversations: N stripping-scrubbing technologies

3/112/2020 11:00h CET – 11:45h CET – TEAMS online meeting

Moderator: Marieke Verbeke (VCM, SYSTEMIC project)

Extra information inserted in this summary after the discussion.

Expert Panel:

SYSTEMIC Demonstration Plants, Outreach Locations and Associated Plants

For more information check out:

https://systemicproject.eu/plants/demonstration-plants/

https://systemicproject.eu/plants/outreach-plants/

https://systemicproject.eu/plants/associated-plants/

General description of the technology

When using the technology on a liquid stream (digestate) you first make sure that the nitrogen becomes available in the form of ammonia as only this form of gaseous nitrogen can be recovered.

This can be done either by increasing the pH with caustic lime ($Ca(OH)_2$) or by sodium hydroxide (NaOH) to a pH of 10-11 preferably, or by heating the liquid fraction to 70 °C for example.

Another way to partly increase the pH is using a CO_2 stripper to remove CO_2. After the pH and temperature of the liquid are increased the liquid fraction is passed over a diffuser or through a stripper tower with a packing material that increases contact surface between liquid and an air flow. Some plants (for example Demo plant Acqua e Sole in Italy) use biogas as stripping gas.

Ammonia (NH3) will transfer from the liquid phase to the gas phase. After this, ammonia is washed or scrubbed from the stripping gas with and acid: nitric acid (HNO_3) or sulphuric acid (H_2SO_4) (same system as an acid air scrubber).

The result is a liquid nitrogen fertiliser, ammonium nitrate (NH_4NO_3) or ammonium sulphate ($(NH_4)_2SO_4$) respectively.

We have to make a distinction between 3 different configurations for the N stripping-scrubbing technology:

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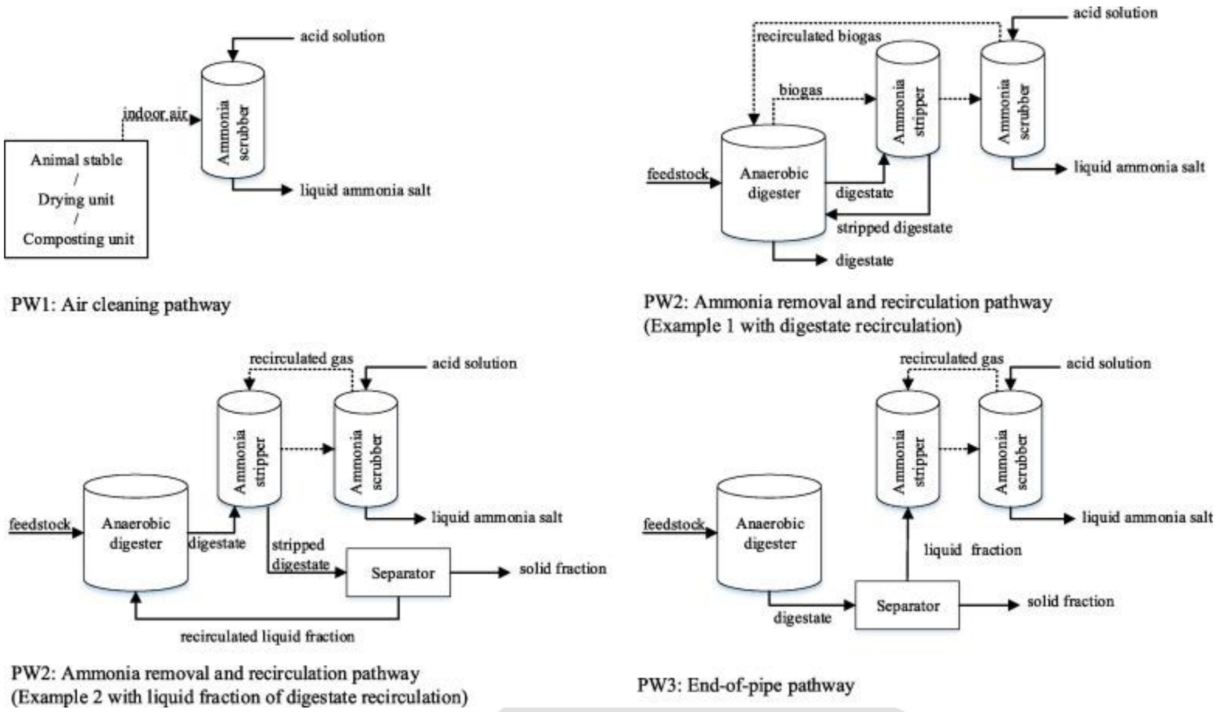

Fig. 1. Pathways (PW) for nitrogen recovery using (stripping-)scrubbing technology.

(i) PW1. Air cleaning pathway

only makes use of scrubbing unit to treat NH_3 rich indoor air from animal stables, drying units and composting installations, especially those mechanically ventilated (Melse and Ogink, 2005). In essence this pathway makes use of capturing volatile NH_3 in its gaseous form by an acid scrubber. A scrubber is a reactor filled with inorganic packing material, with large porosity and large specific area. Water is sprayed with nozzles over the packing material, without leaving any dry area, to prevent the loss of unwashed exhaust air. Part of it is continuously recirculated, the remaining fraction is discharged and replaced by fresh water. Air from animal stables, drying units and composting installations is blown into the system either horizontally (cross-current) or upwards (counter-current). The contact between air and water facilitates the mass transfer between the two phases. In chemical scrubbers, the pH is controlled between 1.5 and 4 by addition of acid substances to the recirculation water, shifting the equilibrium towards ammonium and thus increasing its absorption into the aqueous phase (Van der Heyden et al., 2015).

(ii) PW2. Ammonia removal and recirculation pathway

where (stripping-)scrubbing unit is coupled to an anaerobic digester with the aim to reduce potential NH3 inhibition in the digester by re-circulating the stripped digestate is re-circulated back to the anaerobic digester..

*a. **GNS** has developed a NH_3 stripping-scrubbing technology for digestate of corn and poultry manure, not using any chemicals except Flue Gas Desulphurisation-Gypsum (cheap and Reach-certified). A full scale installation is currently operational at Benas biogas plant in Germany. (read more:https://systemicproject.eu/plants/demonstration-plants/benas-germany/)*

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b. ***DVO has developed a plug flow digester which also includes an NH3 stripping** function. (read more: https://www.dvoinc.com/howitworks.php) and works on chicken manure.*

(iii) ***PW3. End-of-pipe pathway***
where digestate from anaerobic digestion is treated in a (stripping-)scrubbing unit to reduce the ammonium levels in the end product, which is not re-circulated back to the digester.

According to PW2, the use of a stripper can be beneficial when the feedstocks from the digester contain high N levels.
This because too high concentrations of ammonia in the digester can cause inhibition of the methane production (1,5- 7 g.L-1 NH_4^+-N).

Technology provider, UK
If the concentration of NH_3 is very slow and gradually increased the consortium of bacteria has the ability to tolerate higher concentrations of NH_3.

For which digestate types would it be interesting

Poultry manure, waste water treatment sludge, protein rich wastes from food industry

Next to PW2, are there other ways to lower the amount of N in the digester?

Biogas plant in Finland
We don't usually need to prevent high N-levels in digesters, we can recirculate reject water to circulation and as we work in mesophilic conditions and with not that high nitrogen feeds, nitrogen is generally not a problem (usually ~4 g/l as NH4) (with some exceptions, we operate 14 biogas plants). However, we have thought stripping solution for digester N-level adjustment especially if we go to thermophilic.

The motive for stripping for us is (PW3) to clean excess, discharged, reject water (sometimes removing N is enough, and with combination of evapo-stripping you can remove everything else too). In future the motive may be also producing recycled nitrogen.

What is the NH_3 recovery efficiency for such N stripping-scrubbing technologies?

For PW1**: **Air cleaning pathway
Long term monitoring of acid scrubbers at five farm locations was carried out in the study by Melse and Ogink (2005), reporting average NH_3 removal efficiency 90–99% with a minimum and a maximum peak of respectively 40 and 100%.

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For PW3: End of pipe

In the Wings project (https://www.vcm-mestverwerking.be/en/faq/3931/wings) a pilot N stripping-scrubbing unit (Nijhuis Industries) was tested on farm scale in Meerhout (BE), on liquid fraction of dairy cattle manure. 75% of the NH3 from the liquid fraction of the manure could be stripped, meaning 47% of the total N in the liquid fraction. If the manure would be digested first, more ammonia would be available for stripping (70% of total N compared to 50% when not digested).

Results of this test confirmed that it is technically possible to recover nitrogen from non-fermented cattle manure. Unfortunately, at that time, the business case for this stripping and scrubbing installation was not viable and distribution of end products was undefined due to limitations imposed by current legislations.

Theoretically, NH3 recovery efficiencies up to 98-100 %, but they are generally operated to reach 80-90 % recovery in order to reduce the operating costs (Vaneeckhaute 2015).

Biogas Plant in Germany

We have a constant stripping efficiency around 80%, which can be less (75%) if the load of N is higher.

Technology provider in the UK

Stripping efficiency can go up to 100%, especially with the DVO plug flow configuration.

What is used to improve the transfer of NH_4^+ to NH_3

Biogas Plant in Germany

At Benas (the Fiberplus system) we use a CO_2 stripper to increase the pH, no chemicals are added.

Technology provider in the Netherlands

The AMFER system also uses CO_2 stripping.

What about scaling and fouling of the packaging material? Which pre-treatments are necessary?

Scaling and fouling of the packing material of the stripping tower can cause high energy and chemical requirements.

***Scaling**: To prevent scaling a lime-softening step can be installed before stripping, which removes a large part of the Ca, Mg, carbonic acids and carbonates, and increases the pH. In case of high buffering capacity, a preceding CO_2 stripper might also be economical. (Vaneeckhaute 2015).*

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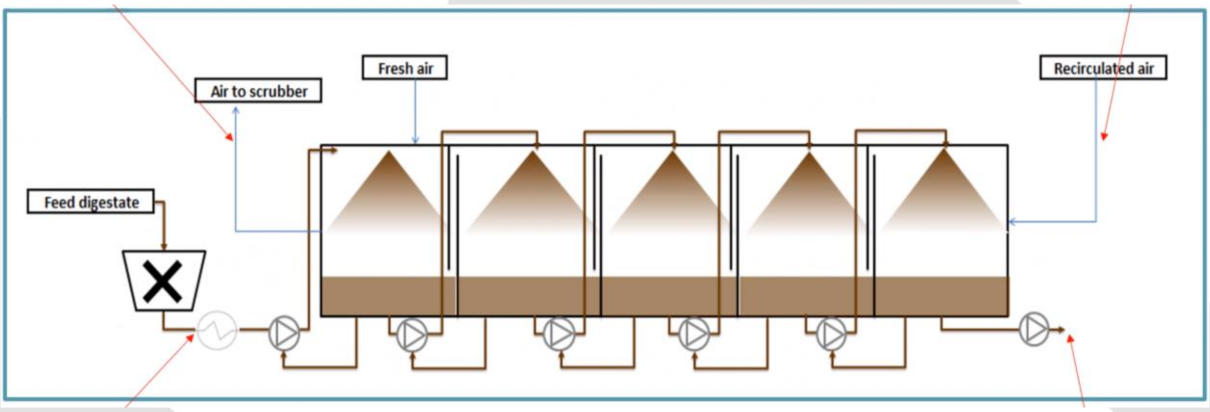
__Fouling__:
This is mostly caused by suspended solids or fibres clogging the carrier material.
Effective and thorough separation and cleaning is therefore essential (Vaneeckhaute 2015).

<u>Biogas Plant in Germany</u>
In most cases it is not necessary to separate the digestate before stripping; an impurity separator and sieves are sufficient, a screw press is also possible.
With our system, we don't have these issues, because we don't work with a packing material to improve the contact surface of liquid and air. We work with multiple vessels, which does require a higher investment cost. However, this is ultimately cheaper in operational costs.

<u>Technology provider in the Netherlands</u>
Colson's AMFER system also works fine on manure or digestate, because it also does not use an internal packing material in the stripping tower but with consecutive vessels.
Because there is no packing material, we can treat streams with a high DM content and no pre-treatment (dewatering, separation) is necessary. You also don't need to clean the tank inside, because there is no packing that could be clogged.

However, it is difficult to design an alternative way of spraying the liquid that increases the contact area to the same degree as a packing material would do.



We work at a low processing temperature (55-65°C) which is easily reached if you have a thermophilic digester and residual heat from the CHP.

The technique is quite complex and high-tech and requires acids and caustic. How much time does the staff need to keep the technology operational?

It is important that the operator or his personnel are adequately trained in chemical processes and safety procedures

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Biogas Plant in Germany

The system can be automated completely, however this is higher in investment costs (programming, PLC). If one would choose to have an operator do the follow-up this increases the operational costs. So, the plant owner has to make this choice themselves.

What is happening now with the end products? Is the market ready for the end products?

Ammonium nitrate

When nitric acid (HNO_3) is used, ammonium nitrate (NH_4NO_3) is produced.
This usually contains 15% nitrogen. (see http://www.digesmart.eu/eng/documentos.html; project on ammonia stripping scrubbing on digested pig manure and producing ammonium nitrate).

This contains both ammonium nitrogen and nitric nitrogen (50/50), meaning that only 50% of the nitrogen is recovered and the other 50% comes from the nitric acid.
Agronomically, nitrate nitrogen is a very fast-acting substance; ammonium nitrogen is gradually absorbed by plant roots.
Alternative niche markets are as a hardener in the production of plywood board and MDF or as an ingredient for fertiliser manufacturers for instance.
Ammonium nitrate can have an explosive character. In practice, pure ammonium nitrate is difficult to detonate. However, the nitrogen content of fertilisers put on the market should not be any higher than 20%.- to prevent intentional misuse (for making explosives)

Technology provider in the Netherlands

In our AMFER system, we standard use nitric acid, producing ammonium nitrate, because this has a higher fertilisation potential.

Ammonium sulphate

When sulphuric acid ($H2\ SO4$) is used, ammonium sulphate ($(NH4)\ 2\ SO4$) is produced.
This usually contains 8% nitrogen.
Ammonium sulphate is a fertiliser that mainly promotes leaf growth. With regular and prolonged use, it is advisable to closely monitor sulphur concentrations in the soil. An excess of sulphur in the soil impairs crop growth.
However, sulphuric acid is cheaper than nitric acid.
The AmS content in the recovered solution ranges from ± 25 % AmS (GNS) and 30 % AmS (Branch Environmental Corp) to 40 % AmS (AMFER, Colsen;) (Vaneeckhaute 2015).

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Biogas Plant in Germany

The products ammonium sulphate solution (AmS) and the solid calcium carbonate (lime) are used on own fields. The organic p-fertilizer (solid fraction) will be also used on own fields of Benas. The produced clean biofibres (a specialty) are used to make paper-products with high market value(https://www.magaverde.de/). This is the business model of Benas. If in other cases the fertilizers must be sold, however, only low market prices can be achieved. Here we want to achieve even better solutions (upgrading the products to complete fertilizers ...).

Legal status

AS: In Flanders there is an exception in Flanders to allow scrubbing water (ammonium sulphate) from chemical air scrubbers to be administered as fertiliser (above 170 kg of animal N/ha), this does not apply to ammonium sulphate derived from liquid (digestate) stripping & scrubbing.
As for ammonium nitrate, although the product has the same characteristics as fertiliser, the status of 'animal fertiliser' currently remains applicable for use on the land according to the provisions of the European Nitrate Directive.

In September 2020 a final report was published on SAFEMANURE, a study performed by the Joint Research Centre (JRC), which goal was to define harmonised criteria for the safe use of nitrogen (N) fertilisers, partially or entirely derived from manure through processing in Nitrates Vulnerable Zones above the threshold established by the Nitrates Directive (170 kg N/ha/year). A new term for Recovered Nitrogen from Manure, RENURE, was introduced. All products mentioned in the document (scrubber salts, mineral concentrates from membrane filtration) are able to comply to the following criteria:

- *RENURE materials should have a mineral N:total N ratio ≥ 90% or a total organic carbon (TOC):total N ratio ≤ 3, where the ratios should be adjusted for any Haber-Bosch-derived N added during the manufacturing process.*
- *RENURE materials should not exceed the following limit values:*
  - *Cu: 300 mg kg^{-1} dry matter;*
  - *Zn: 800 mg kg^{-1} dry matter.*
- *Member States should take the necessary provisions so that the timing and application rates of RENURE are synchronised with plant nutrient requirements to minimise nutrient leaching and run-off losses involving in particular specification of information on the nutrient content of the RENURE and maintaining a living plant cover on the land for as much of the year as possible or equivalent measures.*
- *Member States should take the necessary provisions to prevent and minimise NH_3 emissions during RENURE application on the field, especially*
  - *for RENURE N fertilisers that have > 60% of its total N present in a form other than NO_3^-- N; and*
  - *for RENURE N fertilisers applied on soils of pH_{H2O} > 5,5.*

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- *Member States should take the necessary provisions to prevent and minimise emissions to air resulting from storage through enforcing appropriate storage conditions of RENURE.*

Huygens et al. (Huygens et al. 2020) thus propose criteria that define the point at which N-rich manure-derived materials meet standards to act as 'chemical fertilisers' as defined in the Nitrates Directive. Such materials are referred to as 'REcovered Nitrogen from manURE (RENURE).

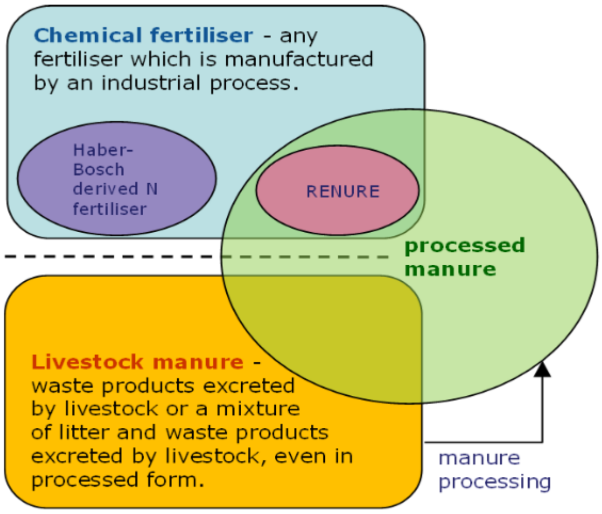

Figure 1 The relation of RENURE to processed manure and livestock manure. Figure from powerpoint presentation of Wim Debeuckelaere (European Commission, DG ENVI).

The report from the SAFEMANURE study, including the proposed criteria are published and now they have to be translated to European Legislation. An amendment of the Nitrate Directive is highly unlikely, but some sort of derogation for these RENURE could be an option. A final legislation is not expected until 2022, and after that member states can still choose how to translate this into national legislation.

Technology provider in the UK

Creating market value for these scrubber salts (AmS and AmN) is very regionally depended. It could only provide revenues in regions with a high nutrient demand.

It can also be interesting to use these products to blend with (dried) solid fraction to create a more tailormade nutrient composition.

Biogas Plant in Germany

The stripping technology is optimized, but an optimal use of the products, the P separation and the further processing of the stripped fermentation residues into pure water are still open issues.

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SYSTEMIC

Circular solutions for biowaste

What are the investment costs and operational cost, maintenance cost, energy use for your treating capacity?

Biogas Plant in Germany

For Benas biogas plant (about 8 to 25 t/h stripping capacity, heat consumption without costs):

	Cost € t^{-1} digestate	Benefit € t^{-1} digestate
Amortized capital cost	3.2	
Electrical energy	1.2	
FGD-gypsum	0.23	
Insurance, maintenance, labour	1.1	
Ammonium sulphate revenue		3.5
Liming substrate revenue		0.78
Heat valorisation		2.8
Total	5.7	7.0

800 m^3/day at 2,400 mg NH_4-N/L (90 % recovery)

Capital costs *of stripping are relatively low compared to biological activated sludge systems for nutrient removal and depend on the method used for pH-increment.*
-chemically:± € 500,000 to € 1.58 million
-physically; € 3.5 million to € 11-15million
(Vaneeckhaute 2015)

Operational costs *depend a lot on the operational temperature, pH, and liquid flow rate.*
90 % NH_3 recovery efficiency , temperature of 70 ºC, a pH of 11, and a flow rate of 70 m^3/h overall costs are estimated at ± 8.1€/ m^3,
90 % NH_3 recovery efficiency , temperature of 30 ºC, a pH of 11, and a flow rate of 70 m^3/h this would be ± four times less, i.e. 2.0 €/ m^3, (Collivignarelli et al., 1998).
(Vaneeckhaute 2015)

Electricity consumption *: 127-400 kWhel/h(1.54-12 kWhel/m^3)*
Heat consumption *2,115-2,333 kWhth/h (62-69 kWhth/m^3; note: ± 50 % could be recovered within the process)*
(Vaneeckhaute 2015)

H_2SO_4 (concentrated at 95-97 %) consumption at 5.5-6.8 ton/day or 7.0-10 kgm^3 digestate.
If NaOH is used for pH-increase, it consumption would amount to 6.0-6.5 kg/m^3
As such, operational costs range between € 1.4 and € 2.5 million/year depending on the system, equivalent to € 4.5-8.6 m^3 of digestate
(Vaneeckhaute 2015)

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Pilot: Nijhuis Industries

For the farm-scale installation tested in the Wings project, with a capacity of 25 m³ of liquid fraction/day at a dairy farm where no fermentation or other heat source was present. Cost 21.30 euro/m³ of manure or 10.50 euro to remove 1 kg of nitrogen, excluding removal/processing of solid fraction and effluent.

Does anyone have experience with crystallisation of ammonium sulphate?

Technology provider in the Netherlands

We tried it and succeeded but when looking at the total financial balance, there was no difference in producing a AmS solution of 30% or crystals of 100% AmS.

Biogas Plant in Germany

We had tried the crystalization with different systems, but it was too expensive. It is not financially feasible to install this only for one plant. Maybe if more plants would work together on this, the advantage of volume could decrease the costs.

Biogas Plant in the Netherlands

Same outcome here, not even for 18.000 ton AS (40% w/w/) per year

The Dutch company Circular Values is setting up a 'crystallisation plant' in Tilburg with the capacity of 60.000tons per year. It will be able to crystallize ammonium sulphate solution and other salt solutions. They still want to investigate how cost-efficient it can be to scale down the crystallizers to fit biogas plant scale or even farm scale.

Huygens, D., G. Orveillon, E. Lugato, and S. Tavazzi. 2020. *Technical Proposals for the Safe Use of Processed Manure above the Threshold Established for Nitrate Vulnerable Zones by the Nitrates Directive (91 / 676 / EEC)*.

Vaneeckhaute, Céline. 2015. "Nutrient Recovery from Bio-Digestion Waste: From Field Experimentation to Model-Based Optimization."

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