

Guideline No.: EN/004

Issue Date: July 2010

Title: Ammonia Works
Issued by: Environment Department

1.0 Introduction

Ammonia is a compound with the formula NH_3 . It is normally encountered as a gas with a characteristic pungent odor. Although ammonia contributes significantly to the nutritional needs of the planet, the gas itself is caustic and can cause serious health damage. Exposure to very high concentrations of gaseous ammonia can result in lung damage and death. It meets the definition of a material that is toxic by inhalation and requires a hazardous safety permit when transported in quantities greater than 13,248 liters (3,500 gallons).

Ammonia used commercially is usually named *anhydrous ammonia*. This term emphasizes the absence of water. Because NH_3 boils at $-33^\circ C$ and freezes at $-77.7^\circ C$, the liquid must be stored under pressure or at low temperature. Its heat of vaporization is, however, sufficiently high that NH_3 can be readily handled in ordinary beakers in a fume hood. *Household ammonia* or *ammonium hydroxide* is a solution of NH_3 in water. It is highly soluble in water, with one column of water absorbing 1.148 volumes of ammonia at $0^\circ C$.

The danger associated with ammonia is that it is explosive when mixed with air in certain proportions, approximately one volume of ammonia to two volumes of air, and is much more so when mixed with oxygen.

Because of its many uses, ammonia is one of the most highly produced inorganic chemicals. Dozens of chemical plants worldwide produced ammonia. The worldwide ammonia production in 2004 was 109 million metric tons. The People's Republic of China produced 28.4% of the worldwide production followed by India with 8.6%, Russia with 8.4% and the United States of America with 8.2%.

These notes apply to all new ammonia production plants and works in which ammonia is stored and handled in anhydrous form in fixed tanks with an aggregate capacity exceeding one hundred (100) tons.

2.0 Industries Emitting Ammonia

Various industries were identified as emitters of ammonia. These include the fertilizer manufacture industry, coke manufacture, fossil fuel combustion, livestock management, and refrigeration methods. Most of the ammonia emitted is generated from livestock waste management and fertilizer production, comprising about 90% of total ammonia emissions.

Fossil fuel combustion is different from the other industries identified in that ammonia is not emitted from the process itself, but from the control technology applied to the source in order to control nitrogen oxide (NO_x) emissions. Selective catalytic reduction and selective non-catalytic reduction are two technologies used to control nitrogen oxides in the post-combustion gases exhausting from combustion sources. These methods reduce nitrogen oxides by injecting urea or ammonia into the exhaust gas to react with the nitrogen oxides, with or without a catalyst present, depending on the method selected. If

the reaction is not complete, a portion of the ammonia may exit the system in the effluent. This condition is known as ammonia slip.

3.0 Emission Limits and Controls

3.1 A single emission limit for ammonia is not readily applicable to this class of works. Design criteria for the discharge from individual plant exists shall be discussed with the Authority and where practicable should aim for concentration of free ammonia (point source limit: 50 mg/m³) shall be so that ambient criterion of 2 ppm (fence line) is met at all times.

3.2 All emissions shall be free from droplets and persistent mist.

3.3 The emission of combustion products from reformer or other furnaces shall be maintained free from visible smoke or fumes during normal operation.

4.0 Control Techniques

The various control technologies available to control ammonia emissions include both add-on control devices and pollution prevention techniques.

4.1 Wet Scrubber – specifically the packed tower has been successfully used to control ammonia emissions, demonstrating control efficiencies up to 99%.

4.2 Condensers – also used to remove ammonia by converting the gas to a liquid. Many times the condensate is returned to the process for reuse.

4.3 Ammonia Recycle – the ammonia is retrieved from the exhaust gas stream and returned to the process, is common pollution prevention. The recycling method is often used in the manufacture of fertilizers, where ammonia is a feedstock and the implementation of recycling benefits the process in addition to controlling emissions. In the case of fossil fuel combustion where ammonia is emitted as a result of the controls implemented to reduce nitrogen oxide emissions, careful application of the nitrogen oxide control method will limit the amount of ammonia that will slip through the process.

With regards to ammonia leakage, good management practices can reduce the amount of ammonia that escapes. For those leaks that cannot be prevented, capture devices such as hoods may be used to collect the ammonia gas, which is then conveyed to a control device for treatment.

5.0 Operational Controls

5.1 Reformer production gas (“make gas”) during start-up or shutdown procedures shall be vented to a suitable flare, or when incombustible, discharged at an agreed height.

5.2 Carbon dioxide discharged to atmosphere from CO₂ absorber-stripper units shall at all time pass through an efficient droplet and spray eliminator system. This shall apply also to emergency venting systems, and extra care shall be taken when absorbents of high toxicity are used.

- 5.3 All gas purged from the synthesis loop during normal operation shall be burned in a suitable furnace or flare.
- 5.4 Gaseous ammonia from pressure relief systems shall, when practicable, be vented to a flare or discharged at an agreed height.
- 5.5 Storage facilities for light liquid hydrocarbon feed stocks shall be fitted either with double-sealed floating roofs, or with a vapor recovery system, or equivalent means for minimizing vapor loss.
- 6.0 Pollution Prevention Techniques
- 6.1 Recycle – for operations that use ammonia as a feedstock, emissions control is intrinsic in the recovery and recycles process. The recycle method benefits the process in that process condensate is collected and reused so less ammonia feedstock is required. In addition, the ammonia emissions are prevented by returning them to the process. With this technique, excess material is reused instead of being wasted and the emissions remain within the system.
- For smaller applications such as refrigeration systems, emissions of ammonia refrigerant may be collected and recycled back to the system for reuse. This decreases the amount of refrigerant that is lost through leakage and therefore reduces the amount of new refrigerant that must be purchased.
- 6.2 Limiting Ammonia Input – ammonia is emitted from post-combustion control systems such as SCR and SNCR which use ammonia or urea to reduce nitrogen oxide emissions from the fossil fuel combustion sources. Although it is nearly impossible to prevent ammonia slip from occurring, the amount of slip can be minimized. This is accomplished by limiting the amount of reducing agent added to prevent ammonia in excess of the amount required to react with the nitrogen oxides. The amount of ammonia or urea added is determined based on the allowed level of ammonia slip and the amount of nitrogen oxides exiting the combustion source. The ammonia to nitrogen oxide ratio must be minimized to keep ammonia slip levels low. Studies have shown that enhancers decrease the amount of ammonia slip since the reaction with nitrogen oxides is more efficient. In addition, the use of ammonia has exhibited lower slip levels than those generated by the use of urea as the reducing agent. Since combustion sources are present at facilities within many different industries, the use of SCR or SNCR is an applicable control method for nitrogen oxides that may be adapted to the concerned stationary combustion source.
- 6.3 Capture Systems – in order to collect ammonia emissions, capture devices such as hoods may be used. These hoods are divided into three categories: enclosure, capture hood, or receiving hood. Enclosures, either partial or complete, encircle the emission source without interrupting the process and prevent emission releases from entering the atmosphere. Capture hoods, or exterior hoods, are placed on the outside of the process and use a powerful air stream to draw emissions into the hood after they are released to the atmosphere. Receiving hoods also capture emissions once they exit the process and are emitted to the atmosphere. These devices use the momentum of certain exhaust streams to facilitate the collection of emissions. Once these streams are collected using capture systems, the streams are often vented to a control device for treatment.

6.4 Maintenance Practices – good maintenance practices may be applied by any source handling ammonia, even small sources. Ammonia leaks occurring from process equipment can be easily controlled by applying capture devices to collect the fugitive emissions. Since leaks often occur around equipment connections, the source of the leaks can be identified and targeted. In addition, there are several leak detection devices available that may be used to identify unknown leak points. After collection, the vapors may be conveyed to a control device such as a filter or wet scrubber for treatment. Ammonia adsorbed by the filter may be retrieved and reintroduced into the process which is economically beneficial. In addition, the equipment must be properly maintained to ensure that worn parts are replaced.

7.0 Chimneys

7.1 Chimney heights [minimum: thirty seven (37) meters] for ammonia works shall be agreed with the Authority on the basis of the expected maximum rate of emission of ammonia or any other significant pollutant, taking into account emergency situations.

7.2 To reduce the possibility of mist formation, chimneys for emissions containing ammonia should be spaced as far as practicable from chimneys discharging acid gases.

8.0 Environmental and Health Effects

Ammonia is found naturally in the environment. You may be exposed to ammonia by breathing air, eating food, or drinking water that contains it, or through skin contact with ammonia or ammonium compounds. Exposure to ammonia in the environment is most likely to occur by breathing in ammonia that has been released into the air.

Ammonia has a very strong odor that is irritating and that you can smell when it is in the air at a level higher than 50 ppm. Therefore, you will probably smell ammonia before you are exposed to a concentration that may harm you. Levels of ammonia in air that cause serious effects in people are much higher than levels you would normally be exposed to at home or work. However, low levels of ammonia may harm some people with asthma and other sensitive individuals.

Outdoors, you may be exposed to high levels of ammonia gas in air from leaks and spills at production plants and storage facilities, and from pipelines, tank trucks, railcars, ships, and barges that transport ammonia. Higher levels of ammonia in air may occur when fertilizer with ammonia or ammonium compounds is applied to farm fields. After fertilizer is applied, the concentration of ammonia in soil can be more than 3,000 ppm; however, these levels decrease rapidly over a few days.

The most important injurious effects of exposure to excessive amounts of ammonia on humans are due to its irritative and corrosive properties. Exposures to ammonia gas cause chemical burns of the respiratory tract, skin, and eyes. Ammonia dissolves in the water present in skin, mucous membranes, and eyes and becomes ammonium hydroxide, which is a highly ionized weak base that causes necrosis of the tissues. Specifically, ammonium hydroxide causes saponification of cell membrane lipids resulting in cell disruption and death. Additionally, it extracts water from the cells, and initiates an inflammatory response, which further damages the surrounding tissues. Contact with liquid ammonia (not ammonium salts) results in cryogenic injury in addition to the alkali burns. Airway blockage and

respiratory insufficiency may be lethal outcomes of exposure to anhydrous ammonia vapors or concentrated aerosols. Ingestion of concentrated ammonium solutions may produce severe burns and hemorrhage of the upper gastrointestinal tract. Survival of the initial insult may be compromised by infections, scarring, and other complications that may develop days or weeks following inhalation or ingestion. Effects that have been observed in humans exposed to ammonia gas and ammonium salt aerosols have also been observed in animals. Hepatic and renal effects have also been reported in animals and humans; however, ammonia does not appear to be a primary liver or kidney toxicant.

Increased systemic ammonia/ammonium salts/ion, or hyperammonemia, is generally not seen following inhalation or dermal exposure, but can result from ingestion and from certain disease states such as cirrhosis of the liver, acute liver failure, and congenital deficiencies of any of the urea cycle enzymes. Liver disease can result in decreased metabolism of ammonia with resultant increased levels of ammonia in the bloodstream and in the brain, which can produce neurological effects such as seizures and coma, and eventually death. The most likely and significant effects of exposure to elevated levels of ammonia are discussed below.

- a. Respiratory Effects – accidental exposures to concentrated aerosols of ammonium salts or high concentrations of ammonia gas have resulted in nasopharyngeal and tracheal burns, airway obstruction and respiratory distress, and bronchiolar and alveolar edema.
- b. Dermal Effects – skin is extremely sensitive to airborne ammonia or ammonia dissolved in water. Dermal exposures to liquid ammonia or concentrated solutions and/or ammonia gas are frequently occupationally related and produce cutaneous burns, blisters, and lesions of varying degrees of severity.
- c. Ocular Effects – good quantitative data are lacking, but symptoms progress as follows: inflamed eyes, lacrimation, swelling of the eyelids, hyperemic conjunctiva, blurred vision, possible transient blindness, corneal abrasions, and sustained corneal damage.
- d. Neurological Effects - Neurological effects in humans following inhalation or dermal exposure to ammonia are usually limited to blurred vision, most likely due to direct contact, but more severe exposures, which result in significant elevation of blood ammonia levels (hyperammonemia), can result in diffuse nonspecific encephalopathy, muscle weakness, decreased deep tendon reflexes, and loss of consciousness. Hyperammonemia in humans can result from certain disease states such as cirrhosis of the liver, acute liver failure, and congenital deficiencies of any of the urea cycle enzymes; hyperammonemia may lead to encephalopathy. Some have suggested that ammonia may be involved in the generation of the symptomatology and progression of Alzheimer's disease as a result of pathological ammonia metabolism in the brain. Cerebral edema and herniation and intracranial hypertension have been noted in animal models of hyperammonemia.