

# Managing Ammonia in Wastewater

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Ammonia is one of the most commonly produced chemicals globally. Efficiently removing it from wastewater streams could allow it to serve as a source of revenue in many applications.

Ammonia is currently the second most commonly produced chemical in the world (after sulfuric acid), with around 200 million metric tons (m.t.) produced in 2018. Nearly 85% of all ammonia produced is used for fertilizers (1). Although nitrogen comprises almost 80% of the earth's atmosphere, because it is inert, it is chemically and biologically unavailable for use in this form. Therefore, ammonia is used in fertilizers to provide the nitrogen source required to increase crop yields.

Ammonia and ammonia byproducts have a multitude of applications. For example, ammonia is often employed as a refrigerant in cooling systems. Compression converts it into a liquid with relative ease. When converted back into a gas, it absorbs heat. The textile industry uses ammonia in the dyeing of wool, cotton, and silk, as well as in the production of nylon. Household floor cleaners and detergents commonly use ammonia. Chemical process industries (CPI) facilities use ammonia for pH control and to manage NO<sub>x</sub>. NO<sub>x</sub>, when combined with ammonia under the correct conditions, produces nitrogen and water. Ammonia is also an important ingredient in fermentation processes — it serves as a source of nitrogen to encourage microorganism growth and adjust the pH.

Although common in nature and widely used industrially, ammonia can damage human health and ecosystems. In many countries, including the U.S., authorities classify ammonia as an extremely hazardous substance. Facilities that produce, store, or use it in significant quantities

must follow strict reporting procedures. In the atmosphere, gaseous ammonia reacts with other pollutants to form tiny particles of ammonium salts that degrade air quality and, by affecting breathing, harm human health (2).

A 2018 study mapped atmospheric ammonia levels with unprecedented precision around the globe (3). Satellite recordings identified 248 nitrogen emission hot spots (defined as areas with diameters of less than 50 km). Eighty-three of those hot spots arise from agricultural activity that involves large numbers of cows, pigs, and chickens. Ammonia emissions from feedlots come primarily from livestock waste. One hot spot found over Eckley-Yuma, CO, coincides with two large cattle feedlots. A fainter hot spot exists over a complex of geothermal power plants in California.

Industrial emissions are responsible for 158 hot spots, primarily locations that produce ammonia-based fertilizers (4). As a general conclusion, it appears that emissions generated from human activities dominate natural ones. Addressing the management and control of ammonia is an ongoing issue.

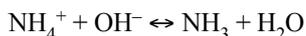
While ammonia is present throughout the solar system, found on most planets, one of the primary naturally occurring sources of ammonia on earth is the decay of organic matter. Ammonia forms as amino acids that degrade during acidogenesis. It also forms as part of the excreta cycle of humans and animals, as the kidneys secrete ammonia to neutralize excess acid. Consequently, it is a commonly encountered water pollutant.

In an age where sustainability, resource recovery, and

the circular economy are essential social themes, this article describes methods to remove, recover, and recycle ammonia from wastewater — particularly wastewater streams from anaerobic digestion processes and landfill leachate. One promising method, thermal ammonia stripping, could use waste heat to remove ammonia from wastewater streams. The article also describes an example of a successful implementation of thermal ammonia stripping in Hong Kong.

## The basic chemistry of ammonia in water

Two forms of ammonia are encountered in wastewater: the ionic form ( $\text{NH}_4^+$ ) and the gaseous form ( $\text{NH}_3$ ). The relationship between ammonia gas and the ammonium ion is:



Dissociated ammonium ( $\text{NH}_4^+$ ) is converted to undissociated ammonia gas ( $\text{NH}_3$ ) by the addition of a base, such as sodium hydroxide. As the temperature of the water increases, the amount of free ammonia gas also increases. The balance of this equation is a function of pH and temperature: Low pH and low temperature push the balance toward  $\text{NH}_4^+$ .

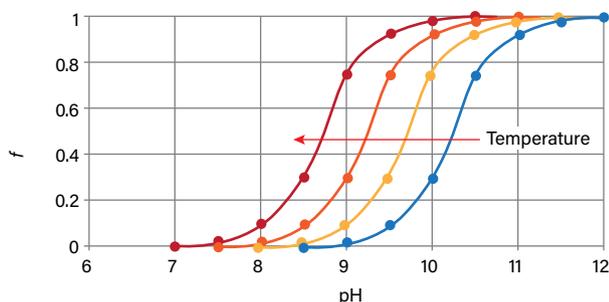
The ratio of ammonia in the gas phase to the total ammoniacal nitrogen, referred to as  $f$ , may be expressed as:

$$f = \text{NH}_3 / (\text{NH}_3 + \text{NH}_4^+)$$

The relationship between pH, temperature, and  $f$  takes the general form depicted in Figure 1. As the temperature increases, denoted by the direction of the arrow, the necessary pH to maintain a value of  $f$  decreases.

## Ammonia in anaerobic digestion

Anaerobic digestion (AD) is a waste management technology for the treatment of organic waste streams. In such waste streams, ammonia content can be fairly high, as it is derived from the nitrogen content in organic substrates. Although ammonia is an essential source of nutrients for



▲ **Figure 1.** As pH increases, the ratio of ammonia in the gas phase to total ammoniacal nitrogen ( $f$ ) increases. As the temperature increases, represented by the direction of the arrow, the necessary pH to maintain a value of  $f$  decreases.

bacterial growth during AD, its inhibitory effect at high concentrations can be toxic to bacteria that benefit from its presence at lower concentrations.

The AD process produces biogas consisting of methane and carbon dioxide, as well as various trace gases. Biogas functions directly as fuel in combined heat and power gas engines, or it can be upgraded to biomethane. Thus, AD is a commercially viable form of renewable energy generation. In addition, the nutrient-rich digestate produced makes for excellent fertilizer.

Protein-rich substrates provide a sound base for methane production, and they are of great interest in commercial biogas production. Unfortunately, high loadings with such materials often correlate with process instability due to the presence of ammonia released during the acidogenic phase of AD. As manufacturers around the world become interested in producing biogas from food waste, ammonia poisoning of AD facilities is happening more frequently (5).

The same issues arise within landfill sites. In Hong Kong, for example, the high loadings of protein in the waste streams entering the landfills, namely meat and meat products, increase the ammonia concentrations of the landfill leachate. Readings of up to 6,000 ppm ammonia are not uncommon.

In the U.K., during the outbreak of bovine spongiform encephalopathy, otherwise known as mad-cow disease, it was necessary to dispose of animal carcasses within sanitary landfills. At such sites, leachate contained ammonia concentrations of up to 9,000 ppm (6).

According to the National Non-Food Crops Centre (NFCC), there are now 486 operational AD plants in the U.K., with another 343 under development. According to the American Biogas Council, the U.S. has 239 AD facilities operating at farms and 1,241 in wastewater treatment plants. The potential for growth in the U.S. is huge.

Both ammonia and ammonium can cause inhibition in an AD system, although primary inhibition occurs as a result of  $\text{NH}_3$ . As ammonium ion concentrations increase in an anaerobic digester, typically above 1,000 ppm, biogas production decreases. Full inhibition of AD occurs at around 5,000 ppm. It is, therefore, a crucial requirement to manage ammonia concentrations, a requirement for which there exists a wide range of options.

In the past, the most commonly employed methods within an AD plant have been to lower the pH, to decrease the free ammonia concentration, or to dilute the digester contents with water. It is also possible to add lignocellulosic biomass with a high C:N ratio to increase the C:N ratio of the substrate in the digester.

Where such approaches are not possible, or not desirable for process efficiency considerations, operators can deploy several technologies to control ammonia. Such approaches

may also be employed to manage landfill leachate. The following section presents several methods of ammonia management, control, and removal (7).

### Ammonia management approaches

Within a typical AD facility, reduction or removal of ammonia may be possible at four locations (Figure 2):

1. before digestion at the hydrolysis-fermentation stage
2. during digestion within the main digester vessel
3. during the digestion in a recycle flow
4. after digestion, before discharge.

Research into the feasibility of removing ammonia during or immediately after the hydrolysis-fermentation stage has resulted in limited success. The practical options are within the digester itself, in a recycle flow, or from the effluent. Stripping ammonia within the digester vessel leaves limited scope for process control. Several researchers have completed work using biogas as a stripping medium. With low-strength ammonia, this may be an option to consider.

The main opportunities for ammonia control in large-scale commercial facilities are, therefore, in recycle and discharge flows. The former impacts the AD process and can improve performance. The latter is a matter of discharge compliance.

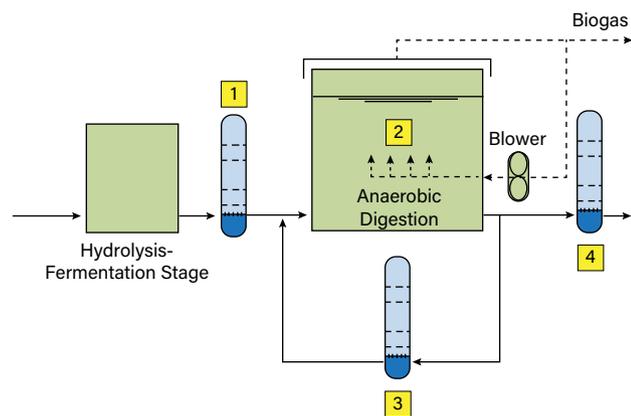
**Biological nitrification.** The removal of ammonia by a two-step biological nitrification and denitrification process (Figure 3) is widely employed, well understood, and generally reliable. In the nitrification step, bacterial activity, supported by introduced oxygen, partially oxidizes ammonia and ammonium to nitrite ( $\text{NO}_2^-$ ) and then to nitrate ( $\text{NO}_3^-$ ). In the second step — denitrification — anoxic bacteria (which use a carbon source for energy) convert nitrates to nitrogen gas ( $\text{N}_2$ ) or, to a lesser extent, nitrous oxide ( $\text{N}_2\text{O}$ ).

Biological nitrification produces varying amounts of sludge and requires the addition of both oxygen and

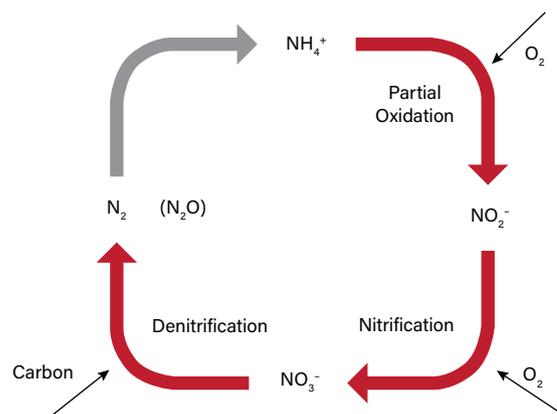
carbon to perform effectively, subject to the organic carbon and ammoniacal nitrogen loadings involved. The process requires large holding volumes, and it may also produce  $\text{N}_2\text{O}$ , a potent greenhouse gas.  $\text{N}_2\text{O}$  has a global warming potential nearly 300 times that of  $\text{CO}_2$ . On average,  $\text{N}_2\text{O}$  emitted today remains in the atmosphere for more than 100 years (8).

For this reason,  $\text{N}_2\text{O}$  has become a target for greenhouse gas reductions. For example, new objectives set in Australia for reducing the carbon footprint of wastewater treatment works have brought this technology under investigation. In Victoria State, one water authority attributes 47% of their carbon footprint to nitrification/denitrification, making the decoupling of nitrogen removal from aerobic processing a principal aim.

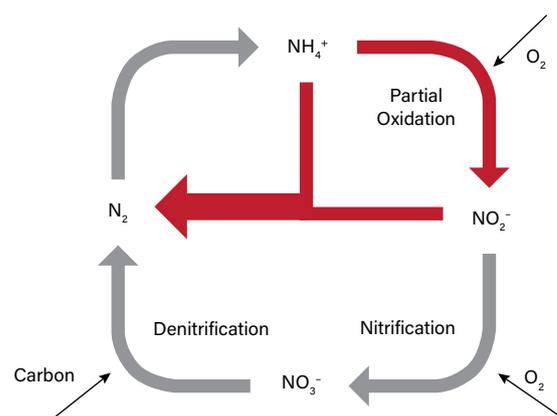
**Anaerobic ammonium oxidation.** In 1995, researchers discovered that ammonia could be converted directly into  $\text{N}_2$  in a fluidized-bed reactor via anaerobic ammonium oxidation (anammox). The process (Figure 4) uses less oxygen than nitrification and does not require carbon. It also



▲ **Figure 2.** Within a typical anaerobic digestion (AD) facility, ammonia can be removed at four different locations, as shown by the yellow boxes.



▲ **Figure 3.** Removal of ammonia by biological nitrification and denitrification is a two-step process.



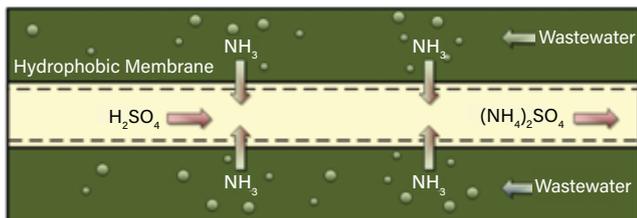
▲ **Figure 4.** Anammox bacteria allow the transformation of ammonia to  $\text{N}_2$  without requiring nitrification or denitrification steps.

produces less sludge than the classic nitrification/denitrification process. The anammox bacteria allow the bypass of the nitrification and denitrification steps. However, anammox bacteria are specialized and slow growing, which increases operational risk (9). Startup can often take several months.

One of the early difficulties of anaerobic ammonium oxidation was washout — the process by which the anammox biomass exits the reactor with the effluent. This challenge was addressed with larger volumes and attached growth systems to try to prevent such washout. However, the preferred approach today is immobilization. For example, the bacteria may be held in a polymeric gel, which prevents washout. The selection of a carrier for immobilization is one of the key decisions to be made in preparation of the immobilization process.

In recent years, wastewater treatment facilities using anammox immobilized cells have received much attention, with advantages that include a high biomass content, higher retention of biomass by prevention of washout, good solid-liquid separation, and lower toxicity to microorganisms. However, in 2018, the Society of Chemical Industry reported that there had been insufficient study of disposal methods and costs involved in anammox immobilization to guide future implementation (10).

**Breakpoint chlorination.** In the breakpoint chlorination



▲ **Figure 5.** In a membrane contactor, ammonia passes through the membrane into a stream of sulfuric acid under osmotic pressure.



▲ **Figure 6.** A thermal ammonia stripper uses heat to remove ammonia from a wastewater stream.

process, dosing pumps add chlorine to wastewater until it removes all free organic compounds and ammonia. The process requires a ratio of approximately 8 mol chlorine to 1 mol ammonia to convert all the ammonia into chloramines. While this is a possible option for discharge flows, it is not suitable for sidestream flows within AD. Addressing the ammonia content of discharge flows can require large additional quantities of chlorine, especially where the organic content of the wastewater is high.

**Zeolite ion exchange.** With zeolite ion exchange technology, ammonium ions in the wastewater replace cations within zeolite adsorbents in an enclosed vessel. The zeolite might be able to remove virtually all ammonia. However, it requires frequent regeneration, which generally limits the use of this technology to final polishing or small-scale applications, such as aquaculture and swimming pools.

**Membrane contactors.** In a membrane contactor (Figure 5), ammonia gas diffuses through a hydrophobic membrane into sulfuric acid under osmotic pressure. It is necessary to increase the wastewater pH to around 10 to ensure that the ammonium ions have been converted to ammonia gas. In many situations, the process must include pH reduction with the addition of acid. Where an operator can accommodate the logistics and cost of managing large quantities of chemicals on-site, this may be a viable option to consider.

**Membrane ion exchange.** In a membrane ion exchange process, ammonia passes through a membrane into an ionic fluid. The process is driven by electrical power. Ammonia can be recovered from the fluid or converted into nitrogen gas. This technology has a small footprint and is fairly effective at removing ammonia. However, one study has reported that it requires 4 kWh per lb of ammonia removed to power this method. A facility removing 5 tons per day would, therefore, require 1.87 MW of electricity or 44.8 MWh per day — a massive amount of energy.

**pH-driven air stripping.** This form of an air stripper requires pH adjustment to above pH 10, which poses a problem similar that of membrane contactors. A substantial airflow is necessary to achieve stripping by this means, usually in the range of 3,000:1 air to wastewater. A facility treating 100 m<sup>3</sup>/hr of wastewater requires an air flowrate on the order of 300,000 m<sup>3</sup>/hr, requiring substantial engineering work. Because it is a physicochemical process, pH-driven air stripping can provide reliable ammonia removal after operating conditions have been reached.

**Thermal ammonia stripping.** Thermally driven air stripping (Figure 6) requires the addition of heat to raise the temperature of the wastewater stream, which has high operational costs. The process can achieve 98.5% removal. In many situations, the process does not need pH adjustment (depending on incoming pH and alkalinity). The airflow

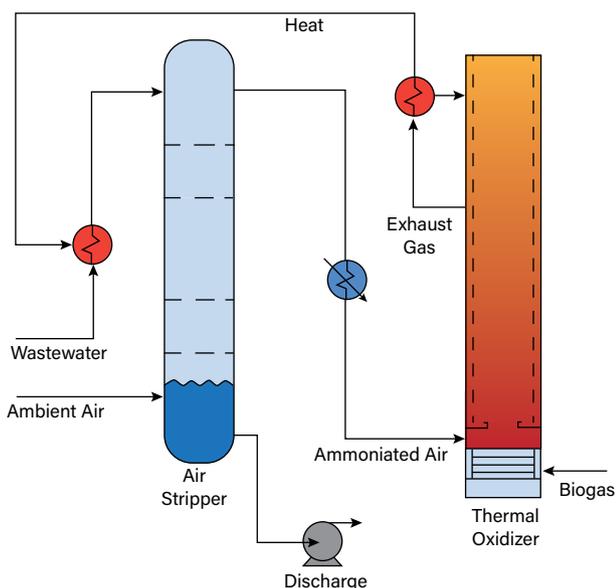
requirement is substantially less than that required for pH-driven air stripping. The relationship in Figure 1 illustrates the fundamental functionality of the thermal ammonia stripper: By raising the temperature, the pH does not need to be increased as much to remove ammoniacal nitrogen from a wastewater stream.

Thermal ammonia stripping and pH-driven ammonia stripping employ similar techniques to achieve ammonia removal. Air-stripping is itself a simple desorption process. Heat, or the addition of a base, breaks the ammonium ion bond. In the case of pH-driven ammonia stripping, the process requires considerably more air, perhaps as much as tenfold. However, the process is not as temperature-dependent as thermally driven air stripping, where a drop in temperature can bring the processes to a halt.

In the thermal ammonia stripping process, wastewater is first preheated and pumped to the top of the stripping column. The wastewater passes countercurrent to airflow in the stripping column, which removes ammonia from the wastewater (Figure 7). From there, a thermal oxidizer destroys the ammonia in the ammoniated air. The heat generated within the thermal oxidizer in turn powers the process.

In the industrial sector, there are no perfect solutions for removing ammonia from wastewater. Each technology has its point of optimum application. However, thermal ammonia stripping has several benefits over the other methods of ammonia removal:

- it can accommodate high removal rates in a relatively small footprint



▲ **Figure 7.** The thermal ammonia stripping process involves preheating the wastewater and passing the wastewater counter-current to an airflow in the stripping column to remove ammonia from the wastewater.

- the process is particularly suited to high-strength ammoniated wastewater
- chemical additions, other than antifoam agents, are not required
- avoidance of nitrous oxide formation mitigates greenhouse gas production
- compared to biological processes, it achieves a relatively rapid start-up (1–2 hr)
- it presents no risk of biology failure
- substantial savings may be available by avoiding carbon-source costs
- it does not form sludge
- the system is relatively easy to operate.

### AD facility in Hong Kong

The West New Territories (WENT) landfill site in Hong Kong uses thermal stripping to remove ammonia from an effluent stream generated by an 80-million cubic yard landfill site. Swire-BFI began operating the thermal stripping system in 1997 (11). Today, the plant is operated by Suez, and it treats double the original anticipated leachate flow from the landfill site (Figure 8).

The first phase had a leachate design flowrate of 1,800 m<sup>3</sup>/day, which has recently been upgraded to 3,350 m<sup>3</sup>/day. The design duty for this first plant was for an influent of 6,700 ppm ammonia to be reduced to a discharge of less than 100 ppm. The WENT facility now removes 14 m.t. of ammonium per day (12). Subsequently, operators installed similar processes on six additional sites around Hong Kong.

When the plant was designed, thermal efficiency was not a performance criterion. However, since commissioning the first plant, thermal efficiency has gradually moved up the list of performance priorities — to a point where it is now



▲ **Figure 8.** The West New Territories (WENT) landfill site in Hong Kong treats a leachate stream using thermal ammonia stripping. The plant is rated at 3,350 m<sup>3</sup>/day.

a tightly measured variable. Landfill site operators initially considered landfill gas to be more of a nuisance than an opportunity. Employing energy recovery, process optimization, and patented technology improvements, the thermal power requirement is now 20% of that of the first facilities. As part of an ongoing development program, there are now options to utilize waste heat sources, such as the heat from engine exhausts. Today, the WENT facility receives its thermal energy from landfill gas.

**Table 1. After the ammonia has been stripped from a wastewater stream, it can be removed from the stripping air by several methods.**

Method	Summary
Thermal oxidation	Where the waste heat source is gas, combustion may convert ammonia directly to nitrogen.
Catalytic oxidation	Catalysts provide a lower-temperature thermal conversion option.
Acid scrubbing	The use of a suitable acid, such as sulfuric acid or phosphoric acid, produces a salt, which may have commercial value.
Cold water scrubbing	Cold water captures the ammonia gas as ammonium hydroxide. The concentration of ammonium hydroxide produces a liquid, which may have commercial value.
Ammonia gas capture	The ammonia-water absorption cycle can concentrate ammonia as a gas. Operators may sell ammonia to realize commercial value, or it may be combusted directly on-site or used to generate electricity.

This improvement in efficiency, coupled with a deeper understanding of the processes at work, has resulted in the technology becoming less specific to Hong Kong, making it more attractive for use in a range of varied applications in other countries.

## Ammonia destruction or recovery

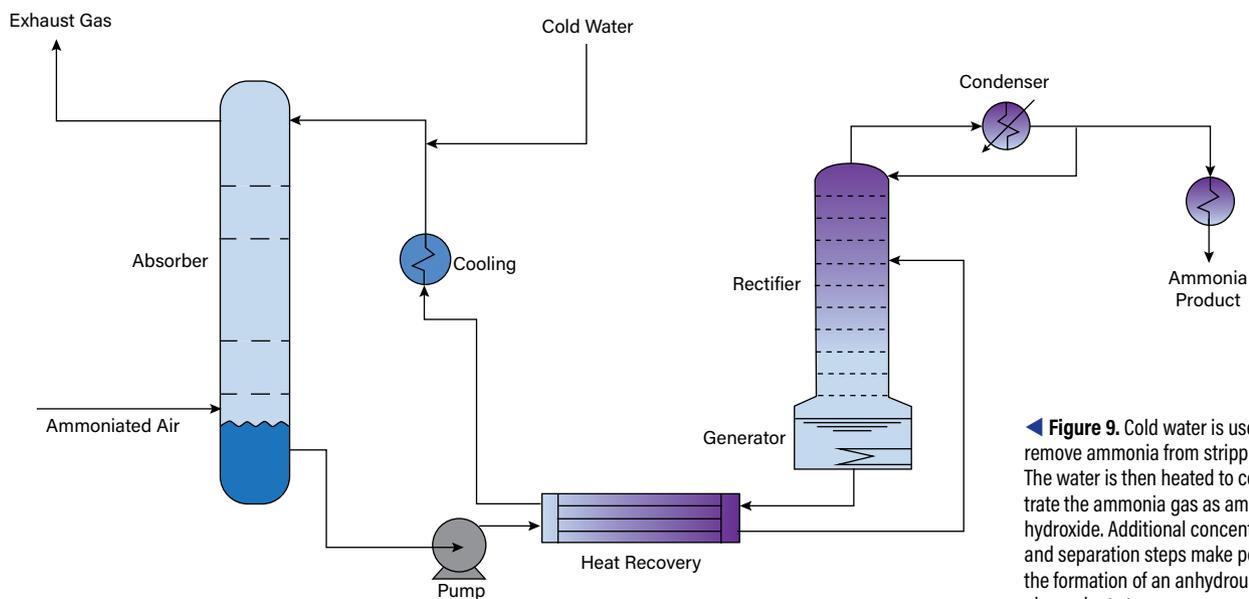
After ammonia is removed from wastewater, engineers must ensure its safe final disposal. Some of the technologies described previously convert ammonia to nitrogen, while others provide a potentially saleable byproduct. If waste heat is used to remove ammonia, such as in the thermal ammonia stripping process, ammonia must then be removed from the stripping air. Table 1 shows several options for treating ammonia in stripping air.

More recently, in conjunction with staff from the Univ. of Warwick Dept. of Engineering in the U.K., we have developed a process that facilitates recovery of either ammonium hydroxide or anhydrous ammonia (Figure 9). This approach employs waste heat and avoids the use of chemicals. Clean, cold water removes ammonia from stripping air. The water is then heated to concentrate the ammonia gas as ammonium hydroxide. Additional concentration and separation can produce anhydrous ammonia.

## Applications for recovered ammonia

After anhydrous ammonia is produced and recovered, many options are available for its use, from simple combustion to commercial application in agriculture, industrial cleaning use, and explosives production.

One possibility that may prove interesting, as we move beyond fossil fuels, is the application of ammonia as a



**Figure 9.** Cold water is used to remove ammonia from stripping air. The water is then heated to concentrate the ammonia gas as ammonium hydroxide. Additional concentration and separation steps make possible the formation of an anhydrous ammonia product stream.

fuel. The useful energy content of liquid ammonia is 18.8 MJ/kg — approximately 30% that of diesel. Fuel cells can use ammonia to produce power, which offers the potential for a local, revenue-generating means of disposal. Although still at a relatively early stage, the development of direct ammonia fuel cells is the focus of interest of many organizations and researchers (13).

High-temperature systems such as molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs) are currently receiving the greatest attention (14). They are particularly suited for use at wastewater treatment facilities for two primary reasons:

- high-temperature operation (typically 1,800°F) allows for internal thermochemical reforming capabilities and acceptance of ammonia as a fuel

- they can achieve higher electrical efficiencies than combustion alternatives because they are not limited by Carnot cycle efficiency.

MCFCs have been found to be less efficient than SOFCs (15). However, researchers are finding it difficult to build a high-temperature ammonia SOFC that is durable through many cycles of performance and that is not prohibitively expensive to fabricate. Now, researchers around the world are investigating medium- and low-temperature fuel cells, which hold some promise for ammonia recycle.

One key attribute of ammonia is that, since it contains no carbon, it cannot produce carbon dioxide, carbon monoxide, hydrocarbons, or soot when it is combusted. This

makes it an ideal fuel to prevent the formation of greenhouse gases. This could be an area of opportunity in the future. For example, with a potential ammonia production of 14 m.t./day, the thermal power available at the Hong Kong WENT landfill site would be around 1.8 MW. While this may be of nominal value in monetary terms, it would make a significant contribution to the challenge of ammonia treatment and disposal.

Ammonia is joining a growing list of substances that require more sustainable technologies for its removal, recycle, and reuse. Using waste heat to meet these objectives helps to ensure a long-term sustainable solution to the challenge of ammonia disposal.

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