STOP POLLUTION

AMERICAS TOUR

Ammonia and urea production:

Incidents of ammonia release from the Profertil urea and ammonia facility, Bahia Blanca, Argentina 2000.

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December 2000

Technical Note: 17/00

GREENPEACE

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THE PROFERTIL FACILITY

The Profertil plant in Bahia Blanca, Argentina is designed to produce 1.1 million tonnes of urea and 775 thousand tonnes of ammonia annually (Profertil 2000). The start-up of the ammonia plant was completed in the first week of October 2000. In recent months, a number of releases of ammonia have occurred at the Profertil plant.

On August 28th, an ammonia leak occurred during start up procedures. The leak is believed to have been caused by excess pressure in a tank holding 200 cubic metres of aqueous ammonia. Measurements taken after the release showed levels of ammonia in the air of between 40 and 100 ppm. The maximum allowable concentration is 35ppm. Levels of ammonia in the air at the time of the release may have been considerably high than these levels, as discussed in Section 3.

People in the vicinity reported burning eyes and respiratory tract, and reported that it was "impossible to breathe". More than 80 people were hospitalised, many requiring breathing assistance. Students at schools near to the industrial complex were evacuated. As a result of the release, the Argentinean regulatory agency Sectretaria de Polytica Ambiental (SPA) ordered the plant to stop production at the facility after August 31.

On November 8th, a leak of ammonia gas occurred during the start-up of the urea plant. The concentration of ammonia was measured at 4-12 ppm for less than one hour at the plant fence line. As a result of the release, the Argentinean regulatory agency Sectretaria de Polytica Ambiental (SPA) ordered the plant to stop production. The ammonia plant remained in operation.

This document covers the production and uses of ammonia and urea, including a discussion of accidental industrial releases of ammonia. The toxicology and legislation of these compounds are also discussed.

1. INTRODUCTION

1.1 Fertilizers

Fertilizers fall into three general categories; nitrogen (N) based, phosphorus (P) based, and combined nitrogen-phosphorus (N-P) based.

The majority of nitrogen based fertilizers are derived from ammonia. In the 1990s, over 95% of all commercial nitrogen fertilizer was derived from synthetic ammonia. Worldwide, the annual production of synthetic ammonia is about 120 million tonnes, of which about 85% is used in fertilizers, including urea (Kroschwitz & Howe-Grant 1995b).

1.2 Ammonia

Ammonia, NH_3, is a comparatively stable, colourless gas at ordinary temperatures, with a boiling point of –33°C. Ammonia gas is lighter than air, with a density of approximately 0.6 times that of air at the same temperature (Marshall 1987). The characteristic pungent odors of ammonia can be detected as low as 1-5ppm (USDHHS 1978).

Ammonia can be highly toxic to a wide range of organisms. In humans, the greatest risk is from inhalation of ammonia vapour, with effects including irritation and corrosive damage to skin, eyes and respiratory tracts. At very high levels, inhalation of ammonia vapour can be fatal. When dissolved in water, elevated levels of ammonia are also toxic to a wide range of aquatic organisms. The toxicology of ammonia is discussed in more detail in Section 4.

Ammonia is highly soluble in water, although solubility decreases rapidly with increased temperature. Ammonia reacts with water in a reversible reaction to produce ammonium (NH_4^+) and hydroxide (OH^-) ions, as shown in equation [1]. Ammonia is a weak base, and at room temperature only about 1 in 200 molecules are present in the ammonium form (NH_4^+). The formation of hydroxide ions in this reaction increases the pH of the water, forming an alkaline solution. If the hydroxide or ammonium ions react further with other compounds in the water, more ammonia with react to reestablish the equilibrium.

$$NH_3 \; + \; H2O \; \leftrightarrows \; NH_4^+ \; + OH^- \qquad\qquad [1]$$

While ammonia-air mixtures are flammable when the ammonia content is 16-25% by volume, these mixtures are quite difficult to ignite (Kroschwitz & Howe-Grant 1995a).

About 85% of the ammonia produced worldwide is used for nitrogen fertilizers. The remainder is used in various industrial products including fibers, animal feed, explosives (Marshall 1987, Kroschwitz & Howe-Grant 1995a).

1.3 Urea

Urea (NH_2CONH_2), which is also known as carbamide, carbonyl diamine, carbamimidic acid, and isourea, was the leading nitrogen fertilizer worldwide in the 1990s (Kroschwitz & Howe-Grant 1995b).

Urea is a stable colourless and odorless solid at room temperature that will melt at 135°C. It is highly water soluble, and will slowly hydrolyse in the presence of water (or water vapour), to give ammonium carbamate which slowly decomposes to ammonia and carbon dioxide (Kroschwitz & Howe-Grant 1995c).

2. PRODUCTION

2.1 Ammonia

Essentially all the processes employed for ammonia synthesis are variations of the Haber-Bosch process, developed in Germany from 1904-1913. This process involves the reaction of hydrogen and nitrogen under high temperatures and pressures with an iron based catalyst. This process also requires large energy consumption (Kroschwitz & Howe-Grant 1995b). Ammonia is generally produced at a few large plants with stream capacities of 1000 tonnes/day or greater (Marshall 1987).

The formation of ammonia from hydrogen and nitrogen is a reversible reaction, as shown in equation [2]. The fraction of ammonia in the final gas mixture is dependent on the conditions employed. Unreacted hydrogen and nitrogen gases separated from the ammonia and are usually recycled. In almost all modern plants, the ammonia produced is recovered by condensation to give liquid ammonia (Kroschwitz & Howe-Grant 1995a).

$$H_2 + 3N_2 \leftrightharpoons 2NH_3 \qquad\qquad [2]$$

The source of nitrogen is always air. Hydrogen can be derived from a number of raw materials including water, hydrocarbons from crude oil refining, coal, and most commonly natural gas. Hydrogen rich reformer off-gases from oil refineries have also been used as a source of hydrogen. Steam reforming is generally employed for the production of hydrogen from these raw materials. This process also generates carbon dioxide, which can then be used as a raw material in the production of urea (Kroschwitz & Howe-Grant 1995a).

Trace impurities in the feed gases, such as sulphur compounds and chlorides, can have a detrimental effect on the production of ammonia by poisoning the catalysts employed. The feed gases, therefore, need to be purified prior to use (Kroschwitz & Howe-Grant 1995a).

2.1.1 Emissions

The production of ammonia is relatively clean compared to other industrial chemical processes. Wastewater effluents may contain ammonia and have high pH values (i.e. alkaline) as a result of dissolved ionized ammonia ($NH_4^+ + OH^-$). A number of methods have been developed for stripping ammonia from wastewaters, and for most modern plants, levels of ammonia in the effluent stream are low (Kroschwitz & Howe-Grant 1995c).

Releases of small quantities of ammonia to air may occur during normal operating procedures. A number of laws cover the maximum allowable concentrations of ammonia in air, these are discussed in Section 5. Of greater concern is the unplanned release of larger quantities of ammonia due to accidents, spills, or equipment failure, as discussed in Section 3.

The reforming of hydrocarbons to produce the hydrogen and carbon dioxide feed gases can result in the production of nitrogen oxides (NO_x) and sulphur oxides (SO_x). Where natural gas is used as the hydrocarbon raw material, the production of sulphur oxides can be greatly reduced by the removal of the low levels of sulphur in the natural gas using a simple adsorption system (Kroschwitz & Howe-Grant 1995a).

It is possible to remove nitrogen and sulphur oxides from the flue gases by a combination of conventional control techniques including low NO_x burners, selective catalytic reduction and flue gas scrubbing (Kroschwitz & Howe-Grant 1995a).

In addition, air emissions from the boilers can include carbon monoxide (CO), nitrogen oxides (NO_x) and sulphur oxides (SO_x).

2.1.2 Storage

Anhydrous ammonia is usually stored as a liquid in refrigerated tanks at –33.3°C and atmospheric pressure, often in doubled-walled tanks with the capacity for hundreds or thousands of tonnes. The low temperature is usually maintained by the venting of ammonia gas. The vented gas is reliquefied for recycling, or absorbed in water to make aqueous ammonia. Relatively small quantities of anhydrous ammonia are sometimes stored under pressure in spherical vessel at ambient temperature (Kroschwitz & Howe-Grant 1995a, Marshall 1987).

Ammonia is corrosive to alloys of copper and zinc and these materials must never be used in ammonia service. Iron and steel are usually the only metals used in ammonia storage tanks, piping and fittings (Kroschwitz & Howe-Grant 1995a).

2.2 Urea

Urea (NH_2CONH_2) is produced from ammonia (NH_3) and gaseous carbon dioxide (CO_2) at high pressure and relatively high temperature. Both reactants are obtained from ammonia synthesis, as discussed in Section 2.1. The production of urea involves the formation of ammonium carbamate (NH_2COONH_4), which is dehydrated to form urea. For all practical purposes, these two reactions take place simultaneously (see equations 3 & 4).

$$2\,NH_3 + CO_2 \leftrightarrows NH_2COONH_4 + heat \qquad\qquad [3]$$

$$NH_2COONH_4 + heat \leftrightarrows NH_2CONH_2 + H_2O \qquad\qquad [4]$$

Both of these reactions are reversible, and therefore ammonia and carbon dioxide exit the reactor along with ammonium carbamate and urea. The components of this mixture are then separated, usually by stripping off gaseous ammonia followed by carbon dioxide, to yield urea.

There are a number of process for handling ammonia in this process, including the once through, the partial recycle and the total recycle processes (Kroschwitz & Howe-Grant 1995b).

2.2.1 Solidification

Urea processes produce an aqueous solution containing 70-87% urea (Kroschwitz & Howe-Grant 1995c). The two most commonly employed methods for the production of solid urea are prilling and granulation.

Prilling
In prilling, molten urea that is almost anhydrous is forced through spray heads or spinner buckets. The droplets of urea fall through a countercurrent stream of air in which they solidify to form prills (pellets). This process has potentially greater pollution problems due to the production of a large volume of air laden with very fine dust that must be processed (Kroschwitz & Howe-Grant 1995b). Many recovery systems have been tried for this process, but all with limited success (Kroschwitz & Howe-Grant 1995c).

Granulation
Granulation is now superceding prilling as the method of choice for urea solidification. In this process, granules are usually formed by the successively spraying and drying (layering) of concentrated urea solution onto recycled granules, in a rotating drum (Kroschwitz & Howe-Grant 1995b).

For both the prilling and granulation processes, formaldehyde (0.2-0.5%) is often added to the urea melt prior to solidification. This is to condition the finished product, improving the particle crushing strength and reducing caking during storage, without lowering the

nitrogen content. The addition of formaldehyde to the pre-solidified urea has also been used to reduce dust formation in both processes (Kroschwitz & Howe-Grant 1995b & 1995c).

2.2.2 Emissions

For every tonne of urea produced, 0.3 tonnes of water are formed. This water is usually discharged from the urea concentration and evaporation section of the plant.

Removal of ammonia and urea from wastewaters can be a problem as it is difficult to remove one in the presence of the other. One method used to overcome this problem is the hydrolysis of urea to ammonium carbamate, which is decomposed to ammonia and carbon dioxide. These gases can then be stripped from the wastewaters. Urea plants are in operation that produce wastewaters with ammonia and urea levels below 1ppm. This water can then be used as boiler feed water (Kroschwitz & Howe-Grant 1995c).

The solidification of urea results in the formation of particulate matter, particularly the prilling process (Kroschwitz & Howe-Grant 1995b).

Of greater concern, however, are one-off accidental releases of ammonia, often due to equipment failure. This is discussed in more detail in Section 3.

3. ACCIDENTAL RELEASES OF AMMONIA

Ammonia is corrosive to a number of metal alloys particularly those of copper and zinc. Iron and steel are usually the only metals used in ammonia storage tanks, piping and fittings (Kroschwitz & Howe-Grant 1995a). However, under certain conditions and with certain steels, anhydrous ammonia is liable to produce embrittlement (Marshall 1987). If stringent protocols are not followed, equipment failure may result in a large release of ammonia liquid or vapour.

Once released, ammonia vapours can disperse extremely quickly. These vapours can be highly toxic by inhalation. The discharge of liquid ammonia, or the absorption of gaseous ammonia, to aquatic systems can also result in conditions that are toxic to aquatic life (see Section 4).

Where ammonia is stored under refrigerated conditions or as a liquefied gas under pressure, if containment is lost a portion of the liquid immediately evaporates (flashes). The proportion flashing depends on temperature conditions (Marshall 1987). While ammonia is less dense than air, there is evidence that some ammonia/air clouds formed by flashing have been denser than the surrounding air, resulting in ammonia clouds at ground level (Marshall 1987).

Liquefied ammonia has a high level of dispersive energy, i.e. the energy available within the ammonia which enables it to be brought into contact with the victims. This is partially due to its relatively high vapour pressure (Marshall 1987).

Where large quantities of liquid ammonia have been released, evaporation will lower the temperature of the liquid. However, the rate of conduction of heat from the surroundings will often maintain the temperature of the ammonia pool sufficiently close to its atmospheric pressure boiling point, to enable continual evaporation (Ball 1970, Shaw & Briscoe, 1978).

Even after large releases of ammonia, it is possible for levels of ammonia vapour in air to return to background levels within a matter of hours, as discussed in Section 3. The rate of dispersal of ammonia clouds is highly dependent of environmental conditions including wind speed and humidity. Levels of ammonia in the air measured only hours after a release do not, therefore, give an accurate measure of the levels present in the air at the time of the release (ACMH 1979, McMullen 1976).

3.1   Large industrial releases

A number of large scale releases of ammonia have occurred from various industrial activities, with varying impacts on humans and the environment, including aquatic systems which can be sensitive to elevated levels of ammonia.

A report in 1979 listed 11 major spills of ammonia which caused a total of 41 fatalities, including a release of 38 tonnes of ammonia from a storage tank at a fertilizer plant in Potchefstroom, South Africa in 1973. This incident resulted in 18 fatalities, 6 of them outside the works fence, up to 200 meters from the tank. An additional 65 cases of non-lethal gassing were reported. A major contributing factor was the failure of the company to have the dished end of the tank stress relieved by heat treatment after a previous repair, resulting in it being very brittle (ACMH 1979 & Lonsdale 1975).

A release of 19 tonnes of ammonia from a road tanker in Houston, Texas in 1976 resulted in 6 fatalities and more than 100 injuries. Only 2.5 hours after the incident, air levels of ammonia had returned to background levels. This clearly demonstrates the inability of air measurements taken only hours after a release to give an accurate measure of the levels present in the air at the time of the release (ACMH 1979 & McMullen 1976).

A spill of 600 tonnes of ammonia from a burst pipe in Floral, Arkansas, USA in 1971 did not result in any human fatalities. However, the released ammonia reached a watercourse and killed thousands of fish (Chemical Engineering 1971).

4. TOXICITY

4.1 Ammonia

Ammonia gas is extremely corrosive and irritating to the skin, eyes, nose, and respiratory tract. Exposure by inhalation causes irritation of the nose, throat, and mucous membranes. Lacrimation and irritation generally begin at 130 to 200 ppm, although symptoms of eye and upper tract respiratory tract irritation have been reported at 30-50ppm. The maximum short exposure tolerance has been reported as being 300-500 ppm for 0.5 to 1 hour (Henderson & Haggard 1943). At 400-700 ppm severe eye and respiratory irritation can occur, with the potential for permanent damage. At 1700 ppm convulsive coughing and bronchial spasms occur, and half hour exposure to this concentration is potentially fatal. Exposure at 3000 ppm is intolerable and exposure to high concentrations (above approximately 2500 ppm) is life threatening, causing severe damage to the respiratory tract, resulting in bronchitis, chemical pneumonitis, and pulmonary edema (build-up of fluid in the lungs), which can be fatal. At 5000-10000 ppm, death can occur from suffocation (NRC 1994, Holness *et al.* 1989, Kroschwitz & Howe-Grant 1995a).

Eye contact with ammonia vapour is severely irritating, and exposure of the eyes to liquid ammonia or mists can result in serious damage, which may result in permanent eye injury and blindness. Skin contact with ammonia vapor, mists, liquid and concentrated aqueous solutions can cause severe irritation and burns; contact with the liquid also results in cryogenic burns. Ingestion of liquid ammonia burns the tissues, causing severe abdominal pain, nausea, vomiting, and collapse and can be fatal. Ammonia has not been found to be carcinogenic or to show reproductive or developmental toxicity in humans (NRC 1994, Trevethick 1973, Marshall 1987).

4.1.1 Aquatic life

Ammonia is a naturally occurring compound though it is usually present in low concentrations in uncontaminated sites (ASTDR 2000).

Ammonia is toxic to a wide range of aquatic organisms at elevated concentrations. Fish are the most sensitive species and cold-water, oxygen-sensitive, fish such as trout are the most vulnerable (Wade 1998).

In aqueous solutions, ammonia exists in both un-ionized (NH_3) and ionized (NH_4^+) forms. The relative concentrations of each species is dependant on a number of factors, including pH and temperature. The toxicity of ammonia is usually due to the concentration of the unionized form, NH_3. In all marine fish species, there is some risk of growth disturbances at ammonia concentrations above 0.11 mg/l (Person-Le Ruyet 1998).

Toxicity by un-ionized ammonia (NH_3) to aquatic life is temperature and pH (acidity/alkalinity) dependant for many species, with higher toxicity being found at lower

temperatures and higher pH. At lower pH, a larger proportion of ammonia will ionize to ammonium ions (NH_4^+), resulting in lower toxic effects (Lewis1988).

Fish sensitivity to total ammonia concentration (NH_3 and NH_4^+) is highly dependent on environmental factors, such as ambient pH and oxygen availability. Their tolerance may also be affected by exposure conditions including acclimation, fluctuating total ammonia levels and exposure duration (Person-Le Ruyet 1998). For example, the survival probability of rainbow trout exposed simultaneously to ammonia and low dissolved oxygen has been shown to be lower than the predicted survival probability derived from the addition of the individual effects of ammonia and hypoxia (Magaud *et al.* 1997).

Organisms closely associated with marine or estuarine sediments may be exposed to higher ammonia concentrations than are found in the water column, especially when sediments are disturbed. Four species of marine or estuarine amphipods (*Rhepoxynius abronius, Eohaustorius estuarius*, *Ampelisca abdita* and *Grandidierella japonica*) exhibit median lethal concentrations (LC50) of between 49.8 mg/liter total ammonia (0.83 mg/liter as un-ionized ammonia) and 148.3 mg/liter total ammonia (3.35 mg/liter un-ionized ammonia), with *A. abdita* being the most sensitive (Kohn *et al.* 1994).

Certain species are considerably more sensitive to low levels of un-ionized ammonia. Nine native New Zealand invertebrate species showed a final acute value (FAV) of 0.15 g/m^3 ammonia (NH_3). This compares with the FAV value of 0.52 g/m^3 NH_3 derived by the US Environmental Protection Agency (EPA) as the basis for the ammonia criterion for salmonid containing waters (Hickey & Vickers 1994).

As for aquatic plants, ammonium concentrations as low as 25 micromoles per litre have been shown to cause toxic effects on the eelgrass *Zostera marina*, with the plants becoming necrotic or dying after five weeks (Van Katwijk *et al.* 1997).

4.2 Urea

Unlike ammonia, urea is classified as a non-toxic compound (Kroschwitz & Howe-Grant 1995c).

5. LEGISLATION

The US Occupational Safety and Health Administration (OSHA) specify the workplace threshold limit value (TVL) to ammonia as 50ppm (25mg/m3), averaged over an 8-hour period (OSHA 2000).

The US National Institute for Occupational Safety and Health (NIOSH) recommend an airborne exposure limit of 25 ppm (18 mg/m^3) averaged over a 10-hour workshift with a limit of 35 ppm (27 mg/m^3) not to be exceeded during any 15 minute work period (NIOSH

2000). NIOSH also specify an Immediately Dangerous To Life or Health Concentration (IDLH) of 300 ppm.

The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a threshold limit value (TVL) of 25ppm, averaged over an 8-hour period (Kroschwitz & Howe-Grant 1995b).

The Agency for Toxic Substances and Disease Registry (ATSDR) set Minimal Risk Levels (MRLs) of ammonia in air at 0.5ppm (acute) and 0.3ppm (chronic). A MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure. They are derived for acute (1-14 days) and chronic (15days and longer) exposure durations (ASTDR 2000).

Most regulatory bodies recommend that respiratory protection should be provided for workers exposed to ammonia, and protective clothing such as rubber aprons, boots, gloves, and goggles should be worn when handling ammonia.

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