# RELIABLE RESOURCE RECOVERY

**Dr. Robert Eden, Organics, UK,** discusses the use of resource recovery to minimise waste generation and preserve natural resources.

In aqueous solution, ammonia exists in two forms: unionised ammonia ($NH_3$) and ionised ammonia ($NH_4$+), with $NH_3$ being the form that is toxic to most fish species, even at low concentrations. Ammonia is also one of the most commonly produced chemicals in the world, with around 200 million t produced in 2018. The fertilizer industry uses approximately 85% of global production. The manufacture of ammonia is, therefore, crucial for the world's agricultural industry. From it, all fertilizers that contain nitrogen are produced. However, when ammonia penetrates through to parts of the environment where it is unwanted, it becomes a source of damage to human health and ecosystems. As such, treatment of ammoniated wastewater streams is a perennial issue to be addressed.

There are many approaches that may be taken to successfully address the problem. The real issue is not so much what can be done, but which of the available options is the best for the specific circumstances under consideration. The increase in annual production of ammonia is just keeping pace with the increasing world population and with its increasing standard of living. It is to be expected that growth in demand will continue.

In terms of ammonia removal options, the classic nitrogen cycle has provided various robust approaches, employing bacteria which are well known and widely applied. These biological nitrogen-removal processes include nitrification, nitritation, and anammox. Oxygen and carbon are variously applied (anammox does not require carbon addition) to manage bacterial colonies which will reduce ammonia, whilst producing varying amounts of sludge and carbon dioxide.

The alternative approach of physical-chemical ammonia management has had a mixed application history. These technologies include breakpoint chlorination, ion exchange, electro-dialysis and, the subject of this article, ammonia stripping. Each method has its optimum point of application but the use of any of these is not as widespread as biological methods.

Ammonia stripping entails the passage of air counter-current to a liquid stream to release and remove ammonia gas. The problem is, however, that ammonia is held as an ion ($NH_4$+), in

**Figure 1.** WENT landfill facility – 3300 $m^3$/day.

**Figure 2.** NENT landfill – 2500 $m^3$/hour.

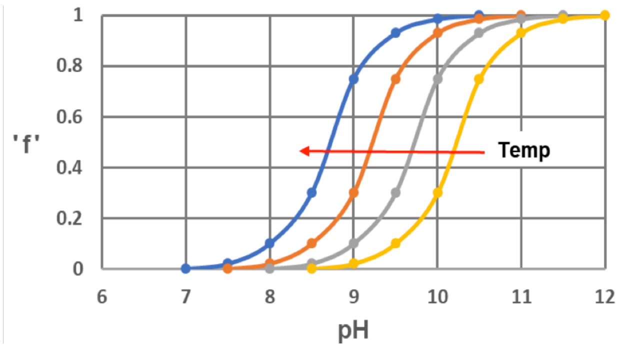


**Figure 3.** The effect of pH and temperature on 'f'.

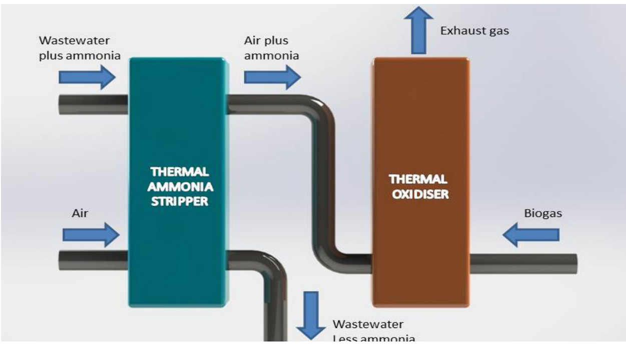


**Figure 4.** Thermal ammonia stripping with thermal oxidation.

wastewater when at around a neutral pH, usually with a carbonate ion, forming ammonium carbonate, $(NH_4)_2CO_3$ – a salt. At ambient temperatures and neutral pH, the ammonium ion will not break to release ammonia gas, $NH_3$. It is, therefore, locked in. The solution to this problem is to either raise the pH or the temperature of the wastewater, or both. An elevated temperature or pH will break the ammonium ion bond and release the ammonia gas into solution, ready for removal.

Both options for breaking the ammonium ion bond require the addition of chemicals or heat. pH adjustment requires the pH to be raised to 10.5 or 11.0, usually meaning the addition of serious quantities of alkali. This is often followed by an obligation to subsequently dose the treated wastewater with acid to bring the pH back down to a compliant range for discharge. With the thermal route, wastewater needs to be heated to above 70°C. Where waste heat is not available, the cost of premium grade fuel or electricity can often be prohibitive.

In 1997, following extensive pilot trials and process evaluation, air stripping was eventually chosen as the core nitrogen removal process for the WENT landfill site in Hong Kong, currently operated by Suez. The plant has been operational since 1998 and has a design flow rate of 1800 $m^3$/ day, recently upgraded to 3350 $m^3$/day (Figure 1). The initial design duty for this first plant was an influent of 6700 mg/l, to be reduced to an effluent of 100 mg/l. The WENT facility now removes 14.5 tpd of ammonium ion. Subsequently, similar processes have been installed on six additional sites around Hong Kong, with the largest single unit having a capacity of 2600 $m^3$/day, with one other site having a total installed treatment capacity of 4000 $m^3$/day. The thermal stripping process was installed as a front-end add-on to an existing biological leachate treatment plant at the NENT landfill, where a change in the consented discharge concentration required considerably lower effluent total nitrogen (Figure 2).

The air-stripping process used at all six sites incorporates two defining features:

- The process is carried out at elevated temperatures, avoiding the need for alkali addition.
- The stripped ammonia is oxidised thermally to nitrogen gas, avoiding the more typical route of scrubbing with sulphuric acid and the consequent problem of its disposal.

For the most part, landfill gas is used as the source of heat for the stripping process, and as a fuel for the thermal oxidation process.

Hong Kong being a densely populated area, there is generally a shortage of available land on which to build biological wastewater treatment facilities. Historically, there has also been a great deal of landfill gas available. The instruction with the first constructed unit was to use as much landfill gas as possible, the balance being simply flared. The unit was designed with a landfill gas flow rate of 6000 cubic m/hour.

Clearly, this is not a replicable situation, except for in Hong Kong. Landfill gas was seen to be more of a nuisance than an opportunity. The electrical grid in Hong Kong is supported by a significant excess capacity, meaning that in 1997 additional small-scale electricity generation was not encouraged.

This position has changed over the years, with the Hong Kong authorities having moved to encourage the production of renewable energy. The landfill sites in question have seen their landfill gas production rates decline with time. The issue of thermal load has moved from a requirement to maximise gas-use to one of minimisation.

Improvements in heat recovery and control of heat losses have made a dramatic impact on thermal loads but the basic plant configuration means there is still a large heat requirement.

The equation governing the relationship between ammonia gas and the ammonium ion may be written as follows:

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

A dissociated ammonia ion ($NH_4^+$) is converted to undissociated ammonia gas ($NH_3$) by the addition of a base ($OH^-$), such as sodium hydroxide. As the temperature of the water increases, so does the amount of free ammonia gas.

The ratio of ammonia in the gas phase to the total ammoniacal nitrogen, referred to as 'f', may be expressed as follows:

$$f = [NH_3] / [NH_3] + [NH_4+]$$

The relationship between pH, temperature, and 'f' takes the general form represented in Figure 3.

Landfill gas, or in one case, biogas from anaerobic digestion, is combusted to raise the system temperature. Steam is produced, and wastewater heated. Once the ammonia gas is released it is transferred into air. This ammoniated-air is then used as secondary combustion-air in a thermal oxidiser, thereby facilitating both combustion and the destruction of ammonia gas. As can be seen in Figure 4, there are therefore two separate heat loads that are required to heat the incoming wastewater and to destroy the ammonia. They are reduced and minimised by means of heat recovery, but they both remain extant.

This technology has been investigated over the years, with varying conclusions as to its relevance in wastewater treatment. A commonly perceived difficulty is that of temperature. Others have concluded that the use of ammonia strippers is too costly because of the volumes of air required. The wind-cooling effect of air passing up a column is also considered to be a source of difficulty, as the ambient temperature approaches zero. A temperature-drop of around 5°C to 6°C has been found to be unexceptional.

The presence of landfill gas from a landfill site, or biogas from an anaerobic digestion facility, adds another dimension to the realistic application of such technology. Such biogas gas can be used to raise the temperature of the wastewater, thus making the removal of ammonia easier and less prone to the problems envisaged or encountered. As the temperature rises, not only does the risk of freezing decline, but the amount of ammonia gas available for removal increases.

The challenge remains, however, to reduce the form of the heat required. Waste heat can be used for system heating but there remains the issue of ammonia destruction by means of thermal oxidation.

One solution to the issue of fuel for thermal destruction is to remove ammonia gas from air by means of acid scrubbing. If sulphuric acid is employed to produce ammonium sulphate, for example, a revenue stream may be added into the equation. Phosphoric or nitric acid may similarly be employed. Nevertheless, in many situations the additional logistics required to manage acid on site, as well as the storage and transport of ammonium salts, have made this option unattractive.

It should be noted that the creation of an ammonium salt is significantly exothermic, leading to a situation where, once started, the overall system may be self-heating. In the case of the WENT unit, 14.5 tpd of removed ammonia would produce approximately 55 tpd of ammonium sulphate, with a commercial value to the order of US$2 million/year. From this, of course, must be deducted operational costs.

Another innovative option developed by Organics, in conjunction with the University of Warwick in England, is to use the mechanics of the ammonia-water thermal absorption cycle to recover ammonia, either as anhydrous ammonia liquid or as ammonium hydroxide (Figure 5) The advantage of the former, apart from commercial value, is that it may be easier to handle,

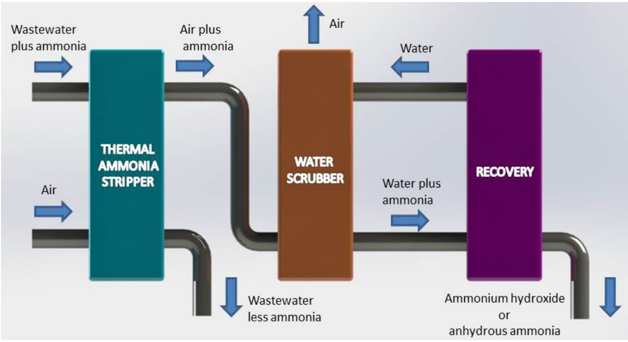


**Figure 5.** Thermal ammonia stripping with ammonia recovery.

whereas the latter also has a commercial value when a concentration of 30% ammonium hydroxide in solution is produced. Production of anhydrous ammonia involves the use of a cold-water scrubber to extract ammonia gas from air, followed by a series of heaters, and a final condenser to produce liquid ammonia.

According to a recent survey of the industry, ammonia costs on average approximately US$2.50/kg to dispose of through municipal sewer systems. A thermal ammonia stripper typically can remove 1 kg of ammonia using 1 kW/hour of electricity, 80 MJ of waste heat, and with no requirement for chemical additions. This represents a significant saving. The heat requirement for a wastewater flow of 2000 $m^3$ /day would typically be 4 MWth for the ammonia stripper, with a similar amount required for thermal destruction. Where either anhydrous ammonia or ammonium hydroxide are produced, the total heat load remains similar but thermal destruction is no longer required.

One particular item which requires some attention, both during design and operation, is the issue of packing cleaning. Once the carbonate ion is released from ammonium carbonate, it can combine with calcium to form calcium carbonate. This, in turn, will precipitate out on the packing, eventually leading to blockage. In Hong Kong, systems have been developed to remove and replace packing relatively quickly. In general, the operators have not found this to be an onerous service requirement. Typically, a packing clean will be required once every three months, taking a couple of days. In-situ, acid-cleaning recirculation loops are also an option.

The advantages of thermal ammonia stripping for the management of nitrogen in wastewater can be summarised as follows:

- Minimal footprint.
- Where used with waste heat, a very low operating cost.
- No sludge production.
- No carbon-source addition required.
- Practically no carbon dioxide production.
- Fast start-up and shut-down.
- Predictable performance which is subject to mechanical process controls.
- The option for revenue generation.

With an ever-increasing demand for natural resources, growing populations, surgent community expectations, and increasing costs, the need to better manage natural resources has become paramount. Resource recovery can minimise waste generation and preserve natural resources, whilst reducing costs and generating additional revenue streams. WF