

# Recovering ammonium fertiliser – an alternative to blowing it away

Tim D. Evans<sup>1</sup> and Andrew Thompson<sup>2</sup>

## Affiliation:

<sup>1</sup> TIM EVANS ENVIRONMENT, Stonecroft, Park Lane, Ashted, Surrey KT21 1EU England

<sup>2</sup> Severn Trent Water

Contact : email [tim@timevansenvironment.com](mailto:tim@timevansenvironment.com) tel: +44 (0) 1372 272 172

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## Abstract:

As a part of remodelling one of its major wastewater treatment works (750,000 pe), Severn Trent Water decided to examine ammonia recovery as an alternative to “conventional” biological treatment of the ammonia load in liquor from dewatering anaerobically digested sludge. This paper will review the technologies, their carbon footprints and their costs.

## Introduction

Nitrogen (N) and phosphate (P) in the liquor from dewatering indigenous digested sludge can be 25% of the load on a wastewater treatment works (WwTW) and can be even more if the works is a treatment centre for imported sludges if the conventional route of returning it to the head of the works (the influent to treatment). Additionally this liquor contributes little BOD to feed the biomass that is needed if it is to be treated biologically. It is a “double whammy” that makes biological removal of phosphate less viable, thus pushing the process selection to chemical-P removal, and increases the requirement for methanol for denitrification and possibly VFA dosing if bio-P is chosen. The objective of this project was to examine whether physico-chemical stripping and recovery of ammonia would be a financially viable and practicably operable alternative.

The economic balance between physico-chemical stripping and biological degradation is influenced by the capital costs of the options, including the implications for the rest of the WwTW, the operating cost of the options, the ease of operating the options, the possible income from recovered fertiliser and the environmental impacts [and potentially taxes] of the options.

Energy prices affect the cost of just about everything and they are forecast to increase. Biological degradation processes could be more energy intensive than stripping. Energy prices are expected to increase because of increasing demand, decreasing resources, measures to reduce climate change and other impacts of using energy. Businesses will be penalised for using electricity because of carbon reduction legislation.

## Fertiliser

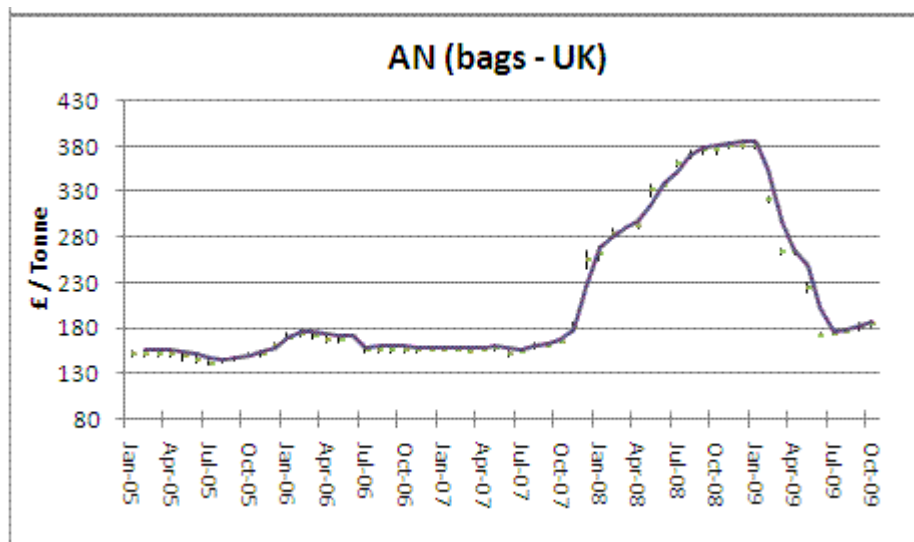
Fundamental questions when considering recovering fertiliser from dewatering liquor is whether there will be a market for the product(s) and what will be the resilience of that market. Crop yields, including grass, are determined by the availability of plant nutrients as well as water, temperature, soil aeration, etc. The maximum potential yield of a crop is determined by the most restricted of these factors. A cereal crop contains about 20 kgN/tonne grain and 7 kgN/t straw. A wheat crop yielding 10 t grain/ha will remove 200 kgN/ha when the straw is chopped and incorporated in the soil, i.e. not removed from the field. This N must come from somewhere. Rainfall contributes maybe 50 kgN/ha but it can also leach N. If the previous crop was a legume,

it will have fixed N from the air and its residues would provide some N to the wheat crop. Manure, biosolids and mineral fertiliser provide the balance. Soils benefit from additions of organic matter because it stimulates stable soil structure but the weight of the equipment used to apply the organic matter reduces this benefit to some extent because of compaction. Zhang et al. (2009) have shown in a preliminary greenhouse study, which is now being transferred to the field, that there are either biostimulants in biosolids that can be assimilated by plants or substances in biosolids that stimulate microbes to produce stress-ameliorating biostimulants that enhance plant growth and tolerance of drought stress.

A requirement for mineral fertiliser is that it should be concentrated so that the minimum weight has to be carried across the field, spreaders have to fill up as infrequently as possible and work rates are fast. Another agronomic requirement is that it should be possible to spread fertilisers evenly and accurately. Some farmers and contractors favour liquid/solution fertilisers because although the mass per unit of nutrient is greater, they can be spread precisely and they are suitable for topdressing, i.e. for applying onto growing crops. Splitting the N fertiliser over several topdressings is preferable to a single application.

Ammonium nitrate (34.5%N) is the principal N-fertiliser in Britain but for the purpose of stripping from dewatering liquor it has two disadvantages compared with ammonium sulphate (i) nitric acid is more hazardous than sulphuric acid and it embrittles plastic if that is used for fabricating the plant and (ii) ammonium nitrate is a powerful oxidising agent with a risk of spontaneous combustion/explosion if mixed with organic matter, which is the reason it is illegal in Ireland.

The prices of mineral fertilisers trebled in 2008 (Figure 1 **Error! Reference source not found.**); subsequently, the global economic crisis caused fertiliser prices to crash to near their historic



level but they are rising again now.

The price of nitrogen fertiliser is related to the price of energy, the demand for fertiliser and the industry's ability to supply. Investment in fertiliser manufacturing capacity was negligible for several years because profits were restricted; therefore when demand increased supply was inelastic and prices rose. Unlike phosphorus, which is quite scarce, nitrogen is abundant; 80% of air is N<sub>2</sub> gas, it just requires energy to "fix" this nitrogen so that it can be used. However given that the global population is expected to increase from 6 bn currently to 9 bn by 2050, that N is

one of the three major plant nutrients, that as per capita wealth increases people want more food and more animal products, that a doubling of agricultural production is expected to be required, and that genetically engineering N-fixation into the major crop plants is a long way off, the demand for N-fertiliser is not going to decrease.

Ammonium sulphate is a useful fertiliser (21%N : 60%SO<sub>3</sub>) for top-dressing crops, either as liquid or solid. Ammonia is a good nitrogen fertiliser. Clean air legislation has removed sulphur emissions and thus S deposition on farmland. S-requirement [deficiency] is widespread in UK, especially [but not exclusively] in oilseed rape (Figure 2). Cereals and grass can also require sulphate-sulphur fertiliser; the amount taken off in crops is similar to the offtake of phosphate.



**Figure 2 Sulphur response of oilseed rape (left received S-fertiliser, the right was the control courtesy Rothamsted Research)**

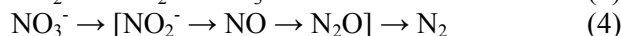
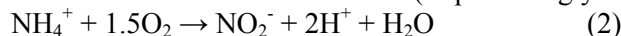
The somewhat specialist companies who apply ammonium sulphate solution and other solution fertilisers desire at least 8%N (i.e. 40% w/w) in order that they are not transporting excessive weights of material (but less than the saturated concentration). Saturation occurs at 541.8 g/L at 25°C, 536.49 g/L at 20 °C, 524.6 g/L at 10°C and 515.35 g/L at 0°C.

Ammonium sulphate has value because of its sulphur content, which is expressed as SO<sub>3</sub> in UK fertiliser practice. A typical application to correct deficiency would be 30-50 kgSO<sub>3</sub>/ha. At 50 kgSO<sub>3</sub>/ha the 8% N ammonium sulphate solution would supply about 20 kgN/ha, which is 10-20% of the total N requirement of most crops. Agronomically and environmentally, it would not be detrimental to increase the application rate of SO<sub>3</sub> in order to increase the application rate of N. N is normally applied split over three applications – as top-dressings.

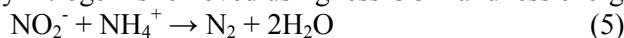
#### Biological removal of nitrogen

The conventional approach to dealing with dewatering liquor at WwTW has been to route it to the head of the works so that suspended solids, N and P can be treated. Inevitably this increases the size of WwTW required. The ratio of food to N and P in dewatering liquor is much less than ideal for biological treatment and in this respect worse than settled sewage.

The N in the dewatering liquor from digested sludge is mostly ammonium salts ( $\text{NH}_4^+$ ); conventional biological treatment (activated sludge process, Arden and Lockett, 1914) involves complete oxidation to nitrate ( $\text{NO}_3^-$ ) (equations 2 and 3), and subsequent reduction of the nitrate to dinitrogen gas ( $\text{N}_2$ ) under anoxic conditions using COD as the energy source. The introduction of oxygen (air) into wastewater for the oxidation of ammonium requires a large amount of energy. Furthermore, the amount of COD present in the wastewater is often limited, making the purchase of COD in the form of methanol (or possible glycerol) necessary.



Due to the long sludge age required for nitrification, large reactors are needed. Some innovations stop at equation 2 (“nitritation”), this only requires 75% of the oxygen (and the energy) of going through to nitrate (equation 3), they then denitrify the nitrite to dinitrogen gas using ammonia as electron donor (equation 5) which requires 40% less COD (e.g. Thomas and de Mooij, 2007). In this way nitrogen is removed using less COD and less energy and with a smaller footprint plant.



However nitritation generates the same amount of acidity as nitrification; if this cannot be neutralised by the inherent buffering capacity (alkalinity) in the liquor, for instance because of ferric dosing to enhance dewatering, there will be a requirement for caustic soda dosing to maintain pH.

Nitritation, nitrification, denitritation and denitrification all “leak” **nitrous oxide** ( $\text{N}_2\text{O}$ ) which is a powerful greenhouse gas (Global Warming Potential factor 298 - ) and it has been shown to be the single most important Ozone Depleting Substance (ODS) emission currently and is expected to remain the largest throughout the 21<sup>st</sup> century.  $\text{N}_2\text{O}$  is unregulated by the Montreal Protocol. Limiting future  $\text{N}_2\text{O}$  emissions would enhance the recovery of the ozone layer from its depleted state and would also reduce the anthropogenic forcing of the climate system, representing a “win-win” for both ozone and climate (Ravishankara, et al., 2009).

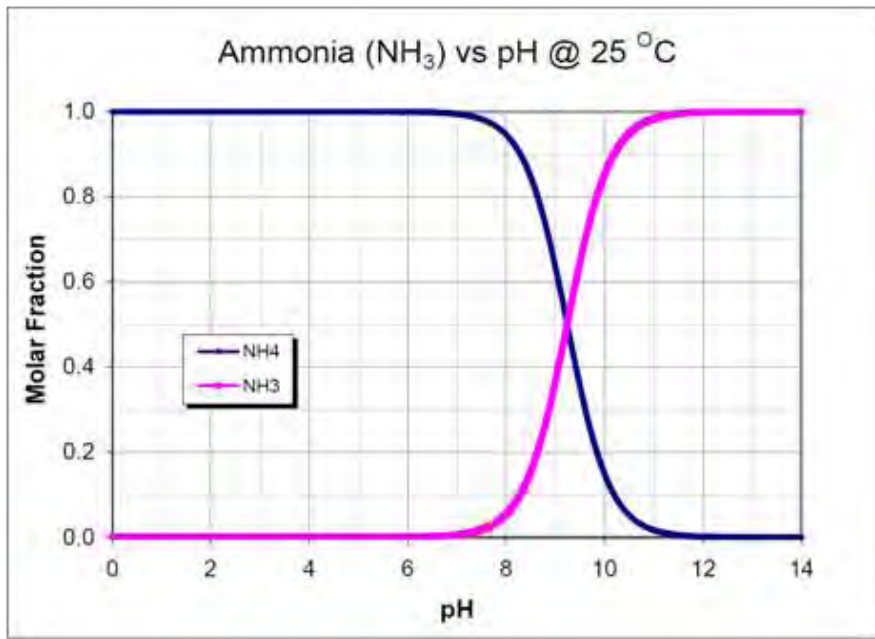
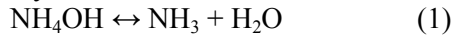
Kampschreura, et al. (2009) reviewed  $\text{N}_2\text{O}$  emission from WwTWs and found there is a wide range of estimates in the literature but that overall it is probably only 3% of the estimated total anthropogenic  $\text{N}_2\text{O}$  emission, however they estimated it is 26% of the greenhouse gas footprint of the total water chain. It is unclear whether nitrifying or denitrifying microorganisms are the main source of  $\text{N}_2\text{O}$  but without doubt reducing N-cycling within a WwTW by stripping it from dewatering liquor will reduce  $\text{N}_2\text{O}$  emission. Kampschreura, et al. reported the main operational parameters are:

- (i) low dissolved oxygen in the nitrification and denitrification stages,
- (ii) increased nitrite concentrations (nitritation/denitritation?), and
- (iii) a low COD/N ratio in the denitrification stage.

So decreasing energy consumption by decreasing aeration actually increases the greenhouse effect (even though it decreases  $\text{CO}_2$  emission) because of the 298 GWP emission factor of  $\text{N}_2\text{O}$ . They also reported that growth on internal storage compounds [for bio-P] can lead to  $\text{N}_2\text{O}$  emission, but the mechanism is unclear and scientific findings are contradictory.  $\text{N}_2\text{O}$  is not accounted currently and emission factors are not reliable but with climate change and ozone destruction it must be a threat to the water industry that it will be included in emission accounting/capping at some time in the future.

#### Physico-chemical ammonia stripping

Ammonia stripping has been practised at the VEAS WwTW in Oslo (population equivalent 650,000) for more than 10 years (Evans, 2007). At VEAS the MAD sludge is treated with lime to kill plant and human pathogens, which means that its pH is favourable for air-stripping but the lime content also means that the stripping tower and packing media must be de-scaled bi-weekly, which is a disadvantage. However, VEAS' operational experience proves that the concept of air-stripping from alkaline dewatering liquor and re-absorption with mineral acid is practicable and very reliable. VEAS recovers 90% of the ammonia from the filtrate (which is 1200-1500 mgN/L). The operational availability has been 99.2% up-time and very little attendance is required. Ammonia gas dissolved in water is in a pH-dependent and temperature-dependent equilibrium with ammonium hydroxide (Figure 3) as temperature increases the solubility of ammonia decreases, i.e. it is easier to strip:



**Figure 3 Relationship of the ammonia - ammonium equilibrium to pH at 25 °C (from DiFilippo, 2006)**

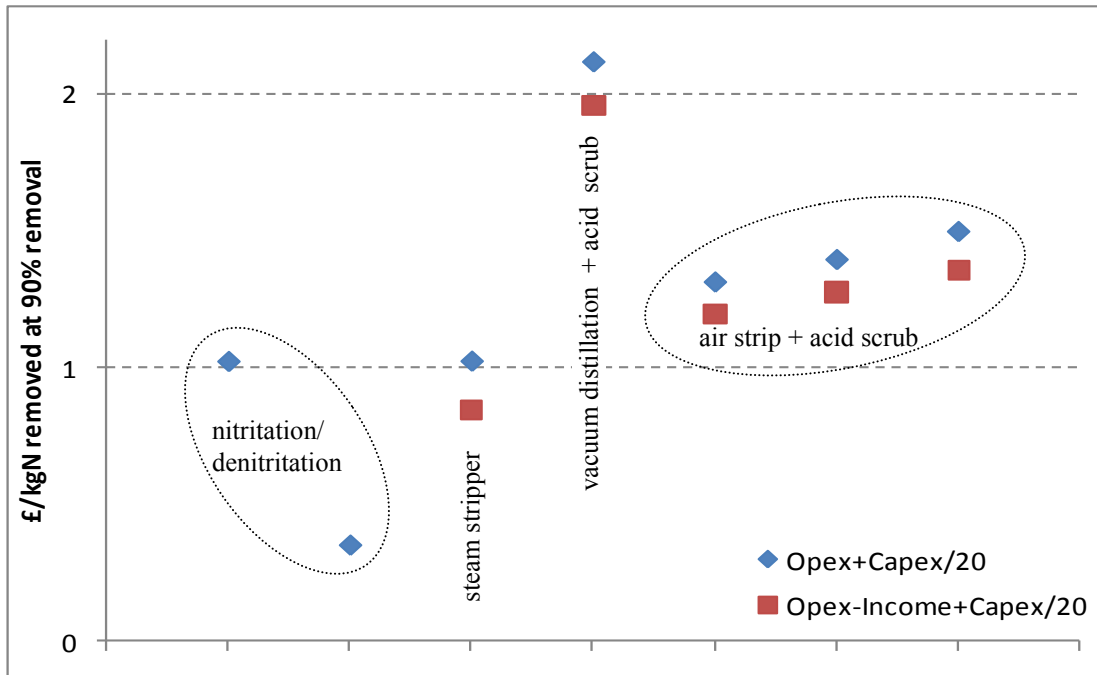
Steam stripping and vacuum stripping are alternatives to air stripping. The former has the advantage that it produces the most concentrated N product, which has the widest diversity of potential uses and therefore the greatest selling price. All of these stripping technologies use established chemical engineering and each is compatible with upstream recovery of phosphate as struvite. Struvite recovery would only result in a small reduction in the ammonia yield, which would not affect the overall economics.

## Results

We assumed that merely building a larger activated sludge plant to nitrify/denitrify, with the associated methanol/glycerol [and VFA] dosing would have been more expensive (Capex and Opex) than side-stream treatment so it was decided it was unnecessary to include this in the evaluation. Companies were selected and invited to submit proposals for side-stream treatment of liquor from centrifuge dewatering of mesophilically anaerobically digested sewage sludge. They were asked for information about capital and operating costs that would be used for budgetary purposes only. They were advised that there would be 2184 kW/h thermal energy in the form of

hot water from engines using biogas from maize biomass crop digesters (forward temperature 85 °C; return temperature 75 °C).

Initially the idea was that stripping would be by adjusting the pH of the liquor to about 10.7 and then stripping the ammonia with a counter current of air in a stripping tower and absorbing the ammonia in a scrubbing tower using sulphuric acid. Whilst investigating suppliers, two alternative technologies were found: steam stripping under reduced pressure (0.25 atm. abs.) and condensation as 25% ammonia solution and vacuum distillation combined with an acid scrubber. Steam distillation produced the product with the highest N concentration (20.6 %N), requires only one tower, whereas the others require two, and does not require acid scrubbing, which is a cost and a safety benefit. The cost data are summarised in Figure 4.



**Figure 4 Unit costs of N removal (£/kgN) with Capex written off over 20 years, with and without allowing for income from selling the recovered ammonia products**

The analysis behind Figure 4 merely divides the Capex by 20 years, it does not allow for renewals, residual values, inflation, carbon cap and trade or loss of revenue on capital. It is not a discounted cash flow. Labour is a negligible part of the cost of any of the options; the processes are all more or less automatic.

Over the course of 20 years we can expect prices of energy, chemicals and fertilisers to inflate and all at different rates. We can also expect that the cost of climate change emissions will become internalised through financial mechanisms that will become increasingly stringent over time.

The lowest unit costs of N-removal were nitritation/denitritation and steam stripping, which were almost identical before the [conservatively estimated] income from selling the product was subtracted (Figure 4). Regarding future proofing, steam stripping (at 0.25 atm. abs.) had the lowest unit electricity use (Figure 5).

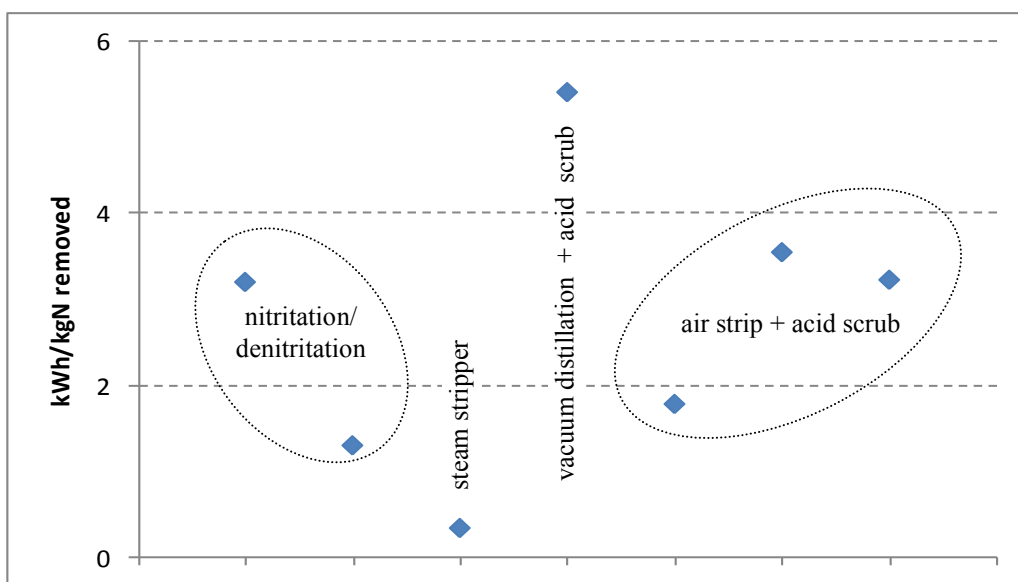


Figure 5 Unit electricity use kWh/kgN removed

## Conclusions

This budgetary investigation has revealed that:

- there is a resilient market for ammonia products recovered from treating dewatering liquors by physico-chemical stripping.
- there is a technology for physico-chemical stripping (based on establish chemical engineering) that is cost competitive with biological N-removal even before allowing for income
- after allowing for income, physico-chemical stripping is less costly than biological N-removal and is more future-proof because it has a smaller carbon footprint; it also has a smaller physical footprint.

## Acknowledgements

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