



Best practices for treating ammonia in landfill leachate

Treating ammonia in landfill leachate requires consideration of several factors to assess which method might be most effective.

Reducing the concentration of ammonia in landfill leachate is often necessary to meet discharge permit requirements. This is true for direct discharge of treated leachate to surface waters and may be required to meet publicly owned treatment works (POTW) discharge permit standards. Ammonia reduction treatment is primarily necessary to prevent toxic impacts on aquatic life in surface waters and to reduce its toxic effects on bacteria populations used in the POTW treatment systems. Ammonia reduction can be accomplished with established wastewater treatment technologies; however, the right treatment depends on the site in question.

Factors to consider

- Ammonia and ammonium ($\text{NH}_3 + \text{NH}_4$ as nitrogen), total Kjeldahl nitrogen (TKN = $\text{NH}_3 + \text{NH}_4$ + organic nitrogen), and total nitrogen (TKN + nitrite-N + nitrate-N) in wastewater are all related by being different constituents of wastewater nitrogen. Each nitrogen species can be analyzed by a laboratory to determine its concentration in wastewater. POTWs can have pretreatment requirements for one or more of these nitrogen constituents, depending on their treatment methods and discharge requirements. Nitrogen is an essential nutrient used in fertilizers, but when present as ammonia, for example, nitrogen constituents can be toxic to aquatic life at low concentrations. While ammonia is toxic to aquatic life, ammonium is less toxic. Thus, it is important to know the acceptable ammonia concentration allowed in the treated leachate before choosing a treatment technology.
- pH is an important wastewater parameter for landfill leachate because pH affects the concentration of ammonia and ammonium present in the wastewater. At a constant temperature (e.g., 20°C) and at a neutral/lower pH (<7), the ionic form—ammonium (NH_4)—is 100 percent present, and at a higher pH (>10) the gaseous form—ammonia (NH_3)—approaches 100 percent present. Leachate, and other wastewaters that have a pH of between 7 and 11.5, have an equilibrium of ammonium and ammonia that changes with the pH (e.g., the lower the pH, the more ammonium is present; the higher the pH, the more ammonia is present at a set temperature).
- Temperature also affects the ammonium/ammonia concentration, with lower temperature leachate having lower concentrations of ammonia when compared with higher temperature wastewater at the same pH. The effect of temperature on the concentration of ammonia in leachate increases with higher leachate pH. For example, a water sample that has a pH of 9 and temperature of 40°F will have approximately 10 percent ammonia and approximately 90 percent ammonium, whereas the same water sample (pH of 9) at 90°F will have approximately 48 percent ammonia and 52 percent ammonium. Both water samples will have the same analytical result for total ammonia ($\text{NH}_3 + \text{NH}_4$), regardless of the temperature.

Other constituents in leachate can also affect the treatment method used to reduce ammonia concentrations because certain methods are also used to treat those other constituents. For example, additional chemicals and treatment processes may be needed to treat ammonia and

other constituents, compared with leachate that only requires a reduction of ammonia.

Treatment methods

Nine of the most effective treatment and/or disposal methods for leachate and other wastewaters with elevated ammonia or total nitrogen are summarized below. The type of treatment process used will depend on several factors:

- The specific nitrogen compounds (e.g., ammonia, ammonium, nitrite, nitrate and organic nitrogen) that require removal or reduction
- The initial concentrations of the nitrogen compounds in the raw leachate
- The target post-treatment concentration requirements (i.e., discharge permit standards)
- Multiple other criteria, including leachate chemistry factors mentioned previously.

Biological treatment: Total ammonia and organic nitrogen can be converted into less toxic nitrites and nitrates ($\text{NO}_2 + \text{NO}_3$) by bacteria through microbiological degradation or “nitrification.”

Nitrification of wastewater is carried out by nitrifiers, (e.g., Nitrosomonas and Nitrobacter bacteria) in an aerated, temperature- and pH-controlled bioreactor or other aeration facility. The nitrifier bacteria require oxygen and carbon as well as alkalinity for pH control. Denitrification is facilitated by denitrifying bacteria (e.g., Pseudomonas and Bacillus bacteria) in an anoxic environment that converts NO_3 to nitrogen (N_2) gas, which is released to the atmosphere.

Several biological treatment methods are particularly effective at removing ammonia, organic nitrogen and total nitrogen from wastewater. For example, a membrane bioreactor (MBR) uses denitrification and nitrification in the “bioreactors” to treat high ammonia concentrations (100 to 2,000 milligrams per liter [mg/L]) and organics (less than 30,000 mg/L biochemical oxygen demand (BOD)) in wastewater. The use of a membrane ultrafilter allows the MBR-treated wastewater to be discharged with minimal suspended solids. Biosolids are retained in an MBR to circulate back through the bioreactor tank(s). Another type of biological treatment is a sequencing batch reactor (SBR) that involves multi-step batch biological processes to treat high-nitrogen wastewaters. More traditional biological treatment methods, such as activated sludge, are only employed for wastewater with a low ammonia concentration (approximately 20 to 40 mg/L ammonia).

POTW discharge/hauling: If a POTW that uses biological treatment is locally available and will allow the landfill to discharge its leachate and wastewater, this option is often the least expensive. A POTW is designed to treat ammonia and other constituents that are found in leachate using the activated sludge method of treatment. However, these facilities are not usually designed to treat concentrated wastewater and the POTW will often charge the leachate generator based on the ammonia concentration, as well as the concentration of other chemicals found in leachate. If a POTW is not locally available, wastewater may be hauled to the POTW, and the leachate generator may incur higher costs.

Breakpoint chlorination: Ammonia nitrogen removal can be accomplished chemically by adding chlorine to wastewater, which causes ammonia to oxidize, primarily to nitrogen gas. This method is generally only used to “polish” effluent wastewater with lower concentrations of ammonia. The theoretical chlorine-to-ammonia ratio of 7.6:1 means that it takes 7.6 pounds of chlorine to oxidize 1 pound of ammonia. However, because other wastewater constituents are often readily oxidizable

(e.g., organics), the amount of chlorine required can be significantly higher. Additional issues include the potential production of nitrogen trichloride (NCl_3) gas, which is toxic and explosive, as well as increasing the concentration of total dissolved solids (TDS) and the need to control pH. Thorough mixing is critical to the effectiveness of breakpoint chlorination, as is pH control. Fifteen mg/L of alkalinity is consumed per mg/L of ammonia oxidized, so alkalinity must be monitored and added if it is not already present as a pH buffer in the wastewater.



Air and steam stripping: By raising the wastewater pH to between 10.8 and 11.5, the wastewater's total ammonia equilibrium is driven toward 100 percent ammonia gas (NH_3). The higher pH wastewater can then be passed through an air or steam stripping tower, where air or steam is forced through cascading wastewater, which causes the ammonia gas to be volatilized or “stripped” from the wastewater. Wastewaters with ammonia concentration greater than 100 mg/L usually require steam stripping; air stripping is ideally for ammonia concentrations between 10 mg/L and 100 mg/L.

Selective ion exchange: Contact with specific ion exchange media can remove ammonia, nitrite and nitrate from leachate through adsorption. One media, used to remove ammonia, is called clinoptilolite. Separate ion exchange media are used for nitrite and nitrate removal, if necessary. Significant pretreatment is required before passing leachate through the ion exchange media, including removal of total suspended solids and competing ions such as those associated with hardness, as well as aluminum and iron.

Ozone and hydrogen peroxide: Total ammonia and organic nitrogen can be removed through the advanced oxidation process of ozone oxidation and hydrogen peroxide. The ozone and hydrogen peroxide reacts to oxidize ammonia to primarily nitrogen gas. Ozone can also assist with effluent disinfection if needed. As with other oxidation processes, competing constituents that can be oxidized will increase the consumption of ozone and peroxide.

Understanding PFAS

After becoming widely embraced by manufacturers in the 20th century thanks to their heat-resistant and water-repellent characteristics, perfluoroalkyl and polyfluoroalkyl substances, or PFAS, have stuck around. Commonly known as “forever chemicals,” PFAS have become notorious for their unique carbon-fluorinated bond that doesn't readily break down, leading to concerns of the compounds' prevalence in landfill leachate and drinking water.

Invented in the 1930s, one of the first uses of PFAS was for non-stick coatings and firefighting foams. Today, more than 3,000 synthetic chemicals are classified as PFAS and have wide-ranging applications, such as in grease-resistant microwave-popcorn bags, carpets that resist stains, and pipes and wires that resist corrosion.

“It’s really easier to talk about where [PFAS] are not expected to be found than where they are,” says Steve Sliver, executive director of the Michigan PFAS Action Response Team (MPART) (<https://www.michigan.gov/pfasresponse/>), which is a division of the Michigan Department of Environment, Great Lakes, and Energy tasked with studying and combating these nationally emerging contaminants.

ADDRESSING THE PROBLEM

PFAS are found globally in both rural and urban environments, and can penetrate the air, dust, food, soil and water. These persistent compounds first gained awareness after concentrations were found in the blood of occupationally exposed workers in the 1970s and, later, in the blood of the general population in the 1990s.

Although some PFAS have been manufactured for close to 100 years, PFAS were not widely documented in environmental samples until the early 2000s. Early detection at low reporting limits was hindered due to analytical limitations arising from the unique surface-active properties of PFAS, according to the Interstate Technology & Regulatory Council (ITRC).

“The analytical methods to detect these [compounds] haven’t been around and perfected for very long,” says Sliver. “[If] you go back to the late 1990s and early 2000s before different media were being investigated for the presence of PFAS, that sort of analytical technology wasn’t available.”

Two classes of PFAS—PFOA and PFOS—have been the most extensively produced and studied of these compounds. PFOA, which is mainly found in the environment around military bases and manufacturing facilities, has been detected in the blood of more than 98 percent of the U.S. population. The presence of this compound in blood has been associated with increased cholesterol and uric acid levels, which can lead to kidney stones and gout.

Other health effects of PFAS exposure include reproductive and developmental problems, such as low infant birth weights, effects on the immune system, cancer (PFOA) and thyroid hormone disruption (PFOS).

FINDING THE SOURCE

Many PFAS-treated consumer goods are eventually disposed of as municipal solid waste (MSW). PFAS present in landfills may not degrade like other waste components, which creates a concern that the compounds could be released through leachate and gas emissions, according to the EPA.

In 2018, the Michigan Department of Environmental Quality (MDEQ) and various waste resource recovery facilities requested that landfills test for PFAS in leachate as part of a statewide effort to better understand the presence of the compounds in the environment in an effort to work towards reducing them.

Of the 35 active Michigan-based MSW landfills involved in the study, PFOA and PFOS were detected in all of them. Leachate samples from participating facilities found PFOA levels ranged from 240 to 3,200 parts per trillion (ppt) and PFOS ranged from 100 to 710 ppt.

“The problem with landfills is [they] perpetuate the cycle,” says Sliver. “Waste goes in, leachate takes the PFAS out and then reintroduces them back into the environment. So, what sort of practices can [the landfill operator] have to exacerbate the levels of PFAS in your leachate, and then how do you manage your leachate once you’ve collected it off your liner so that you don’t perpetuate that cycle by reintroducing it into the environment?”

Some landfill operators have begun investing in treatment methods to address PFAS contamination, including introducing granular activated carbon (GAC), which allows the compounds to pass through a GAC vessel and absorb into the carbon, or ion exchange processes, where leachate passes through resins in a vessel that binds PFAS.

Currently, leachate treatment by wastewater treatment plants (WWTPs) may do little to reduce or remove PFAS. To provide a margin of protection from life-time exposure, the EPA issued a lifetime health advisory in 2016 that limited combined PFOA and PFOS exposure to 70 ppt in drinking water.

Sliver says Michigan is one of a handful of states that is pursuing drinking water standards, with stringent water quality standards (WQS) for both PFOS and PFOA. The applicable WQS for PFOS is 12 ppt for streams that are not used for drinking water and 11 ppt for those that are used as a drinking water source. The applicable WQS for PFOA is much higher at 12,000 ppt for surface waters that are not used for drinking water and 420 ppt for those used as a drinking water source.

On Feb. 20, the EPA proposed regulatory determinations for PFOS and PFOA in drinking water, taking the first steps towards setting an enforceable drinking water standard. If the EPA successfully sets a standard, known as a Maximum Contaminant Level under the Safe Drinking Water Act, utilities will be required to monitor drinking water for PFOS and PFOA and use treatment techniques to keep levels below the standard.

“All of these [measures] at the end of the day are there for protecting public health, and whether it’s in groundwater or surface water, the goal is to reduce exposure to people,” Sliver says.

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Evaporation: Heating wastewater, either with landfill gas or waste heat (e.g., enclosed flare, engine or micro-turbine exhausts) in an evaporator can convert wastewater to water vapor, thereby reducing the wastewater volume by up to 95 percent. Ammonia and other odors (e.g., from sulfides, like H₂S) can be generated as part of the evaporator vapor plume. Concentrated solids resulting from the evaporation process need to be disposed of and are customarily landfilled.

Deep injection well: Wastewater may be injected into the subsurface through specially designed and permitted wells in regions where the regulatory framework supports permitting of a well and where there is appropriate geology for liquid disposal. The subsurface zone where wastewater is

injected is vertically separated by impermeable formations far below the underground sources of drinking water. Special construction methods, including redundant means for environmental protection of below-ground sources of drinking water, are required. Depending on the local geology and leachate or other wastewaters considered for injection, the depth of an industrial wastewater deep injection well can generally range from 3,000 feet to greater than 12,000 feet. Geologic formations that will accept wastewater include porous sandstone and permeable carbonate formations.

Reverse osmosis (RO): The use of permeable membranes can effectively reduce nitrogen and other leachate constituents, including ammonium. The leachate to be treated is pressurized on one side of the RO membrane, and because of the membrane's very small pore size, water molecules pass through the membrane pores leaving concentrated chemical constituents suspended in water on the other side of the membrane. The "concentrate" waste stream can be further treated using even higher-pressure membranes to decrease the concentrate volume to be disposed. Concentrate volume will vary with different leachates but generally ranges between 15 to 35 percent of the original waste stream.

A final word

Consider conducting bench-scale and pilot-scale testing for any nitrogen removal or treatment system that is feasible. If the wastewater/ leachate water quality changes, the makeup of nitrogen compounds remaining in the wastewater effluent may also change. When there are changes to the processes that generate wastewater (e.g., landfills accept new types of waste, etc.), testing the wastewater helps to identify any changes to the concentration of nitrogen compounds. Thus, necessary changes to the treatment processes, such as additional aeration or chemical additions, are easier to identify and implement.

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