HONG KONG: WHILE THE REMOVAL OF AMMONIA FROM WASTEWATER IS A PERENNIAL CHALLENGE FOR WASTEWATER ENGINEERS, THE COUNTRY HAS INCUBATED WORLD-LEADING TECHNOLOGY

Stripping Ammonia in Anaerobic Digesters

Robert Eden discusses thermal stripping in Hong Kong

GIVEN its high population density, coupled with the demanding environmental standards enforced by the Environmental Protection Department, it is not surprising that Hong Kong served as the incubator for our process to remove ammonia from wastewater. What has resulted is a novel thermal ammonia stripping technology, which has low operating costs, high standards, and a small footprint.

Since 1997, the technology has been applied to both leachate from landfill sites, as well as the side-stream flows from an anaerobic digester (AD). While highly focussed on the needs of Hong Kong, the technology is gaining momentum in other countries, where environmental compliance is a serious issue to address. It is also moving from leachate cleanup applications into AD.

To many engineers not involved with AD, the problems caused by ammonia may come as a surprise. It is well known that ammonia is toxic to fish and humans (sniff that floor cleaner if in doubt), so it should not be unexpected that many bacteria are similarly distressed.

THE PROBLEM

Although ammonia is a source of nutrient for bacterial growth during AD, its inhibitory effect at high concentrations can be lethally toxic to bacteria that have thrived on its presence at lower concentrations.

According to the National Non-Food Crops Centre (NNFCC), there are now 486 operational AD plants in the UK, with a further 343 under development. AD is established as a commercially viable form of renewable energy generation. The AD process produces biogas, consisting of methane and carbon dioxide, as well as various trace gases. Biogas can be used directly as fuel, in spark-ignition gas engines or upgraded to natural gas-quality biomethane. The nutrient-rich digestate produced can be used as fertiliser.

With an increasing global interest in producing biogas from food waste, the difficulties encountered with ammonia poisoning of AD facilities are now becoming more frequently encountered.

Protein-rich substrates are valuable for methane production. 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 from the degradation of amino acids during acidogenesis.

There are two forms of ammonia encountered in wastewater. The ionic form (NH_4^+) and the gaseous form (NH_3). They are related by the chemical formula:

$$NH_3 + H^+ \leftrightarrow NH_4^+$$

Both forms can, directly and indirectly, cause inhibition in an AD system, although NH_3 is generally recognised to be the main inhibitor. The balance of this equation is a function of pH and temperature. Low pH and low temperature push the balance towards NH_4^+.

Figures vary, but as ammonium ion concentrations increase in an anaerobic digester, typically above 1,000 mg/L, performance, in terms of biogas production, drops off. Anaerobic digestion is fully inhibited at around 5,000 mg/L. It is, therefore, an essential requirement to manage ammonia concentrations, a requirement for which there exists a wide range of options.

In the past, the most commonly-employed methods 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, there are also several technology variants that may be deployed to control ammonia. It is not so much a lack of choice, which is the issue here, but rather an understanding of the issues that may be encountered with each option.

BIOLOGICAL NITRIFICATION

Biological nitrification is widely employed, well understood, and generally reliable. Biological nitrification produces varying amounts of sludge and requires both oxygen and carbon to perform effectively. Large holding volumes are required. Significant air (oxygen) and carbon-source additions are also required. The process may also produce nitrous oxide (N_2O), a potent greenhouse gas.

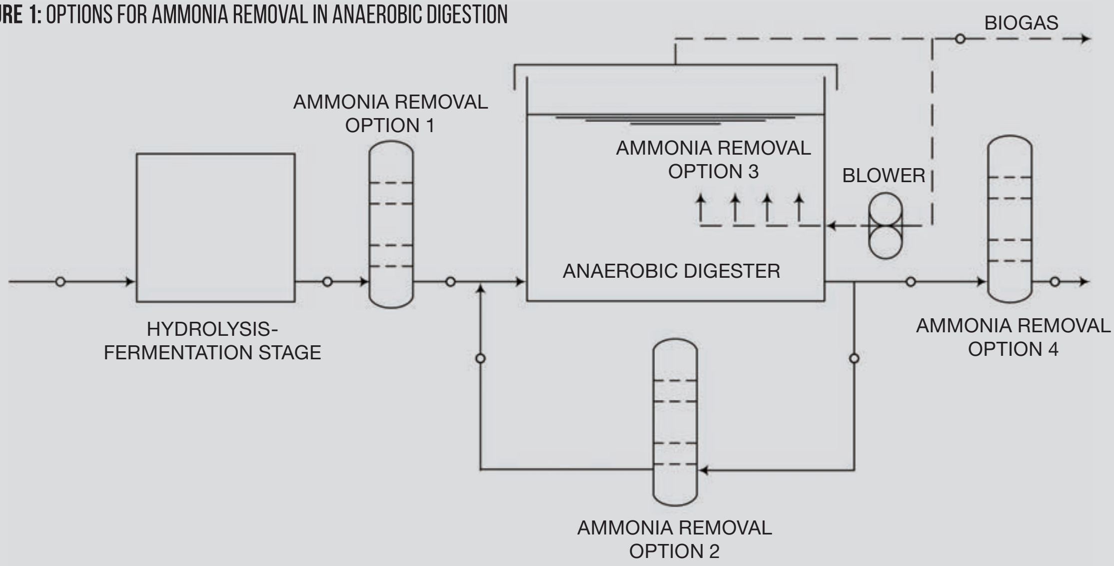
ANAEROBIC AMMONIUM OXIDATION (ANAMMOX)

In 1995 researchers discovered that *Anammox*, a previously unknown bacterium, was converting ammonia directly into N_2 in a fluidised bed reactor. The process that was subsequently developed does not require carbon and produces less sludge. *Anammox* bacteria are specialised and slow growing, which in turn leads to increased operational risk. Startup can be measured in months.

BREAKPOINT CHLORINATION

Chlorine is added to wastewater until all free organic compounds and ammonia are removed. A ratio of approximately 8:1, chlorine to ammonia is required to convert all the ammonia into chloramines. Whilst this is a possible option for discharge flows, it is not suitable for recycle flows. It requires potentially large additional quantities of chlorine where organic content is high.

FIGURE 1: OPTIONS FOR AMMONIA REMOVAL IN ANAEROBIC DIGESTION



ZEOLITE ION EXCHANGE

Ammonium ions are swapped with cations within zeolite, removing virtually all ammonia. The zeolite requires regular regeneration, making application specific to small-scale situations, such as aquaculture and swimming pools.

MEMBRANE ION EXCHANGE

With this technology, ammonia passes through a membrane into an ionic fluid, driven using electrical power. Ammonia may be recovered from the fluid or converted to nitrogen gas. The advantages here are the possibility of compact and high-performance ammonia removal. The electrical load may be an issue for some operators. Removing 5 t/d of ammonia requires approximately 2 MWe.

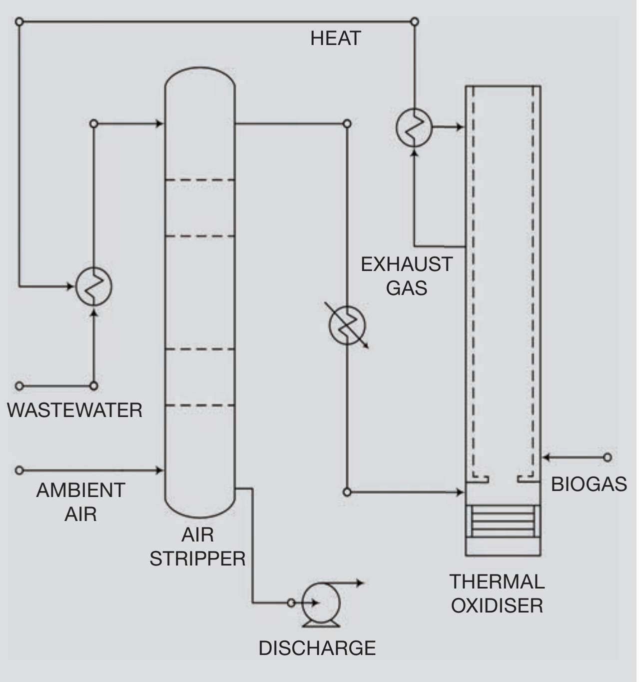
MEMBRANE CONTACTORS

Ammonia diffuses through a hydrophobic membrane into sulfuric acid under osmotic pressure. The wastewater pH needs to be increased to around 10, leading to notable chemical consumption. In many situations, the pH subsequently needs to be reduced by the addition of acid. However, as above, this provides a compact solution where the management of the necessary chemicals can be accommodated.

PH-DRIVEN AIR STRIPPING

This type of air stripper requires pH adjustment to over pH 10. This results in issues similar to those of membrane contactors with the on-site management of chemicals. A substantial airflow is necessary to achieve stripping by this means, usually in the range of 3,000:1, air to wastewater. It is also difficult to achieve better than 80% removal. Where chemicals are available, pH-driven ammonia stripping provides a reliable physicochemical route for ammonia removal.

FIGURE 2: THERMAL AMMONIA STRIPPER PROCESS FLOW DIAGRAM



THERMALLY-DRIVEN AIR STRIPPING

This requires significant additions of heat, which leads to high operational costs where waste heat is not available. Can achieve 98.5% removal. This technology does not usually require chemical additions.

Within a typical AD facility, there are four locations where reduction or removal of ammonia may be possible (*see Figure 1*).

- before digestion at the hydrolysis-fermentation stage;
- during the digestion in a recycle flow;
- during digestion within the main digester vessel; and
- post digestion, prior to discharge.

Research into the feasibility of removing ammonia during or after the hydrolysis-fermentation stage has resulted in limited success. The practical options are either within the digester itself, in a recycle flow or from the discharge.

Stripping ammonia within the digester vessel leaves limited scope for process control. Work has been completed by several researchers 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 leads to improved performance. The latter is a matter of discharge compliance.

THERMAL STRIPPING IN HONG KONG

The systems we have developed in Hong Kong are primarily for discharge flows. Leachate, or in one case digester effluent, is heated to the system operating temperature and passed down through the stripper column, counter-current to a pre-heated airflow. The design ensures that the air collects up to 98.5% of the ammonia gas into the air. The air is then passed directly to a thermal oxidiser where it is combusted, destroying the ammonia and releasing nitrogen, carbon dioxide and water to the atmosphere (*see Figure 2*).

When thermal air stripping was chosen in 1997 as the core nitrogen removal process for the West New Territories (WENT) landfill site in Hong Kong, currently operated by Suez, thermal efficiency was not a performance criterion. With a design flow rate of 1,800 m^3/day, recently upgraded to 3,350 m^3/day, as much landfill gas as necessary was available for use. The first design duty for this first plant was for an influent of 6,700 mg ammonia per litre of wastewater, to be reduced to a discharge of 100 mg/L. The WENT facility now removes 14.5 t/d of ammonium ion. Subsequently, similar processes have been installed on six additional sites around Hong Kong.

Since the commissioning of the first plant, thermal efficiency has gradually moved up the list of performance priorities to a point where it is now a tightly measured variable. Landfill gas in Hong Kong was once seen to be more of a nuisance than an opportunity. Through improved energy recovery, process optimisation, and targeted reduction of the necessary airflow rate, the thermal power requirement has been reduced to 20% of that of the first facilities. Options to utilise waste-heat sources have also been developed.

The use of this technology with AD has also been undertaken in Hong Kong. The application environment is different from that encountered with a typical leachate treatment plant, but the basic principles remain the same. Commissioning in an AD setting is challenging. Unlike a landfill, an AD facility is a more tightly-controlled process environment.

There are several benefits attributable to thermal stripping which indicate situations of optimum deployment:

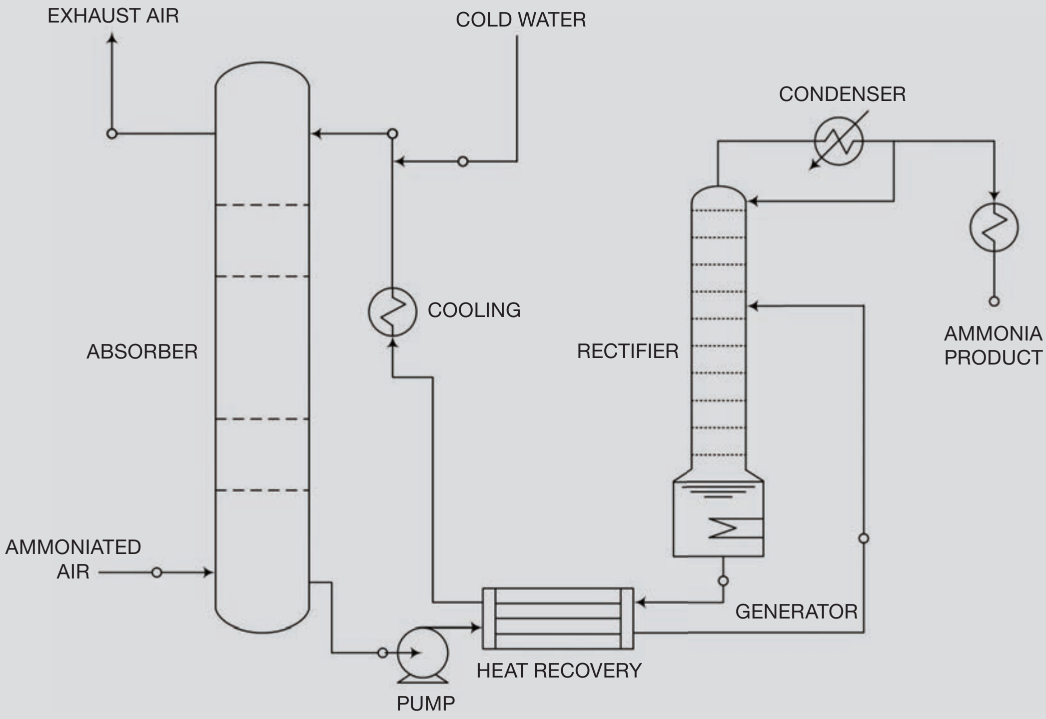
- high removal rates may be achieved in a relatively small footprint;
- the process is particularly suited to high-strength ammoniated wastewater;
- no costs are incurred for chemical additions;
- greenhouse gas production is mitigated by avoiding nitrous oxide formation (N_2O);
- compared to biological processes, relatively rapid startup can be achieved (1 or 2 hours);
- there is no risk of biology failure;
- substantial savings may be available from avoidance of carbon-source costs;
- there is no sludge formation; and
- the system is relatively easy to operate compared to biological processes.

Where waste heat is available in the form of steam or heat (from an engine exhaust, for example) there will be, subsequent to ammonia stripping from wastewater, a requirement to remove ammonia gas from the stripping air. This can be done either by acid scrubbing, ammonia capture, or a catalytic conversion. Using biogas or syngas as a source of heat is, therefore, preferred. Here, employing thermal oxidation, ammonia removed from wastewater can be converted directly into nitrogen and water.

More recently, in conjunction with staff from the University of Warwick Department of Engineering, Organics has developed a

FIGURE 3: WENT AMMONIA STRIPPING PLANT, RATED AT 3,250 M3/DAY

FIGURE 4: AMMONIA RECOVERY PROCESS FLOW DIAGRAM



process which facilitates recovery of either ammonium hydroxide or anhydrous ammonia. This approach further develops two key process themes: employing waste heat, and avoiding the use of chemicals. Ammonia-water systems are well understood and widely applied in refrigeration and adsorption cooling. The process flow diagram (PFD) for a system recovering ammonia is provided in Figure 4. Clean, 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 makes possible the formation of anhydrous ammonia.

AMMONIA IS JOINING THE GROWING LIST OF SUBSTANCES WHICH NEED TO BE PREVENTED FROM POLLUTING THE ENVIRONMENT AND, WHERE PRACTICAL, CAN BE RECYCLED

The production of anhydrous ammonia leads to the question of what to do with it. There exist many options, from simple combustion on-site to commercial use. Ammonia is used in a wide range of applications, from pharmaceuticals and agriculture to industrial cleaning and explosives.

The energy content of liquid ammonia is 11.5 MJ/L, or approximately 30% that of diesel. Ammonia may be used in fuel cells, which offers the potential for a local, revenue-generating means of disposal. Ammonia may also be used in engines and turbines, with ammonia as a fuel. During World War II ammonia was used to power buses in Belgium. And more recently, Hideaki Kobayashi, professor at the Institute of Fluid Science at Tohoku University in Sendai, Japan, developed the world's first technology for direct combustion of ammonia in a gas turbine (https://bit.ly/2JsK2LC). A high-octane rating of 120 and low flame temperature permits the use of high compression ratios without the penalty of high NOx production. Since ammonia contains no carbon, its combustion cannot produce carbon dioxide, carbon monoxide, hydrocarbons, or soot.

Ammonia is joining the growing list of substances that need to be prevented from polluting the environment and, where practical, can be recycled. It is expected that the demand for compact, low operational cost, ammonia removal technologies will increase.

Sectors of growth are where large flows with elevated ammonia concentrations are encountered, such as with landfills taking increased protein loadings, anaerobic digestors taking food waste and industrial processes discharging ammoniated wastewaters – using waste heat to meet these objectives assists with ensuring a long-term sustainable solution to the challenge of ammonia pollution. ■

Robert Eden is Managing Director, Organics Group