

# Ammonium Hydroxide

## Processing

### Identification

**Chemical Name(s):**

Ammonium hydroxide

**Other Names:**

Aqua ammonia, ammonia water, aqueous ammonia, Spirit of Hartshorn

**CAS Number:**

1336-21-6 (ammonium hydroxide)

7664-41-7 (ammonia)

**Other Codes:**

International Numbering System: INS 527

RTECS: BO0875000

DOT ID: 2672 60 (12-44% solution)

2073 15 (44+% solution)

### Summary of Advised Recommendation\*

Synthetic / Non-Synthetic:	Allowed or Prohibited:	Suggested Annotation:
<i>Synthetic</i>	<i>Prohibited</i>	<i>none.</i>

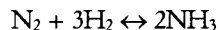
### Characterization

**Composition:**NH<sub>4</sub>OH (or NH<sub>3</sub> • H<sub>2</sub>O)**Properties:**

Colorless liquid, intense, pungent, suffocating odor; acrid taste; strong alkaline reaction; dissolves copper, zinc; fumes are formed when ammonia water is brought near volatile acids; forms exothermic reaction with sulfuric acid; infinitely soluble; specific gravity 0.9 (28% NH<sub>4</sub>OH) at 25° C; pH 11.6 (1.0N solution); boiling point ca. 36°C (ca. 97F); melting point -72C (-98F); stable under ordinary conditions of use and storage.; produces low temperatures by its own evaporation.

**How Made:**

Ammonia is produced by a number of different processes. Historically, one of the oldest, and basis for most currently used methods is the Haber-Bosch process, where natural gas is used to convert atmospheric nitrogen to ammonia (Budavari, 1996). This can be characterized as:



Industrial-scale production requires the maintenance of high temperatures, generally in the range of 700°K to 900°K (427°C - 627°C or 800°F - 1,160°F). Processes generally involve the direct reaction of disassociated hydrogen and nitrogen atoms over a catalytic surface coated with a metallic iron. Ammonium hydroxide is produced by the addition of the resulting ammonia to water.



This reaction is reversible. The existence of undisassociated ammonium hydroxide (NH<sub>4</sub>OH) is considered doubtful, but aqueous solutions of ammonia are basic and behave similarly to metal cation hydroxides, such as

\* This Technical Advisory Panel (TAP) review is based on the information available as of the date of this review. This review addresses the requirements of the Organic Foods Production Act to the best of the investigator's ability, and has been reviewed and commented on by experts on the TAP. The substance is evaluated against the criteria found in section 2119(m) of the OFPA (7 USC 6517(m)). The information and advice presented to the NOSB is based on the technical evaluation against that criteria, and is not intended to incorporate commercial availability, socio-economic impact, or any other factor that the NOSB and the USDA may want to consider in making their decisions.

sodium hydroxide (Czuppon, Knez, and Rovner, 1992). Ammonium hydroxide has an  $\text{NH}_3$  equivalent weight of 48.59 (EPA, 2000).

Most commercial solutions of 28-29%  $\text{NH}_3$  in water, although 44% solutions of  $\text{NH}_3$  are marketed for food processing use.

#### **Specific Uses:**

Ammonia is one of the top industrial chemicals produced in the world. The hydroxide form is petitioned for use as a boiler water additive, but it is also used in processing as a direct food ingredient for leavening, pH control, and as a surface-finishing agent (Lewis, 1989). Ammonium hydroxide is also used to extract food colorants and dyes (Budavari, 1996). Other uses in food processing facilities are as a refrigerant, cleaning agent, wastewater treatment, and reactant, for example, as a starter for a cheese culture (EPA, 1998). Ammonia is also released as a by-product of a number of food processing activities (EPA, 1998).

Ammonia is a precursor to synthesize amino acids, and is used in animal feeds by itself as a nitrogen source. One of the largest uses of ammonia, by production volume, is as a fertilizer, including the ammonium hydroxide form. The review will focus on the ammonium hydroxide form, and the petitioned use as a boiler water additive but some of the other forms, uses, and applications will also be addressed as relevant to the TAP review.

#### **Action:**

Ammonia in solution is alkali in pH, and ammonia ( $\text{NH}_3$ ) reactive. Neutralizes carbonic acid in condensate to prevent corrosion. Used as a boiler additive to neutralize carbonic acid in condensate thus preventing corrosion to boiler equipment. The petition was for use as a boiler water additive. Ammonia is a precursor to amines, will form amines under certain conditions in the presence of certain other co-reactants, and functions similarly to the volatile amines but ammonium hydroxide is technically not a volatile amine.

#### **Combinations:**

Contained in an aqueous solution. Food processing applications are numerous. As a boiler water additive, may be with other volatile amines, such as cyclohexylamine, diethylethanolamine (DEAE), morpholine, and octadecylamine. Combined with other yeast nutrients, with various animal feed ingredients such as molasses, and as a precursor to amino acids for use in livestock feed, as nutritional supplements, and for other applications. It is also used in the manufacture of animal drugs. Ammonia is also used with a variety of cleaners, sanitizers, and disinfectants (Czuppon, Knez, and Rovner, 1992). It is also a waste product in effluent from a number of food processing operations (EPA, 1998).

The largest single use of ammonia has long been as an ingredient in fertilizers (NRC, 1978; Czuppon, Knez, and Rovner, 1992; Johnson, 2000). The next largest use is as a precursor to polymers and to make explosives (Czuppon, Knez, and Rovner, 1992). Applications to the textile industry are also significant. It is also used to tan hides, and is an ingredient in moth-proofing and preservative compounds for leather and furs. It is also widely used in a number of cosmetics (Czuppon, Knez, and Rovner, 1992). Ammonia is used to make or in combination with a large number of industrial chemicals (Czuppon, Knez, and Rovner, 1992).

#### **Status**

##### **OFPA**

May be added to the National List as equipment cleaner (7 USC 6517(c)(1)(B)(i)).  
Prohibited as a synthetic nitrogen fertilizer (7 USC 6508(b)(2)).

#### **Regulatory**

FDA CFR Title 21, Subpart B, Sec. 582.1139 Generally Recognized as Safe (GRAS) is discussed below.

## EPA/NIEHS/Other Appropriate Sources

### EPA -

FIFRA: Residues of ammonium hydroxide are exempted from the requirement of a tolerance when used as a solvent, co-solvent, neutralizer, or solubilizing agent in accordance with good agricultural practices as inert (or occasionally active) ingredients in pesticide formulations applied to growing crops or to raw agricultural commodities after harvest. Also appears on EPA List 3.

CERCLA: Ammonium hydroxide is considered a Hazardous Substance under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (40 CFR 302.4).

SARA/EPCRA: The substance appears on the Superfund Amendments and Reauthorization Act (SARA) Title III and Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) List of Extremely Hazardous Substances (40 CFR 355 Appendix A). It is also subject to SARA reporting requirements contained in 40 CFR 311 and 40 CFR 312. Manufacturers of CHA are subject to Superfund requirements in 40 CFR 313. Ammonia use presents a number of special considerations for food processors to consider (EPA, 1998). Given the numerous uses and sources, special guidance is required for reporting aqueous ammonia (EPA, 2000).

CWA: Ammonia discharges from certain types of meat processing facilities are regulated under the Clean Water Act (40 CFR 432.45 *inter alia*).

CAA: Does not appear on the Clean Air Act list of Volatile Organic Chemicals.

NIEHS - The National Toxicology Program does not consider ammonium hydroxide to be a carcinogen. The NTP database does not include data on either ammonia or ammonium hydroxide. The NOSB may want to consider supporting a petition to have the NTP review ammonia and ammonium hydroxide.

### Other sources -

Occupational Safety and Health Administration (OSHA) revised the limits for Final Rule on Air Contaminants Project (54 Fed Reg. 2324). This rule was remanded by the U.S. Circuit Court of Appeals and the limits are not currently in force. OSHA's former exposure limit for ammonia was 50 ppm as an 8-hour TWA [Time Weighted Average]. OSHA proposed to revise this limit to 25 ppm TWA and to add a 35-ppm 15-minute short-term exposure limit (STEL), based on the limits established by the ACGIH. However, in the final rule, the Agency has determined that it is not appropriate to establish a 25-ppm TWA limit for ammonia; the final rule does revise OSHA's exposure limit to 35 ppm as a 15-minute STEL. . .

Ammonia is a primary eye and upper respiratory tract irritant. Ammonia concentrations in the range of 20 to 25 ppm elicited complaints of discomfort from workers engaged in blueprinting and copying operations (Detroit Department of Health, 1986). Pigs exposed to ammonia also showed systemic effects (Stombaugh et al., 1969). Thus the ACGIH established both a full-shift TWA of 25 ppm to protect against chronic effects and a 35-ppm STEL to protect against ammonia's irritant effects.

OSHA also considered NIOSH's recommended 5-minute ceiling limit for ammonia of 50 ppm. NIOSH relied on several reports that ammonia concentrations as low as 50 ppm are moderately irritating. Their findings concluded that the "irritating or annoying effects...[of exposure to ammonia are] more dependent upon concentration than length of exposure," and that "a standard expressed as a time-weighted average is inappropriate since it would permit fluctuations to concentrations considerably higher than 50 ppm.(NIOSH, 1974).

Some workers experience eye and upper respiratory tract irritation. For example, one source cites that 5-minute exposures to 32 ppm caused nasal dryness in 10 percent of exposed volunteers, and that 5-minute exposures to 50 ppm ammonia caused nasal irritation and dryness in 20 percent of exposed volunteers (Proctor, Hughes, and Fischman).

Pigs exposed continuously to between 103 and 145 ppm ammonia reduced their consumption of food and lost weight (Stombaugh, Teague, and Roller, 1960 cited in ACGIH, 1986). The ACGIH interprets this study to mean that systemic toxicity occurs as a result of chronic exposure to ammonia. However, OSHA interprets this

study differently, believing instead that it shows a secondary effect of the irritation traditionally associated with ammonia exposure. OSHA considered this as evidence that the pigs were experiencing too much respiratory and eye irritation to be interested in their food (OSHA, 1989). OSHA concluded that the eye and upper respiratory tract irritation associated with ammonia exposure constitute material impairments of health and pose a significant risk to exposed workers.

### **Status Among U.S. Certifiers**

Most US certifiers do not include it on their materials lists, and prohibit boiler water additives according to the Organic Good Manufacturing Practices established by the NOSB in 1995. Oregon Tilth Certified Organic classifies ammonium hydroxide as 'regulated' but this appears to be unique among certifiers worldwide. See the discussion regarding boiler water additives in the background paper Steam Generation in Organic Food Processing Systems (Steam Paper).

### **International**

**Canada** – Not included in the list of permitted non-organic additives substances for organic food products (CGSB, 1999).

**CODEX**- Not in Annex 2, Table 4, 'Processing Aids' (FAO/WHO, 1999).

**EU 2092/91** – Not in Annex VI, 'Processing Aids' (EU 2092/91).

**IFOAM** – Not on Appendix IV, approved processing aids and other products (IFOAM, 2000).

**Japan** – Not on the list of approved food additives (Woolsey, 2000).

## **OFPA 2119(m) Criteria**

- 1. The potential of such substances for detrimental chemical interactions with other materials used in organic farming systems.*  
As this is a processing material, the substance is prohibited from synthetic sources for use in organic farming systems as a synthetic nitrogen source. Use from natural sources (e.g. manure) is generally restricted. Chemical interactions within a processing environment is discussed in the Steam Paper.
- 2. The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment.*  
See processor criteria 3 below.
- 3. The probability of environmental contamination during manufacture, use, misuse or disposal of such substance.*  
This is considered below under item (2).
- 4. The effect of the substance on human health.*  
The effects of ammonia on human health have a vast literature associated with it. Two of the best summaries have been prepared by the National Research Council's Committee on Medical and Biologic Effects of Environmental Pollutants (1979) and the World Health Organization's International Programme on Chemical Safety (1986). The TAP review will limit consideration of those factors related to the effect on nutrition (3) below as well as the consideration of GRAS and residues (5) below.

5. *The effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock.*

Ammonia's chemical interactions in the agroecosystem and physiological effects on soil organisms are the subject of significant study (NRC, 1979) but is beyond the scope of the petitioned processing use. While some food handling uses may result in the release of significant amounts of ammonia into the agroecosystem, this TAP review assumes that disposal takes place outside the organic farming system.

6. *The alternatives to using the substance in terms of practices or other available materials.*

See discussion of alternatives in the Steam Paper.

7. *Its compatibility with a system of sustainable agriculture.*

This is considered more specifically below in the context of organic handling in (6) below.

### Criteria from the February 10, 1999 NOSB Meeting

*A PROCESSING AID OR ADJUVANT may be used if;*

1. *It cannot be produced from a natural source and has no organic ingredients as substitutes.*

Ammonia is naturally occurring in foods at low levels in both aqueous and ammonium hydroxide forms. It is commonly found in manure and decaying organic matter. However, all commercial sources are synthetically manufactured from atmospheric nitrogen, usually using natural gas as a fuel source.

As for substitutes for the petitioned use, steam can be produced from water without the addition of boiler water additives. A list of substances that are FDA approved for boiler water contact is attached. When considering chemical means to condition steam lines in boiler systems, the additives to the steam lines must be volatile, so that they purposely travel along with the steam. There are no known non-synthetic boiler additives that can serve this purpose. The alternatives are discussed in greater depth in the Steam Paper.

2. *Its manufacture, use, and disposal do not have adverse effects on the environment and are done in a manner compatible with organic handling.*

Ammonia production does not generate any significant waste stream. Production of ammonia requires a significant energy input to drive the synthetic reaction (Budavari, 1996). Ammonia production—primarily for fertilizer—continues to account for one of the largest uses of energy of all chemicals produced (Johnson, 2000). Coal production methods may cause significant air pollution. About two-thirds of all ammonia production involves the use of natural gas as a fossil fuel (Czuppon, Knez, and Rovner, 1992).

Ammonium hydroxide is an irritant and must be handled properly. There are significant worker health issues that could be a problem if it is improperly handled. Exposure to humans and other mammals by ammonium hydroxide is a serious toxicological concern. It is toxic by all routes (inhalation, ingestion, and dermal contact (Toxnet, 2001). Various published guidelines for use of this material all prescribe the use of protective equipment, for eyes, lungs, skin, and ingestion (NIOSH, 1979; NTP, 2001). Short-term exposure can result in irritation of the eyes, throat, skin, and mucous membranes, as well as dyspnea, bronchospasm, and pulmonary edema; ingestion can cause burning pains in the throat, mouth, stomach, and thorax; brief exposure to higher concentrations (5000 ppm) can be fatal (Budavari, 1996; Chermishinoff). Long-term exposure can result in chronic irritation to the eyes and respiratory tract (NIOSH, 1978).

Ammonium hydroxide produces a pungent odor that is an irritant. It is an air and water pollutant. For example, ammonia is considered a greenhouse gas (NRC, 1978). Ammonia produced as the effluent of sparged boiler water is a potential water pollutant. Ammonia is a plant nutrient. As an effluent, it will favor some species over others and may be a factor in contributing to eutrophication (NRC, 1978). Ammonia is also toxic to fish and other aquatic animals (IPSC, 1986).

3. *If the nutritional quality of the food is maintained and the material itself or its breakdown products do not have adverse effects on human health as defined by applicable Federal regulations.*

Acute oral exposure and ingestion are linked to liver damage (NRC, 1978) and hepatic coma (IPCS, 1986). Ammonium hydroxide has an acid taste, and can affect the flavors of foods; as it participates in a strong alkaline reaction with a variety of materials, the resultant products can be made bitter. Ammonia has a pungent odor and imparts a distinct flavor defect, even at relatively low rates. For example, the threshold value for detection in water is  $3.4 \times 10^{-1}$  or about 35 ppm (Fazzalari et al., 1978, cited by petitioners; supported by IPCS, 1986).

The full effects of reactions between ammonium hydroxide and foodstuffs are not as well documented as other forms of exposure in the scientific literature (NRC, 1978; IPCS, 1986). There is substantial disagreement among researchers as to the long-term effects of exposure (IPCS, 1986). It would appear that it has minimal adverse effects on human health if used as intended (IPCS, 1986). However, there have been incidents and indications that ammonia can have documented adverse effects on human health at relatively low levels, not far above the levels at which workers and consumers could potentially be exposed. Accidental exposure is also a possibility when a chemical is being handled in a food processing operation. Ammonia will form nitrates and nitrites under certain conditions (NRC, 1978). Nitrates and nitrites are prohibited by the Organic Foods Production Act (7 USC 6510(a)(3)).

The Federal Centers for Disease Control reported that the accidental release of ammonia resulted in non-lethal acute poisoning of schoolchildren from consumption of contaminated milk. These children reported severe burning of the mouth and throat, as well as nausea. The symptoms developed within 1 hour of drinking the contaminated milk (CDC, 1986). There has been a noted case where milk was contaminated by ammonium hydroxide during processing (CDC). Especially when considering that the ammonium hydroxide would be contacting foodstuffs under heated conditions, reactivity is likely in at least some cases. The reaction of this synthetic material with organic foodstuffs may create a variety of synthetic by-products, the health implications of which are not completely known, especially over the long-term.

There is no indication that addition of aqua ammonia to the processing stream has a beneficial effect on the nutritional quality of food. The petition does not provide a food safety benefit for allowing its use. Furthermore, ammonium hydroxide is a good solvent for many materials, including certain metals such as copper and zinc (Budavari, 1996), which could result in the toxic accumulation of these metals in organic food products, if the material is not used with caution, or is used in incompatible steam systems.

Ammonium hydroxide is an eye and respiratory tract irritant. Another characteristic is that under certain common conditions, aqueous ammonia can damage metals and cause rather than prevent corrosion (Bradford, 1993). For example, ammonium hydroxide is corrosive of copper and zinc (Budavari, 1996). Ammonia in high pH systems or beyond the optimum level will actually increase the amount of copper in boiler water copper-nickel systems above a zero-treatment control (Burgmayer, 1989). While copper and zinc are essential trace elements, both can be toxic in excess. This is a concern where copper or zinc are used as either sacrifice coatings or as the primary materials in the waterside wall of boilers. Ammonia will also react with chlorine-based disinfectants in water to form chloramines (EPA, 1998).

4. *Its primary purpose is not as a preservative or used only to recreate/improve flavors, colors, textures, or nutritive value lost during processing except in the latter case as required by law.*

The petitioned use is not to change the quality of the food, but rather to maintain and prevent corrosion of the boiler and steam line equipment used to produce steam that is in contact with the food. Ammonium hydroxide as a boiler water additive is not intended to have any technical or functional effect on the food product. If used, however, some of the material will come into contact with organic foods, thus the reason for the petition. Other uses will have a functional effect, such as in chocolate processing, as an extractant for glycyrrhizin (licorice); and as a synthetic nitrogen source in a feed additive. These functions are not covered in the TAP review.

5. *Is Generally Recognized as Safe (GRAS) by FDA when used in accordance with Good Manufacturing Practices (GMP), and contains no residues of heavy metals or other contaminants in excess of FDA tolerances.*

Ammonium hydroxide is listed as GRAS by FDA (21 CFR 184.1139) food with no limitation other than current good manufacturing practices for the following uses:

Leavening agent	21 CFR 170.3(o)(17)
pH control agent	21 CFR 170.3(o)(23)
surface-finishing agent	21 CFR 170.3(o)(30)
boiler water additive	21 CFR 173.310
Feed additive	21 CFR 582.1139.

FDA requires that as an ingredient used in food it cannot exceed levels used in current good manufacturing practice. When used as a boiler water additive, levels also are not to exceed current good manufacturing practice. The GMPs do not cite a quantitative level that can be carried over in steam, in contrast to some of the other boiler water additives that have been petitioned.

6. *Its use is compatible with the principles of organic handling.*

As a general rule, ammonia products are not considered compatible with organic production or handling. The NOSB considered the issue of boiler chemicals in 1995, and determined that boiler water additives are not allowed to be in live steam that is in direct contact with organic food. While this did not specify ammonia and volatile amines, this particular application was excluded for use. All organic production and processing certification standards are based on the premise that synthetic toxic substances should not be used in a way that brings them in contact with organic foods.

As ingredients in processed food products, an exception was made to ammonium carbonates used in baked goods. However, the NOSB voted to prohibit ammonium phosphate and ammonium soaps in organic handling. The NOSB has already recommended that several be listed. Different additives have different functionalities. As a caustic, sodium carbonates, potassium carbonate, potassium hydroxide, sodium hydroxide.

Ammonium carbonates are on the National List as an alternative yeast food. No petitioner has requested any use other than as a boiler chemical, although some certifiers have reportedly encountered these other uses by processors.

See the Steam Paper and the reviewers' comments below for a further discussion.

7. *There is no other way to produce a similar product without its use and it is used in the minimum quantity required to achieve the process.*

Live steam can be generated without the use of any boiler chemicals. There are boiler chemicals that are already on the National List. These include other caustics, such as potassium hydroxide and sodium hydroxide. There are methods to keep live steam from coming into direct contact with food. These include the use of heat exchangers, traps, filters, and other equipment. See the Steam Paper for further discussion.

## TAP Reviewer Discussion\*

### TAP Reviewer Comments

#### Reviewer 1 [Food Science and Nutrition Professor with inspection and certification experience]

Ammonium hydroxide  $\text{NH}_4\text{OH}$  is considered a strong alkali which is manufactured from both natural gas and atmospheric nitrogen to ammonia gas which is readily soluble in water at concentrations of 28 to 44%. Most ammonium hydroxide is marketed to food processing operations at 44% being more concentrated which reduces the liquid handling and shipping cost of water, but presents perhaps more of a dangerous environmental impact issue should spillage occur.

Ammonium hydroxide is considered a neutralizing amine with the highest distribution ratio of 10 when compared to the other neutralizing volatile amines (Betz, 1980). This means it has a greater percentage in the vapor phase rather than the aqueous phase. Therefore its effectiveness may be based on its distribution ratio. This may be the main argument as to why the industry has not embraced the options of using sodium carbonate, sodium bicarbonate, potassium carbonate, potassium hydroxide or sodium hydroxide. However, if boiler feed water is deaerated followed by ion exchange, these alternatives may be as effective since the internal rate of corrosion of steam lines will be reduced. However, if optimization of alternatives is considered coupled with boiler feed water treatments, then a satisfactory solution or alternative is provided.

Overall, the toxicity of ammonium hydroxide and gaseous ammonia is well documented as eye and respiratory tract irritant. In the baking industry, ammonium bicarbonate decomposes to ammonia gas and carbon dioxide and serves as leavening agent for cracker food products. However, the ammonia gas must be exhausted or ammonium hydroxide will form which will cause a yellow discoloration of the wheat flour based cracker as well as contribute to a strong, astringent off flavor in the product.

Since there are no FDA limitations on its use, the potential for excessive use exists resulting in high concentrations of ammonia in the steam (i.e. greater than 25 ppm). Therefore due to environmental and worker safety issues, toxicity issues and the potential for direct contact (as with all volatile amine boiler additives) of ammonium hydroxide to organic food products, I recommend that it be prohibited for all organic food processing operations where there is direct steam contact with the food.

#### Summary Recommendation:

1. Synthetic
2. Prohibited
3. Suggested annotation: for processing operations where there is direct steam or food contact.

#### Reviewer 2 [Consultant to organic certifiers]

Although ammonia does result from natural fermentative processes and can be found in nature as such, collection of the gas from these sources for use in processing systems is not practical and not done. For the purposes of this TAP review, ammonium hydroxide is considered a synthetic material.

*[A]mmonium hydroxide . . . [is used] as an additive to steam [that] comes into direct contact with organic foods during processing. The function of the aqua ammonia is to neutralize carbonic acid which forms from the steam generation system; neutralization of the acidic condensate stream reduces corrosion of boiler equipment most notably steam lines.*

Ammonium hydroxide may be used in the synthesis of other compounds which might subsequently be used in food processing, such as leavening agents. Such materials should be deemed beyond the scope of this review. The NOSB has already reviewed some such materials which the NOP placed on the National List (ammonium carbonate and ammonium bicarbonate) as allowed non-organic ingredients for processing organic foods. Other ammonium compounds have traditionally been prohibited in organic production systems, for agriculture,

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\* OMRI's information is enclosed in square brackets in italics. Where a reviewer corrected a technical point (e.g., the word should be "intravenous" rather than "subcutaneous"), these corrections were made in this document and are not listed here in the Reviewer Comments. The rest of the TAP Reviewer's comments are edited for identifying comments, redundant statements, and typographical errors. Any text removed is identified by ellipses [ . . . ] Statements expressed by reviewers are their own, and do not reflect the opinions of any other individual or organization.



livestock, and processing applications. The only noted exception in the NOP rule is the allowance of ammonium carbonate in insect traps (no contact with soil or crops allowed). (7 CFR 205)

#### Comments on the Criteria

Organic certifiers in the United States, if they take a position at all on this issue, are consistent in repeating the prohibition recommended by the NOSB. The NOSB did make exceptions to this by allowing ammonium carbonate and ammonium bicarbonate as leavening agents, but has recommended prohibitions on other ammonium products. The reason for the exceptions made for the leavening agents is unknown to this reviewer, but judging by the processing techniques and materials available to processors of organic foods, it would seem more consistent if those materials were also removed from the National List. Adding another ammonium product does not seem compatible, especially given the other considerations mentioned in this review.

Live steam can be and is produced in many processing systems without the use of any boiler additives that carry over onto the food products. Boiler water can be treated in advance of use in the system by a variety of methods to soften, deionize, filter, and otherwise purify it. These steps reduce the need for addition of synthetic materials not on the National List to the boiler system. In some applications, the steam or heating system for the food may be changed to one where live steam is not the active agent, but rather heating (of food contents directly, or of steam in contact with food) is done via a heat exchange system. The wide variety and individuality of processing systems which exist is indicative of the many ways in which the full range of processed food products can be made without the need for toxic boiler additives to be used in contact with organic foods. This reviewer does not know of any food product type that absolutely requires ammonium hydroxide in steam which contacts organic food.

Justification of use of ammonium hydroxide by the petitioners is based on the constraints of their particular boiler and steam systems as they currently exist, and on the financial and/or logistical challenges involved with changing those systems so as to avoid contact of the organic food by the aqua ammonia. However, economic considerations are clearly not one of the criteria (either in OFPA or the final NOP rule) for determining the suitability of materials used in organic production systems.

History shows that quite often it has been the case that an organic operator (producer or handler) has had to make substantial changes to their system in order to be compliant with organic standards. These changes often involved redesigning of systems, practices, and techniques. In many cases, such changes resulted in the need for financial investment, as well as an investment in time. Some creativity on the part of the operator was often needed, to devise a new system. This has indeed been the case for certain processors, who made adjustments to their boiler systems or manufacturing practices in order to comply with the prohibition of contact of organic foodstuffs by synthetic boiler chemicals. The inconvenience of having to retool or readjust systems should not be the determining factor in whether or not such materials are added to the National List.

For certain processors, where organic processing events are not frequent, the boiler may be operated without the ammonium hydroxide for a limited time, without significant affect on the boiler or steam line system. For these operations, no retooling may be needed; instead, a procedure can be designed whereby it is verifiable that the volatile boiler chemical has been exhausted from the system prior to handling the organic goods.

For processors who intend to process frequently enough, or for long enough run times, redesigning of the system will be necessary, in one way or another. Prohibition on the use of volatile boiler chemicals can exist without consigning processors to premature deterioration of their equipment. It is often the case in industry that the creative process involved in redesigning systems has unpredicted benefits (short- and long-term) to the operator and the environment, in terms of long-term cost-effectiveness and sustainability; efforts in this direction should be encouraged, especially if not doing so results in a compromise of organic principles.

In fact, running boiler equipment designed for use with synthetic additives without the additives in place does lead to deterioration, and consequent lower efficiency of the system, which generally means greater energy consumption (Kohan, 1997). While greater efficiency of energy consumption seems undoubtedly to be desirable (both economically and ecologically), energy balance as a whole has not been considered as factor by the NOSB or certifiers when making determinations on the compatibility or allowability of materials or

methods. To use such a factor as a criterion in the case for the volatile boiler additive is therefore inconsistent with the rest of the paradigm, and should not be a determining factor at this time.

### Summary and Recommendation

Ammonium hydroxide should be deemed a synthetic, prohibited material, and not be added to the National List for any purpose.

#### Reviewer 3 [University staff in Food Science with inspection, consulting, and certification experience]

Ammonium Hydroxide (NH<sub>3</sub>) is petitioned for use as a steam additive chemical to reduce corrosion in pipes. There could be direct food contact in many processing operations when steam is used to cook or heat food, such as in a blancher, cooker, canner, or other operations. NH<sub>3</sub> has no functionality toward the food.

#### Comments on the Criteria

*[The] . . . environmental impact [of the petitioned use] is likely to be negligible. [However, g]enerally ammonium products are not considered compatible [with organic production and processing].*

There are other solutions that could be used to produce the desired result (no corrosion of piping). To summarize many of the citations reviewed, 'use of stainless steel piping completely solves the problem of corrosion.' The justification statement in the petition and the alternative control methods do not mention this as a possible solution. They do mention the costs of capital equipment and provide anecdotal evidence of the life expectancy and replacement needs should boiler water additives not be used, but provide no data to support this. There are numerous tests that can and should be performed periodically to determine the corrosion rates, (even with the use of inhibitors) to insure that equipment is being operated and maintained in a safe and efficient manner. Without confirming studies to show the differences in corrosion rates with and without the use of corrosion inhibitors, it appears that these petitioners are using anecdotal evidence to justify their continued use of cheap toxic chemicals instead of more expensive, but viable alternatives. There are several cited alternatives: stainless steel piping (suitable for all operations); discontinued use during organic processing (some operations); steam to steam heat exchanger (suitable for some operations); secondary boiler for food contact application only (suitable for all operations) that could be used. None of these are necessarily cheap, but all offer a viable alternative to the use of toxic chemicals.

In spite of the minimal health and environmental impact of ammonium hydroxide, alternatives exist with even lower impacts. Because of ammonium hydroxide's GRAS status and minimal health and environmental concerns, I could see reviewing its use with restrictions on concentration, if studies indicate the necessity for its use. Such studies would have to be completed in a timely fashion (1-2 years) and demonstrate a significant improvement in the life expectancy of a boiler and it's piping systems. Studies demonstrating no adverse impact on the composition, flavor or nutritional parameters of the food at the recommended concentrations should also be undertaken prior to granting approval. Additional studies and regulations to insure worker exposure safety should also be included prior to further review.

### Conclusion

The reviewers unanimously consider ammonium hydroxide to be synthetic, and unanimously advise the NOSB to not add it to the National List. Use should remain prohibited in organic handling.

### References

See the Steam Paper.



# Occupational Health Guideline for Ammonia

## INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

## SUBSTANCE IDENTIFICATION

- Formula:  $\text{NH}_3$
- Synonyms: Anhydrous ammonia
- Appearance and odor: Colorless gas with a penetrating, pungent, suffocating odor; it can be a liquid under pressure.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for ammonia is 50 parts of ammonia per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 35 milligrams of ammonia per cubic meter of air ( $\text{mg}/\text{m}^3$ ). NIOSH has recommended that the permissible exposure limit be changed to a ceiling of 50 ppm ammonia ( $35 \text{ mg}/\text{m}^3$ ) averaged over a five-minute period. The NIOSH Criteria Document for Ammonia should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

- Routes of exposure  
Ammonia can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It may also affect the body if it is swallowed.
- Effects of overexposure
  1. *Short-term Exposure:* Ammonia is a severe irritant of the eyes, respiratory tract, and skin. It may cause burning and tearing of the eyes, runny nose, coughing, chest pain, cessation of respiration, and death. It may cause severe breathing difficulties which may be delayed in onset. Exposure of the eyes to high gas

concentrations may produce temporary blindness and severe eye damage. Exposure of the skin to high concentrations of the gas may cause burning and blistering of the skin. Contact with liquid ammonia may produce severe eye and skin burns. Contact of the eyes, nose, throat, and skin with solutions of ammonia may produce severe burns.

2. *Long-term Exposure:* Repeated exposure to ammonia gas may cause chronic irritation of the eyes and upper respiratory tract.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to ammonia.

### • Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to ammonia at potentially hazardous levels:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and respiratory tract should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Ammonia causes human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Ammonia is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. *Periodic Medical Examinations:* The above medical examinations should be repeated on an annual basis, except that an x-ray is necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

### • Summary of toxicology

Ammonia vapor is a severe irritant of the eyes, especially the cornea, the respiratory tract, and skin. Inhalation of concentrations of 2500 to 6500 ppm causes dyspnea,

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These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Public Health Service Centers for Disease Control  
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR  
Occupational Safety and Health Administration

bronchospasm, chest pain and pulmonary edema which may be fatal; production of pink frothy sputum often occurs. Consequences can include bronchitis or pneumonia; some residual reduction in pulmonary function has been reported. In a human experimental study which exposed 10 subjects to various vapor concentrations for 5 minutes, 134 ppm caused irritation of the eyes, nose, and throat in most subjects and 1 person complained of chest irritation; at 72 ppm, several reported the same symptoms; at 50 ppm, 2 reported nasal dryness and at 32 ppm only 1 reported nasal dryness. In a survey of 8 workers in a blueprint shop, ammonia concentrations of 4 to 29 ppm caused "barely noticeable" to "moderate" eye irritation; no respiratory irritation was reported. Tolerance to usually irritating concentrations of ammonia may be acquired by adaptation, a phenomenon frequently observed among workers who became inured to the effects of exposure; no data are available on concentrations that are irritating to workers who are regularly exposed to ammonia and who presumably have a higher irritation threshold. Liquid anhydrous ammonia in contact with the eyes may cause serious eye injury or blindness; on the skin it causes first- and second-degree burns which are often severe, and if extensive, may be fatal. Vapor concentrations of 10,000 ppm are mildly irritating to the moist skin, while 30,000 ppm or greater causes a stinging sensation and may produce skin burns and vesiculation. Increased cancer has been reported in workers exposed to high levels of ammonia and amines, although lack of details makes evaluation difficult.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data

1. Molecular weight: 17
2. Boiling point (760 mm Hg): -33.4 C (-28 F)
3. Specific gravity (water = 1): Liquid 0.67 at boiling point
4. Vapor density (air = 1 at boiling point of ammonia): 0.6
5. Melting point: -77.7 C (-108 F)
6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere
7. Solubility in water, g/100 g water at 20 C (68 F): 51
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Reactivity

1. Conditions contributing to instability: Elevated temperatures may cause containers to explode.
2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions. Contact with calcium, hypochlorite bleaches, gold, mercury, and silver may form highly explosive products. Contact with halogens may cause violent spattering.
3. Hazardous decomposition products: None.
4. Special precautions: Liquid ammonia will attack some forms of plastics, rubber, and coatings.

### • Flammability

1. Flash point: Not applicable
2. Autoignition temperature: 651 C (1204 F)
3. Flammable limits in air, % by volume: Lower: 16; Upper: 25
4. Extinguishant: Stop flow of gas.

### • Warning properties

1. Odor Threshold: The AIHA *Hygienic Guide* states that "ammonia is a colorless gas with a characteristic odor detectable at 1 to 5 ppm."
2. Eye Irritation Level: Grant states that "ammonia is slightly irritant to human eyes at a concentration of 140 ppm in air and immediately irritating at 700 ppm."
3. Other Information: The *Hygienic Guide* states that "irritation of the respiratory tract in workers inhaling 100 ppm has been found, but 55 ppm was unobjectionable."
4. Evaluation of Warning Properties: Because of its low thresholds of odor and irritation, ammonia is treated as a material with good warning properties.

## MONITORING AND MEASUREMENT PROCEDURES

### • Eight-Hour Exposure Evaluation

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

### • Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of ammonia. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

### • Method

Sampling and analyses may be performed by collection of vapors using an adsorption tube with a subsequent chemical analysis of the adsorption tube. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure ammonia may be used. An analytical method for ammonia is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

## RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

## PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid anhydrous ammonia or aqueous solutions of ammonia containing more than 10% by weight of ammonia and to prevent the skin from becoming frozen from contact with vessels containing liquid anhydrous ammonia.
- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing 10% or less by weight of ammonia.
- Where there is any possibility of exposure of an employee's body to liquid anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.
- Non-impervious clothing which becomes contaminated with anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight should be removed immediately and not reworn until the ammonia is removed from the clothing.
- Non-impervious clothing which becomes wet with solutions containing 10% ammonia by weight or less should be removed promptly and not reworn until the ammonia is removed from the clothing.
- Clothing wet with liquid anhydrous ammonia or aqueous solutions of ammonia should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of ammonia

from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the ammonia, the person performing the operation should be informed of ammonia's hazardous properties.

- Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight contacting the eyes.
- Employees should be provided with and required to use splash-proof safety goggles where solutions containing 10% ammonia by weight or less may contact the eyes.
- Where there is any possibility that employees' eyes may be exposed to liquid anhydrous ammonia or aqueous solutions containing more than 10% ammonia by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

## SANITATION

- Skin that becomes contaminated with liquid anhydrous ammonia or solutions containing more than 10% ammonia by weight should be immediately washed or showered to remove any ammonia.
- Skin that becomes wet with solutions containing 10% ammonia by weight or less should be promptly washed or showered to remove any ammonia.
- Employees who handle liquid anhydrous ammonia or aqueous solutions of ammonia should wash their hands thoroughly before eating, smoking, or using toilet facilities.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to ammonia may occur and control methods which may be effective in each case:

Operation	Controls
Use as a chemical in manufacture of fertilizers, as solvent in manufacture of textiles, leather, and pulp and paper processing; as a stabilizer in rubber manufacture	Process enclosure; local exhaust ventilation; general dilution ventilation; personal protective equipment

## Operation

Use in organic and inorganic synthesis of nitric acid, urea, plastics, fibers, synthetic resins, pharmaceuticals, pesticides, explosives, rocket fuels, cyanides, amides, dyestuffs, amines, flame retardants, and household cleaners

Use in mining/metallurgy ore extraction and purification, treatment of scrap metal, annealing, atomic hydrogen welding, electronics, nitriding steel

Use in petroleum refining as a neutralizing agent; manufacture and recovery of cracking catalysts; and in dewaxing of lubrication oils

Use as a refrigerant in food installations, production of ice, cold-storage, food lockers, deicing

Use during blueprinting and photography, electroplating, and as a laboratory reagent

## Controls

Process enclosure; local exhaust ventilation; personal protective equipment

Local exhaust ventilation; general dilution ventilation; personal protective equipment

Process enclosure; local exhaust ventilation; personal protective equipment

Local exhaust ventilation; general dilution ventilation; personal protective equipment

Local exhaust ventilation; general dilution ventilation; personal protective equipment

## EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

### • Eye Exposure

If liquid anhydrous ammonia, solutions containing ammonia, or high concentrations of ammonia gas get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

### • Skin Exposure

If liquid anhydrous ammonia, strong solutions of ammonia, or high concentrations of ammonia gas get on the skin, immediately flush the contaminated skin with water. If liquid anhydrous ammonia, strong solutions

containing ammonia, or high concentrations of ammonia gas penetrate through the clothing, remove the clothing immediately and flush the skin with water. If irritation or burns are present after washing, get medical attention.

### • Breathing

If a person breathes in large amounts of ammonia, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

### • Swallowing

When ammonia has been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the ammonia. Do not attempt to make the exposed person vomit. Get medical attention immediately.

### • Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

## SPILL AND LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If ammonia is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak to disperse gas.
2. If in gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
3. If in liquid form, allow to vaporize.

## REFERENCES

- American Conference of Governmental Industrial Hygienists: "Ammonia," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
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- Gleason, M. N., Gosselin, R. E., Hodge, H. C., and Smith, R. P.: *Clinical Toxicology of Commercial Products* (3rd ed.), Williams and Wilkins, Baltimore, 1969.
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- Spector, W. S. (Vols. I, II), Negherbon, W. O. (Vol. III), Grebe, R. M. (Vol. IV), and Dittmer, D. S. (Vol. V) (eds.): *Handbook of Toxicology*, Saunders, Philadelphia, 1956-1959.

## RESPIRATORY PROTECTION FOR AMMONIA

Condition	Minimum Respiratory Protection* Required Above 50 ppm
Gas Concentration	
100 ppm or less	<p>Any chemical cartridge respirator with an ammonia cartridge(s).</p> <p>Any supplied-air respirator.</p> <p>Any self-contained breathing apparatus.</p>
300 ppm or less	A chemical cartridge respirator with a full facepiece and an ammonia cartridge(s).
500 ppm or less	<p>A gas mask with a chin-style or a front- or back-mounted ammonia canister.</p> <p>Any supplied-air respirator with a full facepiece, helmet, or hood.</p> <p>Any self-contained breathing apparatus with a full facepiece.</p>
Greater than 500 ppm** or entry and escape from unknown concentrations	<p>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</p> <p>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.</p>
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	<p>Any gas mask providing protection against ammonia.</p> <p>Any escape self-contained breathing apparatus.</p>

\*Only NIOSH-approved or MSHA-approved equipment should be used.

\*\*Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of ammonia; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 500 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.



(Gas) Density: Not pertinent; Ratio of Specific Heats of Vapor (Gas): Not pertinent; Latent Heat of Vaporization: Not pertinent; Heat of Combustion: Data not available; Heat of Decomposition: Not pertinent; (iv) **Health Hazards Information** — Recommended Personal Protective Equipment: Respirator for nuisance dust; Symptoms Following Exposure: Inhalation of dust irritates nose and throat. Contact with eyes causes mild irritation; General Treatment for Exposure: INHALATION: remove to fresh air. EYES OR SKIN: flush with water; Toxicity by Inhalation (Threshold Limit Value): Data not available; Short-Term Exposure Limits: Data not available; Toxicity by Ingestion: Data not available; Late Toxicity: Data not available; Vapor (Gas) Irritant Characteristics: Data not available; Liquid or Solid Irritant Characteristics: Data not available; Odor Threshold: Data not available.

**Ammonium Hydroxide (< 20 % Aqueous Ammonia)** — (i) **Chemical Designations** — Synonyms: Ammonia Water, Aqueous Ammonia, Household Ammonia; Chemical Formula:  $\text{NH}_4\text{OH}-\text{H}_2\text{O}$ ; (ii) **Observable Characteristics** — Physical State (as normally shipped): Liquid; Color: Colorless; Odor: Pungent; (iii) **Physical and Chemical Properties** — Physical State at 15 °C and 1 atm.: Liquid; Molecular Weight: Not pertinent; Boiling Point at 1 atm.: Not pertinent; Freezing Point: Not pertinent; Critical Temperature: Not pertinent; Critical Pressure: Not pertinent; Specific Gravity: 0.89 at 20°C (liquid); Vapor (Gas) Density: Not pertinent; Ratio of Specific Heats of Vapor (Gas): Not pertinent; Latent Heat of Vaporization: Not pertinent; Heat of Combustion: Not pertinent; Heat of Decomposition: Not pertinent; (iv) **Health Hazards Information** — Recommended Personal Protective Equipment: Rubber boots, gloves, apron, and coat; broad-brimmed rubber or felt hat; safety goggles. Use of protective oil will reduce skin irritation from ammonia; Symptoms Following Exposure: Contact of liquid or vapor with skin, mucous membranes, lungs, or gastroenteric tract causes marked local irritation. Ingestion causes burning pain in mouth, throat, stomach, and thorax, constriction of throat, and coughing. This is soon followed by vomiting of blood or by passage of loose stools containing blood. Breathing difficulty, convulsions, and shock may result. Brief exposure to 5000 ppm of ingestion of 3-4 ml may be fatal; General Treatment for Exposure: INHALATION: give artificial respiration and oxygen if needed; enforce rest. INGESTION: do NOT induce vomiting; lavage stomach with water or lemon juice, milk, or demulcents; delay may cause perforation of esophagus or stomach; swelling of glottis may necessitate tracheostomy. EYES OR SKIN: wash with plenty of

water; Toxicity by Inhalation (Threshold Limit Value): ppm; Short-Term Exposure Limits: (ammonia gas ppm for 30 min.; 500 ppm for 10 min.); Toxicity by Ingestion: Grade 3; oral rat,  $\text{LD}_{50}$  350 mg/kg; Toxicity: Data not available; Vapor (Gas) Irritant Characteristics: Vapors cause moderate irritation such personnel will find high concentrations intolerable effect is temporary; Liquid or Solid Irritant Characteristics: Causes smarting of the skin and first-degree burns on short exposure; may cause second-degree on long exposure; Odor Threshold: 50 ppm.

**Ammonium Iodide** — (i) **Chemical Designation** — Synonyms: No common synonyms; Chemical Formula:  $\text{NH}_4\text{I}$ ; (ii) **Observable Characteristics** — Physical State (as normally shipped): Solid; Color: White; Odor: None; (iii) **Physical and Chemical Properties** — Physical State at 15 °C and 1 atm.: Solid; Molecular Weight: 149.09; Boiling Point at 1 atm.: Not pertinent (sublimes); Freezing Point: Not pertinent; Critical Temperature: Not pertinent; Critical Pressure: Not pertinent; Specific Gravity: 2.20 at 20°C (solid); Vapor (Gas) Density: Not pertinent; Ratio of Specific Heats of Vapor (Gas): Not pertinent; Latent Heat of Vaporization: Not pertinent; Heat of Combustion: Not pertinent; Heat of Decomposition: Not pertinent; (iv) **Health Hazards Information** — Recommended Personal Protective Equipment: Dust mask; goggles or face shield; rubber gloves; Symptoms Following Exposure: Inhalation causes irritation of nose and throat. Contact with skin causes irritation; General Treatment for Exposure: INHALATION: remove to fresh air. INGESTION: significant amount has been ingested, get medical attention. EYES: flush with water; Toxicity by Inhalation (Threshold Limit Value): Data not available; Short-Term Exposure Limits: Data not available; Toxicity by Ingestion: Data not available; Late Toxicity: Data not available; Vapor (Gas) Irritant Characteristics: Data not available; Liquid or Solid Irritant Characteristics: Data not available; Odor Threshold: Odorless.

**Ammonium Lactate** — (i) **Chemical Designation** — Synonyms: Ammonium Lactate Syrup; dl-Lactic Ammonium Salt; Chemical Formula:  $\text{C}_2\text{H}_5(\text{OH})\text{COONH}_4$ ; (ii) **Observable Characteristics** — Physical State (as normally shipped): Solid or liquid; Color: White; Odor: None; (iii) **Physical and Chemical Properties** — Physical State at 15 °C and 1 atm.: Solid; Molecular Weight: 107.11; Boiling Point at 1 atm.: Not pertinent; Freezing Point: Not pertinent; Critical Pressure: Not pertinent; Critical Temperature: Not pertinent; Specific Gravity: 1.2 at 15°C (solid); Vapor (Gas) Density: Not pertinent.

and symptoms including nausea, flushing of face, increased blood pressure; weakness; convulsions

Other causes of convulsions are differentiated from 2-aminopyridine. These include idiopathic convulsive encephalopathies, such as hypoglycemia, and porphyria, such infections and exposure to other convulsants.

Convulsions occur, diagnosis includes analysis of calcium, urea nitrogen

If splashed in the eyes, immediately flush with water. If convulsions, diazepam or phenobarbital may be given intramuscularly. In a dose of 5 to 10 mg Valium into a large vein over 1 minute and repeated every two minutes. Rapid injection may cause cardiac arrest. The alternative, phenobarbital, may also be given in a dose of 200 mg, to be repeated every four hours. If unresponsive to these doses of phenobarbital, it is worth trying occasional seizure-inducing consequences than drug-induced coma that would require doses of medication.

Preplacement screening emphasizes on detecting eye disorders. Such persons are at risk from exposure.

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3. A.C.G.I.H.: 2-Aminopyridine. Documentation of the TLVs for Substances in Workroom Air. ed. 3, p. 11. Cincinnati, 1976.  
4. Adams, R. D.: The convulsive state and idiopathic epilepsy. In Thorn, G. W., et al. (eds.): Harrison's Principles of Internal Medicine. ed. 8, pp. 127-135. New York: McGraw-Hill, 1977.

AMMONIA

NH<sub>3</sub> 1977 TLV 25 ppm

Synonyms: Ammonia gas

Physical Form: Colorless gas

Uses: Refrigeration; petroleum refining; manufacture of fertilizers, nitric acid, explosives, plastics and other chemicals

Exposure: Inhalation

Toxicology: Ammonia is a severe irritant of the eyes, respiratory tract, and skin.

Exposure to and inhalation of concentrations of 2500 to 6500 ppm cause severe corneal irritation, dyspnea, bronchospasm, chest pain, and pulmonary edema, which may be fatal; production of pink frothy sputum often occurs. Consequences can include bronchitis or pneumonia; some residual reduction in pulmonary function has been reported.<sup>1</sup>

In a human experimental study which exposed ten subjects to various vapor concentrations for five minutes, 134 ppm caused irritation of the eyes, nose, and throat in most subjects, and one person complained of chest irritation; at 72 ppm, several reported the same symptoms; at 50 ppm, two reported nasal dryness, and at 32 ppm only one reported nasal dryness.<sup>2</sup> In a survey of eight workers in a blueprint shop, ammonia concentrations of 4 to 29 ppm caused "barely noticeable" to "moderate" eye irritation; no respiratory irritation was reported.<sup>3</sup>

Tolerance to usually irritating concentrations of ammonia may be acquired by adaptation, a phenomenon frequently observed among workers who became inured to the effects of exposure; no data are available on concentrations that are irritating to workers who are regularly exposed to ammonia and

who presumably have a higher irritation threshold.

Liquid anhydrous ammonia in contact with the eyes may cause serious eye injury or blindness; on the skin, it causes first- and second-degree burns, which are often severe and, if extensive, may be fatal. Vapor concentrations of 10,000 ppm are mildly irritating to the moist skin, while 30,000 ppm or greater cause a stinging sensation and may produce skin burns and vesiculation.<sup>4</sup>

The TLV is set at a level to prevent irritation to the eyes and respiratory tract.<sup>5</sup>

Diagnosis: Signs and symptoms include eye, nose, throat irritation; dyspnea, bronchospasm, chest pain, pulmonary edema, pink frothy sputum; skin and eye burns and vesiculation.

Differential Diagnosis: In mild exposure resulting in mucous membrane irritation, the symptoms may mimic a viral upper respiratory tract infection. The latter may be characterized by fever, myalgias, and lymphocytosis. As the tracheobronchial tree and pulmonary parenchyma become involved, the symptoms and signs must be differentiated from cardiogenic pulmonary edema, severe viral or bacterial pneumonia, and adult respiratory distress syndromes.

Special Tests: Diagnostic studies should include electrocardiogram, sputum gram stain and culture, differential white blood count, and arterial blood gas analysis.

Treatment: If the liquid is splashed in the eyes or on the skin, immediately flush with water. If severe exposure is suspected, immediate hospitalization and observation for 72 hours for delayed onset of severe pulmonary edema are advisable.

Refer to Therapeutic Maneuvers in Treatment of Respiratory Irritants, Chapter 6. Obtain chest X-ray and examine for infiltrates. Perform analysis of arterial blood gases. Maintain P<sub>O</sub><sub>2</sub> above 60 mm Hg by instituting, in stepwise fashion, the following measures as needed:

1. Administration of 60 to 100 per cent oxygen by mask or cannula
  2. Intubation and mechanical ventilation
  3. Positive end expiratory pressure breathing
- Fluid balance must be maintained; use of a diuretic may be required. Steroids may be administered on a short-term basis (two to

four days) to decrease the inflammatory response of the lung.

**Medical Control:** Preplacement and annual physical examinations with emphasis on examination of the respiratory system, eyes, and skin; pulmonary function testing, such as FVC and FEV (1 sec.); 14" x 17" chest roentgenogram.

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3. Hygienic Guide Series: Anhydrous ammonia. Am. Ind. Hyg. Assoc. J., 32:139, 1971.

##### Supplemental

4. Patty, F. A.: Alkaline materials. In Fasset, D. W., and Irish, D. D. (eds.): Toxicology. vol. 2. In Patty, F. A. (ed.): Industrial Hygiene and Toxicology. 2, pp. 859-862. New York: Interscience, 1963.
5. A.C.G.I.H.: Ammonia. Documentation of the TLVs for Substances in Workroom Air. ed. 3, p. 289. Cincinnati, 1976.

#### AMMONIUM SULFAMATE

$\text{NH}_4\text{SO}_3\text{NH}_2$  1977 TLV 10 mg/m<sup>3</sup>

**Synonyms:** Ammate

**Physical Form:** Hygroscopic crystals

**Uses:** Manufacture of weed-killing compounds and fire-retardant compositions

**Exposure:** Inhalation

**Toxicology:** Ammonium sulfamate is of low toxicity; there are no reports of effects in humans.

Repeated application of a 4 per cent solu-

tion to the anterior surface of one arm of each of five human subjects for five days caused no skin irritation.<sup>1</sup>

In rats, the intraperitoneal injection of 0.8 g./kg caused the death of six of ten animals; effects were stimulation of respiration and then prostration.<sup>1</sup>

The TLV is recommended as a guide for good industrial hygiene practice for agents of low toxicity.<sup>3</sup>

**Diagnosis:** There are no known signs and symptoms.

**Differential Diagnosis:** None is specific.

**Special Tests:** None is specific.

**Treatment:** Remove from exposure; flush eyes and skin with water.

**Medical Control:** None required.

#### References

1. Ambrose, A. M.: Studies on the physiological effects of sulfamic acid and ammonium sulfamate. J. Ind. Hyg. Toxicol., 25:26, 1943
2. A.C.G.I.H.: Ammonium sulfamate (ammate). Documentation of the TLVs for Substances in Workroom Air. ed., 3, p. 12. Cincinnati, 1976.

#### n-AMYL ACETATE

$\text{C}_7\text{H}_{14}\text{O}_2$  1977 TLV 100 ppm

**Synonyms:** Amyl acetic ether; pear oil

**Physical Form:** Liquid

**Uses:** Manufacture of lacquers, artificial leather, photographic film, artificial glass, celluloid, artificial silk and furniture polish

**Exposure:** Inhalation; minor skin absorption

**Toxicology:** n-Amyl acetate is an irritant of mucous membranes; at high concentrations it causes narcosis in animals, and it is expected that severe exposure will produce the same effect in humans.

Human subjects exposed to 900 ppm for 30 minutes experienced irritation of the eyes, nose, and throat, with cough and slight fatigue.<sup>1</sup> Early reports of systemic injury in

humans may have been caused by the n-amy acetate.<sup>1</sup> This sul-  
fating agent, and prolonged  
produce dermatitis.<sup>1</sup>

Narcosis occurred in guinea  
ppm but not at 2000 ppm;  
showed injury to the lungs, l  
neys.<sup>2</sup> Several drops of the li  
eyes caused temporary cornea  
injury.<sup>3</sup>

n-Amyl acetate may be rec  
centrations of 7 ppm by the  
characteristic of esters.<sup>2</sup>

The TLV was set to preve  
the eyes and respiratory passag

**Diagnosis:** Signs and sympto  
tion of the eyes, nose, an  
mautis. By analogy with eff  
animals; signs and symptoms  
vous system depression may  
from sustained exposure to h  
lions.

**Differential Diagnosis:** Diff  
other causes of conjunctiviti  
membrane irritation, such as vi  
the upper respiratory tract and

**Special Tests:** None is specifi  
**Treatment:** Institute app  
dures such as removal from e  
top of skin areas, and irrigatic  
water.

**Medical Control:** Preplac  
naire with emphasis on detecti  
chronic respiratory disease o  
Such persons may be at incre  
exposure.

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Thomas, 1974.

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tion of the TLVs for Subst  
Workroom Air. ed. 3, pp. 12-  
1976.

Cosce (in list)

... contains particles that readily ad...  
... conjunctiva; they often induce ulcera...  
... orneal epithelium and stromal opaci...  
... ly penetrate to the iris or lens. It is...  
... ssential to wash out the conjunctiva...  
... ly. A .01-.05 M near-neutral solution...  
... etate (EDTA) is said to be useful to...  
... ent particles. See also Calcium Salts

Unknown d.

... long chronically exposed workers, ce...  
... itis assumes many forms: skin dryness...  
... rophy of nails, eczematous rashes, etc...  
... f cement dermatitis have been widely...  
... st American authorities regard the...  
... wet cement (pH about 12), its abra...  
... perhaps its hygroscopicity as the...  
... s that make it hazardous to skin and...  
... rbanes. Several European dermatol...  
... ver, have reported skin hypersensitiv...  
... dent chromium (see Chromium trioxi...  
... dex) among cement workers. Because...  
... an cements (e.g., from Switzerland)...  
... iderable amounts of chromates, chro...  
... has been regarded as a contributory...  
... ent dermatitis (Calnan, 1960, 1973). A...  
... 4 found no evidence that allergies to...  
... ickel or cobalt were importantly re...  
... natitis in the American cement indus...  
... et al., 1974). Because the older Euro...  
... e has not been adequately explained...  
... ot satisfactorily resolved. Acute der...  
... s to wet cement are usually treated...  
... s. Obviously gloves, impervious boot...  
... otective gear should be worn when...  
... ent.

1973; Perone et al., 1974; Rowe and

... and dishwasher products. The most al...  
... orrosive substance in such mixtures. A...  
... solution in water has a pH of about 12...  
... ively high buffer capacity. Dangerous...  
... eyes and on all mucous membranes.

... usually has a mole ratio of 2.0 to 2.5...  
... the ratio (e.g., the less sodium) the...  
... lubility and alkalinity. Less soluble...  
... than sodium metasilicate, which has

mole ratio of 1:1 (see latter above). The acute oral  
LD<sub>50</sub> in the rat varies from 1.1 to 1.6 gm./kg. Forms  
gelatinous mixtures with water. Except for nonspe-  
cific irritation of skin, cornea and mucous mem-  
branes, and perhaps corrosive lesions with the

See also: Lye, Reference Congener in Section III.

Ref.: Morris, 1953; Task Force on the Health Effects of non-NTA Detergent Builders, 1981.

more alkaline mixtures, no toxic actions are rec-  
ognized. Said to be partly absorbed and excreted  
in the urine; thus excretion during chronic expo-  
sures may contribute to the production of urinary  
calculi.

59 Potassium Phosphate (Tribasic)

59

Aqueous solutions are alkaline and may produce a  
caustic burn like Trisodium Phosphate. See also

Potassium salts in the index.

See also: Lye, Reference Congener in Section III.

60 Trisodium Phosphate

60

Sodium phosphate tribasic

Aqueous solutions are highly alkaline and may produce a caustic burn.

See also: Lye, Reference Congener in Section III.

Ref.: Cann and Verhulst, 1958a.

61 Lithium Hydride

61

Lithium hydride has many uses in space and nu-  
clear technology. It reacts vigorously when placed  
in water to liberate hydrogen and form lithium  
hydroxide. If powdered, lithium hydride may ignite  
spontaneously in humid air or on contact with  
moist mucous surfaces. The resulting tissue injury  
may have features of both thermal damage and  
strong alkali corrosion. The accidental explosion of

a cylinder of lithium hydride sprayed material in  
the eye of a physicist and caused him to swallow a  
small amount of the dust. The resulting burns  
caused scarring of both corneas, stricture of the  
larynx, trachea, bronchi and esophagus. Despite  
intensive surgical treatment this case eventually  
terminated fatally.

See also: Lye, Reference Congener in Section III.

Ref.: Cracovaner, 1964.

62 Calcium Carbide

62

Used to generate acetylene for lighting purposes.  
Inert when dry, but reacts quickly with water to  
form acetylene and calcium hydroxide in a vigor-  
ously exothermic reaction. In contact with moist  
mucous membranes this reaction would probably  
result in a severe thermal and caustic burn. Pre-

sumably the acetylene produced would be of less  
toxic significance than the local lesion. Contact of  
calcium carbide dust with the eye or moist areas of  
the skin may produce marked irritation. Systemic  
effects do not occur.

See also: Lye, Reference Congener in Section III.

Ref.: Manufacturing Chemists' Assoc., 1948b.

Ammonia and amines that form strongly alkaline solutions

63 Ammonia

63

Ammonia water, Ammonium hydroxide, Ammonia gas

Most freshly opened bottles of household ammonia  
range from 5 to 10% (w/v) ammonia (NH<sub>3</sub>). Dilute  
ammonia water (USP) is 9 to 10% (w/v) NH<sub>3</sub>,  
whereas strong ammonia solution (USP) is 27 to  
30% (w/v) NH<sub>3</sub>. When ingested, any of these solu-  
tions is capable of producing a corrosive esophagi-  
tis, sometimes with an associated gastritis. The

inhalation of anhydrous ammonia gas accidentally  
released in industrial accidents has produced acute  
and chronic respiratory disease. Anhydrous liquid  
ammonia produces second-degree burns on the  
skin and extensive destruction of the anterior  
chamber in the eye.

See also: Ammonia, Reference Congener in Section III.

64 Monoethanolamine (and Salts)

64

2-Aminoethanol, β-Aminoethyl alcohol, β-Hydroxyethylamine, β-Ethanolamine

Toxicity Rating: 3. A somewhat viscous, clear, hy-  
droscopic fluid. Used to remove H<sub>2</sub>S and CO<sub>2</sub> from

natural gas, also as an emulsifier in polishes and  
hair wave solution and as a dispersing agent for

can initiate base-catalyzed polymerizations of acrylonitrile, acrylonitrile, allyl alcohol, and other organic unsaturates susceptible to polymerization, often resulting in explosions.

Most hazardous reactions of potassium hydroxide are similar to those of caustic

soda, and many are well documented (NFPA 1986). Explosions occurred when caustic potash was added to liquid chlorine dioxide (Mellor 1946), nitrogen trichloride, *N*-nitrosomethyl urea in *n*-butyl ether (NFPA 1986), and maleic anhydride (MCA 1960). Reaction with phosphorus yields

TABLE 6.1

Compound/Synonyms/  
CAS No.

Rubidium hydroxide  
dium hydrate

TABLE 6.1 Toxicity and Hazardous Reactions of Miscellaneous Alkalies

Compound/Synonyms/ CAS No.	Formula/ MW	Toxicity	Hazardous Reactions
Lithium hydroxide (lithium hydroxide [1310-65-2]; lithium hydroxide monohydrate [1310-66-3])	LiOH 23.95 LiOH·H <sub>2</sub> O 41.97	Highly corrosive, very irritating to skin and eyes; caustic effects similar to caustic soda but to a lesser extent; low toxicity; systemic toxicity similar to other compounds of lithium; DOT Label: Corrosive Material, UN 2679 (for anhydrous salt), UN 2680 (for hydrate)	Explosive polymerization may occur when in contact with certain unsaturate organics; strongly alkaline but less caustic to sodium hydroxide; expected to undergo many hazardous reactions similar to caustic soda
Ammonium hydroxide (aqueous ammonia, aqua ammonia, ammonia solution, ammonia water) [1336-21-0]	NH <sub>4</sub> OH 35.06	Highly caustic and corrosive; contact with eyes and skin can cause severe irritation; concentrated solutions emit ammonia, which can cause lachrymation and severe irritation of respiratory tract and acute pulmonary edema (see Section 20.1); static 24-hr median lethal tests with channel catfish indicated that while ammonia was lethal with LC <sub>50</sub> value of 1.45 NH <sub>3</sub> -N mg/L, NH <sub>4</sub> ion from NH <sub>4</sub> Cl was essentially nontoxic to channel catfish at the same pH (Sheehan and Lewis 1986); moderately toxic by ingestion; LD <sub>50</sub> oral (rats): 350 mg/kg; DOT Label: Corrosive Material, NA 2672 (for 12-44% ammonia content)	Reacts violently with many silver salts, such as silver nitrate, silver oxide, silver perchlorate, and permanganate, causing explosions—attributed to the formation of shock-sensitive silver nitride or silver complexes; explosion may occur when its reaction products with gold and mercury with variable compositions are heated and dried; in concentrated solution it reacts with excess of iodine to form nitrogen iodide, which may detonate on drying (Mellor 1946, Suppl. 1964); produces flame and/or explosion when mixed with fluorine; reacts violently with dimethyl sulfate (NFPA 1986); exothermic reactions occur when its concentrated solution is mixed with concentrated acids

Barium hydroxide, caustic [17194-00-2]

Calcium hydroxide, lime, calcium [1305-62-0]

Potassium carbonate (dipotassium pearl ash, potash) [584-08-7]

Sodium carbonate (soda ash) [497-19-8]

(continued)

New York: Van Nostrand Reinhold





# EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW SECTION 313 Guidance for Reporting Aqueous Ammonia

Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) requires certain facilities manufacturing, processing, or otherwise using listed toxic chemicals to report their environmental releases of such chemicals annually. Beginning with the 1991 reporting year, such facilities also must report pollution prevention and recycling data for such chemicals, pursuant to section 6607 of the Pollution Prevention Act, 42 U.S.C. 13106. When enacted, EPCRA section 313 established an initial list of toxic chemicals that was comprised of more than 300 chemicals and 20 chemical categories. EPCRA section 313(d) authorizes EPA to add chemicals to or delete chemicals from the list, and sets forth criteria for these actions.

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## FOREWORD

This document is an updated version of the previous document, EPA 745-R-95-012. This version has the following updates:

- Under Section 1.4. *de minimis* concentrations on page 4, the second sentence is modified to clarify *de minimis* concentration for aqueous ammonia; and
- References to *List of Toxic Chemicals within the Water Dissociable Nitrate Compounds Category and Guidance for Reporting* (EPA #745-R-00-006, Revised December, 2000) are added in the last sentence on page 8, in the example 6 on page 9, and in the example 7 on page 10.



## Section 1. Introduction

On June 30, 1995 EPA finalized four actions in response to a petition received in 1989 to delete ammonium sulfate (solution) from the list of toxic chemicals subject to reporting under section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), 42 U.S.C. 11001. The four actions taken are summarized as follows: (1) deleted ammonium sulfate (solution) from the EPCRA section 313 list of toxic chemicals, (2) required that threshold and release determinations for aqueous ammonia be based on 10 percent of the total aqueous ammonia present in aqueous solutions of ammonia, (3) modified the ammonia listing by adding the following qualifier: ammonia (includes anhydrous ammonia and aqueous ammonia from water dissociable ammonium salts and other sources; 10 percent of total aqueous ammonia is reportable under this listing), and (4) deleted ammonium nitrate (solution) as a separately listed chemical on the EPCRA section 313 list of toxic chemicals. All actions are effective for the 1994 reporting year for reports due July 1, 1995, with the exception of the deletion of ammonium nitrate (solution) as a separately listed chemical, which is effective for the 1995 reporting year for reports due July 1, 1996. At the time that these actions were finalized, EPA indicated that the Agency would develop, as appropriate, interpretations and guidance that the Agency determines are necessary to facilitate accurate reporting for aqueous ammonia. This document constitutes such guidance for reporting under the ammonia listing.

### Section 1.1 Who Must Report

A facility is subject to the provisions of EPCRA section 313, if it meets all three of the following criteria:

- It is included in Standard Industrial Classification (SIC) Code 10 (except SIC Codes 1011, 1081, and 1094); SIC Code 12 (except SIC Code 1241); SIC Codes 20 through 39; SIC Code 4911 (limited to facilities that combust coal and/or oil for the purpose of generating power for distribution in commerce); SIC Code 4931 (limited to facilities that combust coal and/or oil for the purpose of generating power for distribution in commerce); SIC Code 4939 (limited to facilities that combust coal and/or oil for the purpose of generating power for distribution in commerce); SIC Code 4953 (limited to facilities regulated under the Resource Conservation and Recovery Act, Subtitle C, 42 U.S.C. Section 6921 *et seq.*); SIC Code 5169; SIC Code 5171; and SIC Code 7389 (limited to facilities primarily engaged in solvent recovery services on a contract or fee basis); and
- It has 10 or more full-time employees (or the equivalent 20,000 hours per year); and
- It manufactures, imports, processes, or otherwise uses any of the toxic chemicals listed on the EPCRA section 313 list in amounts greater than the "threshold" quantities specified in Section 1.2.

## Section 1.2 Thresholds

Thresholds are specified amounts of toxic chemicals used during the calendar year that trigger reporting requirements.

If a facility *manufactures* or *imports* any of the listed toxic chemicals, the threshold quantity will be:

- ! 25,000 pounds per toxic chemical or category during the calendar year.

If a facility *processes* any of the listed toxic chemicals, the threshold quantity will be:

- 25,000 pounds per toxic chemical or category during the calendar year.

If a facility *otherwise uses* any of the listed toxic chemicals (without incorporating it into any product or producing it at the facility), the threshold quantity is:

- 10,000 pounds per toxic chemical or category during the calendar year.

## Section 1.3 Chemical Sources of Aqueous Ammonia

If a facility manufactures, processes, or otherwise uses anhydrous ammonia or aqueous ammonia, they must report under the ammonia listing. EPA is providing a table of Chemical Abstract Service (CAS) numbers and chemical names to aid the regulated community in determining whether they need to report under the ammonia listing for aqueous ammonia. This table includes a list of water dissociable ammonium salts which, when placed in water, are a source of aqueous ammonia. The table contains only commonly used ammonium salts and therefore is not exhaustive. If a facility manufactures, processes, or otherwise uses aqueous ammonia, regardless of its source, it must report under the ammonia listing, even if the source of the aqueous ammonia is not listed in the table provided in this document.

## Section 1.4 *De Minimis* Concentrations

The ammonia listing is subject to the one percent *de minimis* concentration. Thus, mixtures containing total aqueous ammonia at concentrations equal to or in excess of *one percent* should be factored into threshold and release determinations.

## Section 2. Guidance for Reporting Aqueous Ammonia

Note: for the purposes of reporting under the ammonia listing for aqueous ammonia, water dissociable ammonium salts means that the ammonium ion dissociates from its counterion when in solution.

### Section 2.1 Determining Threshold and Release Quantities for Ammonia

If a facility manufactures, processes, or otherwise uses *anhydrous ammonia*, the quantity applied towards threshold determinations for the ammonia listing is the total quantity of the anhydrous ammonia manufactured, processed, or otherwise used. The quantity reported when calculating the amount of ammonia that is released, transferred, or otherwise managed is the total quantity of *anhydrous ammonia* released or transferred.

If the facility manufactures, processes, or otherwise uses *anhydrous ammonia* in quantities that exceed the appropriate threshold and subsequently dissolves some or all of the *anhydrous ammonia* in *water*, then the following applies: 1) threshold determinations are based on 100 percent of the *anhydrous ammonia*; 2) release, transfer, and other waste management quantities for the *aqueous ammonia* are calculated as 10 percent of total ammonia; and 3) release, transfer, and other waste management quantities for the *anhydrous ammonia* are calculated as 100 percent of the *anhydrous ammonia*.

If a facility manufactures, processes, or otherwise uses *aqueous ammonia*, the quantity applied toward threshold determinations for the ammonia listing is 10 percent of the total quantity of the *aqueous ammonia* manufactured, processed, or otherwise used. The quantity reported when calculating the amount of ammonia that is released, transferred, or otherwise managed is 10 percent of the total quantity of *aqueous ammonia* released or transferred.

If a facility dissolves a water dissociable ammonium salt in water that facility has manufactured *aqueous ammonia* and 10 percent of the total *aqueous ammonia* manufactured from these salts is to be included in manufacturing threshold determinations under the ammonia listing.

If *aqueous ammonia* from water dissociable ammonium salts is processed or otherwise used, then 10 percent of the total *aqueous ammonia* is to be included in all processing and otherwise use threshold determinations under the ammonia listing.

**Example 1:** In a calendar year, a facility places 25,000 lbs of anhydrous ammonia in water for processing and processes 25,000 lbs of aqueous ammonia from an ammonium salt. The facility must include all of the 25,000 lbs of anhydrous ammonia in the determination of the processing threshold, but only 10 percent (or 2,500 lbs) of the aqueous ammonia from the ammonium salt in the processing threshold determination.

Total aqueous ammonia is the sum of the two forms of ammonia (un-ionized,  $\text{NH}_3$ , and ionized,  $\text{NH}_4^+$ ) present in aqueous solutions. A precise calculation of the weight of total aqueous ammonia would require determining the ratio of the two forms of ammonia present using the pH and temperature of the solution. The weight of total aqueous ammonia can be more easily calculated by assuming that aqueous ammonia is comprised entirely of the  $\text{NH}_4^+$  form or the  $\text{NH}_3$  form. For the purpose of determining threshold and release quantities under EPCRA section 313, EPA recommends that total aqueous ammonia be calculated in terms of  $\text{NH}_3$  equivalents (i.e., for determining weights, assume total ammonia is comprised entirely of the  $\text{NH}_3$  form). This method is simpler than using pH and temperature data to determine the ratio of the two forms present and is consistent with the presentation of total ammonia toxicity in a separate EPA document, *Ambient Water Quality Criteria for Ammonia* (EPA document #440/5-85-001, January 1985).

## **Section 2.2 Chemical Sources of Aqueous Ammonia**

Aqueous ammonia may be generated in solution from a variety of sources that include the release of anhydrous ammonia to water and the dissociation of ammonium salts in water. Water dissociable ammonium salts are not reportable in their entirety under the ammonia listing; these salts are reportable to the extent that they dissociate in water, and only 10 percent of the total aqueous ammonia that results when these salts dissociate is reportable. If these salts are not placed in water, they are not reportable.

If ammonium salts are purchased neat or as solids by a facility, then placed in water by that facility, the facility is *manufacturing* aqueous ammonia.

### **Section 2.2.1 Reporting Aqueous Ammonia Generated from Anhydrous Ammonia in Water**

If the source of aqueous ammonia is anhydrous ammonia in water, total aqueous ammonia (calculated in terms of  $\text{NH}_3$  equivalents) is equal to the quantity of anhydrous ammonia manufactured, processed, or otherwise used. A hypothetical scenario demonstrating the calculations involved in reporting aqueous ammonia generated from anhydrous ammonia in water is given in Example 2.

Example 2: In a calendar year, a facility uses 30,000 pounds of anhydrous ammonia to neutralize acids in a waste water stream. The neutralized waste stream (containing aqueous ammonia from dissociated ammonium salts) is then transferred to a POTW. The quantity to be applied toward threshold determinations is the total quantity of anhydrous ammonia used in the waste stream neutralization, or 30,000 pounds. The quantity of ammonia reported as transferred is 10 percent of the total quantity of aqueous ammonia transferred, or 3,000 pounds.

### **Section 2.2.2 Reporting Aqueous Ammonia Generated from the Dissociation of Ammonium Salts (Other Than Ammonium Nitrate)**

If the source of aqueous ammonia is the dissociation of ammonium salts in water, total aqueous ammonia (calculated in terms of NH<sub>3</sub> equivalents) is calculated from the weight percent (wt%) of the NH<sub>3</sub> equivalents of the ammonium salt. The NH<sub>3</sub> equivalent wt% of an ammonium salt is calculated using the following equation:

$$\text{NH}_3 \text{ equivalent wt\%} = (\text{NH}_3 \text{ equivalent weight})/(\text{MW ammonium salt}) \times 100.$$

If the source of aqueous ammonia is a monovalent compound (such as ammonium chloride, NH<sub>4</sub>Cl, ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub>, or ammonium bicarbonate, NH<sub>4</sub>HCO<sub>3</sub>), the NH<sub>3</sub> equivalent weight is equal to the MW of NH<sub>3</sub> (17.03 kg/kmol). If divalent compounds are involved (such as ammonium carbonate, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>), then the NH<sub>3</sub> equivalent weight is equal to the MW of NH<sub>3</sub> multiplied by two. Similarly, if trivalent compounds are involved, then the NH<sub>3</sub> equivalent weight is equal to the MW of NH<sub>3</sub> multiplied by three.

#### Example 3:

The NH<sub>3</sub> equivalent wt% of ammonium chloride is calculated as follows:

$$\text{NH}_3 \text{ equivalent wt\%} = (\text{NH}_3 \text{ equivalent weight})/(\text{MW ammonium chloride}) \times 100$$

$$\text{NH}_3 \text{ equivalent wt\%} = (17.03)/(53.49) \times 100$$

$$\text{NH}_3 \text{ equivalent wt\%} = 31.84\%$$

The NH<sub>3</sub> equivalent wt% of ammonium carbonate is calculated as follows:

$$\text{NH}_3 \text{ equivalent wt\%} = 2 \times (\text{NH}_3 \text{ equivalent weight})/(\text{MW ammonium carbonate}) \times 100$$

$$\text{NH}_3 \text{ equivalent wt\%} = 2 \times (17.03)/(96.09) \times 100$$

$$\text{NH}_3 \text{ equivalent wt\%} = 35.45\%$$

To aid the regulated community in reporting under the ammonia listing for aqueous ammonia, the table of chemical sources of aqueous ammonium provided in Section 3 of this document includes, in addition to CAS number, chemical name, and molecular weight, the NH<sub>3</sub> equivalent wt% of the commonly used, water dissociable ammonium salts listed in Table 1.

Example 4: In a calendar year, a facility uses 100,000 pounds of ammonium chloride, NH<sub>4</sub>Cl, *in aqueous solution* which is released to waste water streams, then transferred to a POTW. The NH<sub>3</sub> equivalent wt% of ammonium chloride is 31.84% (taken from Table 1 in section 3 below or calculated as in Example 3 above). The total quantity of aqueous ammonia present in solution is 31.84% of the 100,000 pounds of ammonia chloride used, or 31,840 pounds. The quantity applied towards threshold determinations for the ammonia listing is 10 percent of the total quantity of aqueous ammonia present in solution, or 3,184 pounds. The quantity of ammonia reported as released or transferred is 10 percent of the total quantity of aqueous ammonia released or transferred, or 3,184 pounds.

Example 5: In a calendar year, a facility uses 500,000 pounds of ammonium carbonate, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, and 400,000 pounds of ammonium bicarbonate, NH<sub>4</sub>HCO<sub>3</sub>, *in aqueous solution* which is released to waste water streams, then transferred to a POTW. The NH<sub>3</sub> equivalent wt% of ammonium carbonate is 35.45%, and the NH<sub>3</sub> equivalent wt% of ammonium bicarbonate is 21.54% (taken from Table 1 in Section 3 below or calculated as in Example 3 above). The quantity of aqueous ammonia present in solution from ammonium carbonate is 35.45% of the 500,000 pounds of ammonia carbonate used, or 177,250 pounds. The quantity of aqueous ammonia present in solution from ammonium bicarbonate is 21.54% of the 400,000 pounds of ammonia bicarbonate used, or 86,160 pounds. The total quantity of aqueous ammonia present in solution is 263,410 pounds. The quantity applied towards threshold determinations for the ammonia listing is 10 percent of the total quantity of aqueous ammonia present in solution, or 26,341 pounds. The quantity of ammonia reported as released or transferred is 10 percent of the total quantity of aqueous ammonia released or transferred, or 26,341 pounds.

### **Section 2.2.3 Reporting Aqueous Ammonia Generated from the Dissociation of Ammonium Nitrate**

Some sources of aqueous ammonia may be reportable under other EPCRA section 313 category listings. Ammonium nitrate (solution) is relevant to reporting under the ammonia listing to the extent that 10 percent of the total aqueous ammonia that results when ammonium nitrate dissociates is reported when determining thresholds and calculating releases. However, under the nitrate compounds category listing, ammonium nitrate (and other mixed salts containing ammonium and nitrate) must be reported in its entirety. When reporting ammonium nitrate under this category listing, the total nitrate compound, including both the nitrate ion portion and the ammonium counterion, is included when

determining threshold quantities. However, only the nitrate ion portion is included when determining the amount of ammonium nitrate that is released, transferred, or otherwise managed in wastes. The calculations involved in determining threshold and release quantities for reporting under the nitrate compounds category listing are described in a separate directive, *List of Toxic Chemicals within the Water Dissociable Nitrate Compounds Category and Guidance for Reporting* (EPA #745-R-00-006, Revised December, 2000). Note: reporting ammonium nitrate under the ammonia listing and the nitrate compounds category listing is effective for the 1995 reporting year for reports due July 1, 1996.

Example 6: In a calendar year, a facility uses 1,250,000 pounds of ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , in aqueous solution which is released to waste water streams, then transferred to a POTW. The  $\text{NH}_3$  equivalent wt% of ammonium nitrate is 21.28% (taken from Table 1 in Section 3 below or calculated as in Example 3 above). The total quantity of aqueous ammonia present in solution is 21.28% of the 1,250,000 pounds of ammonia chloride used, or 266,000 pounds. The quantity applied towards threshold determinations for the ammonia listing is 10 percent of the total quantity of aqueous ammonia present in solution, or 26,600 pounds. The quantity of ammonia reported as released or transferred is 10 percent of the total quantity of aqueous ammonia released or transferred, or 26,600 pounds. For determining thresholds and calculating releases under the nitrate compounds category listing, see the separate directive, *List of Toxic Chemicals within the Water Dissociable Nitrate Compounds Category and Guidance for Reporting* (EPA #745-R-00-006, Revised December, 2000).

Example 7: In a calendar year, a facility transfers 100,000 pounds of nitric acid ( $\text{HNO}_3$ ) to an on-site treatment facility. The nitric acid is neutralized with anhydrous ammonia, and treatment efficiency is 95 percent (the nitrate compound formed as a result of the treatment is ammonium nitrate,  $\text{NH}_4\text{NO}_3$ ). The neutralized waste stream (containing aqueous ammonia from dissociated ammonium nitrate) is then transferred to a POTW. The quantity of nitric acid neutralized is 95 percent of 100,000 pounds or 95,000 pounds. The quantity of nitric acid neutralized is converted first to kilograms then to kilomoles using the following equations:

$$\begin{aligned}\text{Kilograms HNO}_3 \text{ neutralized} &= (\text{lbs HNO}_3 \text{ neutralized}) \times (0.4536 \text{ kg/lb}) \\ \text{Kilomoles HNO}_3 \text{ neutralized} &= (\text{kg HNO}_3) \div (\text{MW of HNO}_3 \text{ in kg/kmol}).\end{aligned}$$

Substituting the appropriate values into the above equations yields:

$$\begin{aligned}\text{Kilograms HNO}_3 \text{ neutralized} &= 95,000 \text{ lbs} \times 0.4536 \text{ kg/lb} \\ &= 43,092 \text{ kg} \\ \text{Kilomoles HNO}_3 \text{ neutralized} &= 43,092 \text{ kg} \div 63.01 \text{ kg/kmol} \\ &= 683.9 \text{ kmol}.\end{aligned}$$

*(Example 7 is continued below)*

*(Example 7, continued)*

The quantity of anhydrous ammonia used in kilomoles in the acid neutralization and the quantity of ammonium nitrate generated in kilomoles from the neutralization are equal to the quantity of nitric acid neutralized (683.9 kmol). The quantity of anhydrous ammonia used in kilograms and pounds in the acid neutralization is calculated as follows:

$$\text{Kilograms NH}_3 \text{ used} = (\text{kmol NH}_3) \times (\text{MW of NH}_3 \text{ in kg/kmol}).$$

$$\text{Pounds NH}_3 \text{ used} = (\text{kg NH}_3) \times (2.205 \text{ lbs/kg}).$$

Substituting the appropriate values into the above equations yields:

$$\text{Kilograms NH}_3 \text{ used} = (683.9 \text{ kmol}) \times (17.03 \text{ kg/kmol}).$$

$$= 11,647 \text{ kmol}.$$

$$\text{Pounds NH}_3 \text{ used} = (11,647 \text{ NH}_3) \times (2.205 \text{ lbs/kg}).$$

$$= 25,682 \text{ pounds}.$$

The quantity reported applied towards threshold determinations for the ammonia listing is the total quantity of anhydrous ammonia used in the acid neutralization, or 25,682 pounds. The quantity of ammonia reported as released or transferred is 10 percent of the total quantity of aqueous ammonia released or transferred, or 2,568 pounds. For determining thresholds and calculating releases under the nitrate compounds category listing, see the separate directive, *List of Toxic Chemicals within the Water Dissociable Nitrate Compounds Category and Guidance for Reporting* (EPA #745-R-00-006, Revised December, 2000).



### Section 3. CAS Number List of Some Chemical Sources of Aqueous Ammonia

EPA is providing the following table of CAS numbers and chemical names to aid the regulated community in determining whether they need to report under the ammonia listing for aqueous ammonia. If a facility manufactures, processes, or otherwise uses, *in aqueous solution*, a chemical which is listed below, they must report 10 percent of the total aqueous ammonia that is the result of the dissociation of this chemical. However, this list is not exhaustive. If a facility manufactures, processes, or otherwise uses, *in aqueous solution*, a water dissociable ammonium compound, they must report 10 percent of the total aqueous ammonia that is the result of the dissociation of the compound, even if the compound does not appear in the following table.

Table 1. Listing by CAS Number and Molecular Weight of Some Chemical Sources of Aqueous Ammonia			
Chemical Name	Molecular Weight*	NH <sub>3</sub> Equivalent Wt%	CAS Number
Ammonium acetate	77.08	22.09	631-61-8
Ammonium aluminum sulfate (Ammonium aluminum disulfate)	237.14	7.181	7784-25-0
Ammonium antimony fluoride (Diammonium pentafluoroantimonate)	252.82	13.47	32516-50-0
Ammonium arsenate (Ammonium arsenate, hydrogen) (Ammonium arsenate, dihydrogen)	158.97	10.71	13462-93-6
Ammonium arsenate (Diammonium arsenate) (Diammonium arsenate, hydrogen) (Diammonium arsenate, monohydrogen)	176.00	19.35	7784-44-3
Ammonium arsenite	124.96	13.63	13462-94-7
Ammonium azide	60.06	28.35	12164-94-2
Ammonium benzenesulfonate	175.20	9.720	19402-64-3
Ammonium benzoate	139.15	12.24	1863-63-4
Ammonium bromate	145.94	11.67	13843-59-9
Ammonium bromide	97.94	17.39	12124-97-9
Ammonium cadmium chloride (Ammonium cadmium trichloride)	236.81	7.191	18532-52-0
Ammonium carbamate	78.07	21.81	1111-78-0
Ammonium carbonate carbamate	157.13	21.68	8000-73-5
Ammonium carbonate (Diammonium carbonate)	96.09	35.45	506-87-6

Ammonium carbonate, hydrogen (Ammonium bicarbonate)	79.06	21.54	1066-33-7
Ammonium cerium nitrate (Ammonium hexanitratocerate) (Ammonium hexanitratocerate (IV)) (Diammonium cerium hexanitate)	548.23	6.213	16774-21-3
Ammonium cerous nitrate (Ammonium cerous nitrate, tetrahydrate)	486.22	7.005	13083-04-0
Ammonium chlorate	101.49	16.78	10192-29-7
Ammonium perchlorate	117.49	14.49	7790-98-9
Ammonium chloride	53.49	31.84	12125-02-9
Ammonium chromate (Ammonium chromate (VI)) (Diammonium chromate)	152.07	22.40	7788-98-9
Ammonium chromate (Ammonium dichromate) (Ammonium dichromate (VI)) (Ammonium bichromate) (Diammonium dichromate)	252.06	13.51	7789-09-5
Ammonium chromium sulfate (Ammonium chromic sulfate)	265.17	6.422	13548-43-1
Ammonium citrate (Ammonium citrate, monohydrogen) (Ammonium citrate, dibasic) (Diammonium citrate) (Diammonium citrate, hydrogen)	226.19	15.06	3012-65-5
Ammonium citrate (Ammonium citrate, tribasic) (Triammonium citrate)	243.22	21.01	3458-72-8
Ammonium cobalt sulfate (Ammonium cobaltous sulfate)	289.14	11.78	13596-46-8
Ammonium cupric chloride (Ammonium chlorocuprate (II)) (Diammonium copper tetrachloride) (Diammonium tetrachlorocuprate)	241.43	14.11	15610-76-1
Ammonium cyanate (Ammonium isocyanate)	60.06	28.35	22981-32-4
Ammonium cyanide	44.06	38.65	12211-52-8
Ammonium cyanoaurate, monohydrate (Ammonium tetracyanoaurate, monohydrate)	319.07	5.337	14323-26-3

Ammonium cyanoaurate (Ammonium dicyanoaurate)	267.04	6.377	31096-40-9
Ammonium ferricyanide (Ammonium hexacyanoferrate (III)) (Triammonium hexacyanoferrate)	266.07	19.20	14221-48-8
Ammonium ferrocyanide (Ammonium hexacyanoferrate (II)) (Tetraammonium ferrocyanide) (Tetraammonium hexacyanoferrate)	284.11	23.98	14481-29-9
Ammonium fluoride	37.04	45.98	12125-01-8
Ammonium fluoride (Ammonium difluoride) (Ammonium bifluoride) (Ammonium fluoride, hydrogen) (Ammonium difluoride, hydrogen) (Ammonium bifluoride, hydrogen)	57.04	29.86	1341-49-7
Ammonium fluoroborate (Ammonium tetrafluoroborate)	104.84	16.24	13826-83-0
Ammonium fluorogermanate (IV) (Ammonium hexafluorogermanate (IV)) (Diammonium hexafluorogermanate)	222.66	15.30	16962-47-3
Ammonium fluorophosphate (Ammonium hexafluorophosphate)	163.00	10.45	16941-11-0
Ammonium fluorosulfate (Ammonium fluorosulfonate)	117.10	14.54	13446-08-7
Ammonium formate	63.06	27.01	540-69-2
Ammonium gallium sulfate	282.90	6.020	15335-98-5
Ammonium hydroxide	35.05	48.59	1336-21-6
Ammonium iodide	144.94	11.75	12027-06-4
Ammonium iridium chloride (Ammonium chloroiridate (III)) (Ammonium hexachloroiridate) (Triammonium hexachloroiridate)	459.05	11.13	15752-05-3
Ammonium iron sulfate (Ammonium ferric sulfate) (Ammonium iron disulfate)	269.02	6.330	10138-04-2
Ammonium iron sulfate (Ammonium ferrous sulfate) (Diammonium iron disulfate) (Diammonium ferrous disulfate)	286.05	11.91	10045-89-3

Ammonium lactate (Ammonium 2-hydroxypropionate)	107.11	15.90	515-98-0
Ammonium laurate (Ammonium dodecanoate)	217.35	7.835	2437-23-2
Ammonium magnesium sulfate	252.50	13.49	14727-95-8
Ammonium malate	168.15	20.26	6283-27-8
Ammonium malate, hydrogen (Ammonium bimalate)	151.12	11.27	5972-71-4
Ammonium molybdate (Diammonium molybdate)	196.01	17.38	13106-76-8
Ammonium molybdate (Ammonium heptamolybdate) (Ammonium molybdate, hydrate) (Ammonium molybdate, tetrahydrate) (Ammonium <i>para</i> molybdate, tetrahydrate)	1163.8	8.780	12054-85-2
Ammonium nickel chloride, hexahydrate	183.09	9.301	16122-03-5
Ammonium nickel sulfate (Ammonium nickel sulfate, hexahydrate) (Ammonium nickel disulfate, hexahydrate) (Diammonium nickel disulfate, hexahydrate)	286.88	11.87	7785-20-8
Ammonium nitrate	80.04	21.28	6484-52-2
Ammonium nitrate sulfate	212.18	24.08	12436-94-1
Ammonium nitrite	64.04	26.59	13446-48-5
Ammonium oleate	299.50	5.686	544-60-5
Ammonium oxalate	124.10	27.45	1113-38-8
Ammonium palladium chloride (Ammonium chloropalladate (II)) (Ammonium tetrachloropalladate (II)) (Diammonium tetrachloropalladate)	284.31	11.98	13820-40-1
Ammonium phosphate (Ammonium orthophosphate)	149.09	34.27	10124-31-9
Ammonium phosphate (Ammonium biphosphate) (Ammonium phosphate, hydrogen) (Ammonium phosphate, dihydrogen) (Ammonium orthophosphate, dihydrogen) (Ammonium phosphate, monobasic)	115.03	14.80	7722-76-1

Ammonium phosphate (Ammonium phosphate, hydrogen) (Ammonium orthophosphate, monohydrogen) (Ammonium phosphate, dibasic) (Ammonium orthophosphate, dibasic) (Diammonium phosphate) (Diammonium orthophosphate) (Diammonium phosphate, hydrogen) (Diammonium phosphate, monohydrogen) (Diammonium orthophosphate, hydrogen)	132.06	25.79	7783-28-0
Ammonium phosphinate (Ammonium hypophosphite)	83.03	20.51	7803-65-8
Ammonium phosphite (Ammonium biphosphite) (Ammonium phosphite, dihydrogen)	99.03	17.20	13446-12-3
Ammonium picramate	216.15	7.879	1134-85-6
Ammonium propionate	91.11	18.69	17496-08-1
Ammonium rhodium chloride (Ammonium chlororhodate (III)) (Ammonium hexachlororhodate (III)) (Triammonium rhodium hexachloride) (Triammonium hexachlororhodate)	369.74	13.82	15336-18-2
Ammonium salicylate (Ammonium 2-hydroxybenzoate)	155.15	10.98	528-94-9
Ammonium selenide	115.04	29.61	66455-76-3
Ammonium silicon fluoride (Ammonium fluorosilicate) (Ammonium hexafluorosilicate) (Diammonium silicon hexafluoride) (Diammonium fluorosilicate) (Diammonium hexafluorosilicate)	178.15	19.12	16919-19-0
Ammonium stearate (Ammonium octadecanoate)	301.51	5.648	1002-89-7
Ammonium succinate (Diammonium succinate)	152.15	22.39	2226-88-2
Ammonium sulfamate (Ammonium amidosulfate) (Ammonium amidosulfonate)	114.12	14.92	7773-06-0
Ammonium sulfate (Diammonium sulfate)	132.13	25.78	7783-20-2

Ammonium sulfate (Ammonium bisulfate) (Ammonium sulfate, hydrogen) (Ammonium sulfate, monohydrogen)	115.10	14.80	7803-63-6
Ammonium persulfate (Ammonium peroxydisulfate) (Ammonium peroxydisulfate) (Diammonium persulfate) (Diammonium peroxydisulfate)	228.19	14.93	7727-54-0
Ammonium sulfide (Ammonium bisulfide) (Ammonium sulfide, hydrogen)	51.11	33.32	12124-99-1
Ammonium sulfide (Ammonium monosulfide) (Diammonium sulfide)	68.14	49.99	12135-76-1
Ammonium sulfide (Diammonium pentasulfide)	196.39	17.34	12135-77-2
Ammonium sulfite, monohydrate (Diammonium sulfite, monohydrate)	116.13	29.33	7783-11-1
Ammonium sulfite (Ammonium bisulfite) (Ammonium sulfite, hydrogen)	99.10	17.18	10192-30-0
Ammonium tetrachloroaurate (III), hydrate	356.82	4.772	13874-04-9
Ammonium thiocarbamate	94.13	18.09	16687-42-6
Ammonium thiocarbonate (Diammonium trithiocarbonate)	144.27	23.61	13453-08-2
Ammonium thiocyanate (Ammonium isothiocyanate) (Ammonium sulfocyanate) (Ammonium rhodanate) (Rhodanid)	76.12	22.37	1762-95-4
Ammonium dithionate	196.19	17.36	60816-52-6
Ammonium thiosulfate (Ammonium hyposulfite) (Diammonium thiosulfate)	148.20	22.98	7783-18-8
Ammonium tin bromide (Ammonium bromostannate (IV)) (Ammonium hexabromostannate (IV)) (Diammonium hexabromostannate)	634.19	5.371	16925-34-1

Ammonium tin chloride (Ammonium chlorostannate (IV)) (Ammonium hexachlorostannate (IV)) (Diammonium tin hexachloride) (Diammonium hexachlorostannate)	367.48	9.269	16960-53-5
Ammonium titanium fluoride (Ammonium fluorotitanate (IV)) (Ammonium hexafluorotitanate (IV)) (Diammonium titanium hexafluoride) (Diammonium hexafluorotitanate)	197.95	17.21	16962-40-6
Ammonium titanium oxalate, monohydrate (Diammonium dioxalatooxotitanate, monohydrate)	276.00	12.34	10580-03-7
Ammonium tungstate (Ammonium tungstate (VI)) (Ammonium <i>para</i> tungstate) (Hexaammonium tungstate)	1779.2	5.743	12028-06-7
Ammonium tungstate (Ammonium tungstate (VI)) (Ammonium <i>para</i> tungstate) (Decaammonium tungstate)	3058.6	5.568	11120-25-5
Ammonium valerate (Ammonium pentanoate)	119.16	14.29	42739-38-8
Ammonium zinc chloride (Ammonium chlorozincate) (Ammonium tetrachlorozincate) (Diammonium tetrachlorozincate)	243.27	14.00	14639-97-5

\* For hydrated compounds, e.g. ammonium sulfite, monohydrate, the molecular weight excludes the weight of the hydrate portion.





Kirk-Othmer  
© 1992**AMMONIA**

Ammonia [7664-41-7],  $\text{NH}_3$ , a colorless alkaline gas, is lighter than air and possesses a unique, penetrating odor. The preparation of ammonium salts dates back to the early Egyptians in the fourth century BC. Ammonia gas was first produced as a pure compound by Priestly in 1774.

The value of nitrogen compounds as an ingredient of mineral fertilizers was recognized in 1840. Nitrogen is an essential element to plant growth and ammonia is the primary nitrogen source used in fertilizers (qv). Until the early 1900s, the nitrogen source in farm soils was entirely derived from natural sources: from mineral resources such as Chilean nitrates, from manure and the putrefaction of vegetable wastes; and from ammonium sulfate from coal coking, seed meals, sewage sludges, and food processing by-products. The synthesis of ammonia directly from hydrogen [1333-74-0] (qv) and nitrogen [7727-37-9] (qv) on a commercial scale was pioneered by Haber and Bosch in 1913, for which they were awarded Nobel prizes. Further developments in economical, large scale ammonia production for fertilizers have made a significant impact on increases in the world's food supply.

**Physical Properties**

Table 1 lists the important physical properties of ammonia; Table 2 gives the densities at 15°C; Figure 1 is a Mollier diagram giving additional thermodynamic data for ammonia. The flammable limits of ammonia in air are 16 to 25% by volume; in oxygen the range is 15 to 79%. Such mixtures can explode although ammonia-air mixtures are quite difficult to ignite. The ignition temperature is about 650°C.

Ammonia is readily absorbed in water to make ammonia liquor. Figure 2 summarizes the vapor-liquid equilibria of aqueous ammonia solutions and Figure 3 shows the solution vapor pressures. Additional thermodynamic properties may be found in the literature (1,2). Considerable heat is evolved during the solution of ammonia in water: approximately 2180 kJ (520 kcal) of heat is evolved upon the dissolution of 1 kg of ammonia gas.

Ammonia is an excellent solvent for salts, and has an exceptional capacity to ionize electrolytes. The alkali metals and alkaline earth metals (except beryllium) are readily soluble in ammonia. Iodine, sulfur, and phosphorus dissolve in ammonia. In the presence of oxygen, copper is readily attacked by ammonia. Potassium, silver, and uranium are only slightly soluble. Both ammonium and beryllium chloride are very soluble, whereas most other metallic chlorides are slightly soluble or insoluble. Bromides are in general more soluble in ammonia than chlorides, and most of the iodides are more or less soluble. Oxides, fluorides, hydroxides, sulfates, sulfites, and carbonates are insoluble. Nitrates (eg, ammonium nitrate) and urea are soluble in both anhydrous and aqueous ammonia making the production of certain types of fertilizer nitrogen solutions possible. Many organic compounds such as amines (qv), nitro compounds, and aromatic sulfonic acids, also dissolve in liquid ammonia. Ammonia is superior to water in solvating organic compounds such as benzene (qv), carbon tetrachloride, and hexane.

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**Table 1. Physical Properties of Anhydrous Ammonia**

Property	Value
molecular weight	17.03
boiling point, °C	-33.35
freezing point, °C	-77.7
critical temp, °C	133.0
critical pressure, kPa <sup>a</sup>	11,425
specific heat, J/(kg·K) <sup>b</sup>	
0°C	2097.2
100°C	2226.2
200°C	2105.6
heat of formation of gas, $\Delta H_f$ , kJ/mol <sup>b</sup>	
0 K	-39,222
298 K	-46,222
solubility in water, wt %	
0°C	42.8
20°C	33.1
40°C	23.4
60°C	14.1
specific gravity	
-40°C	0.690
0°C	0.639
40°C	0.580

<sup>a</sup>To convert kPa to psi, multiply by 0.145.

<sup>b</sup>To convert J to cal, divide by 4.184.

**Table 2. Density of Aqueous Ammonia at 15°C**

Ammonia, wt %	Density, g/L
8	0.970
16	0.947
32	0.889
50	0.832
75	0.733
100	0.618

### Chemical Properties

Ammonia is comparatively stable at ordinary temperatures, but decomposes into hydrogen and nitrogen at elevated temperatures. The rate of decomposition is greatly affected by the nature of the surfaces with which the gas comes into contact: glass is very inactive; porcelain and pumice have a distinct accelerating effect; and metals such as iron, nickel, osmium, zinc, and uranium have even more of an effect. At atmospheric pressure, decomposition begins at about 450–500°C, whereas in the presence of catalysts, it begins as low as 300°C and is nearly complete at 500–600°C. At 1000°C, however, a trace of ammonia remains. Ammonia decomposition, a source of high purity hydrogen and nitrogen for use in metals processing, can also be promoted electrically or photochemically.

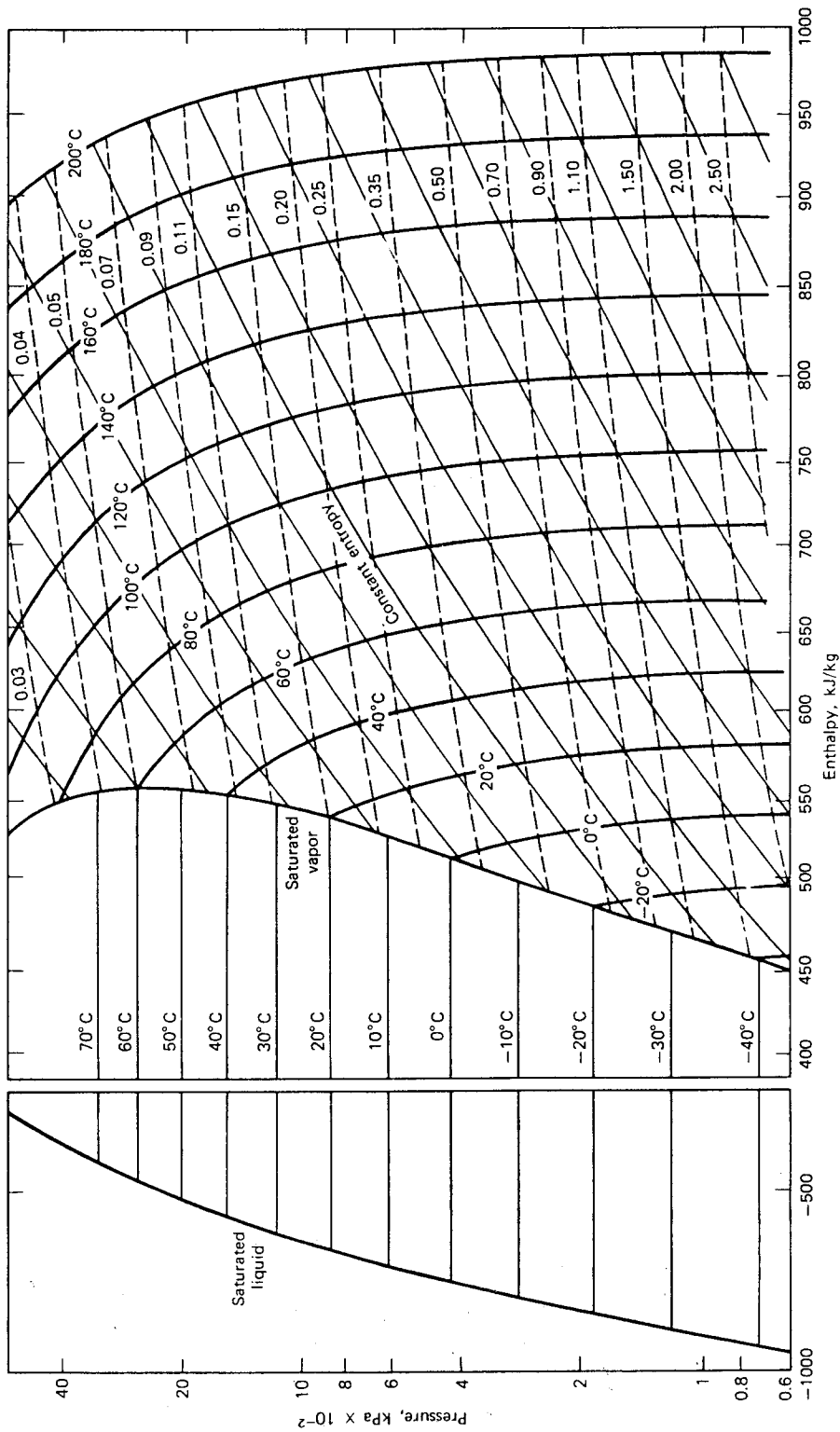


Fig. 1. Mollier diagram for ammonia. Numbers on dashed lines represent specific volume values in m<sup>3</sup>/kg. To convert from kPa to psi, multiply by 0.145. To convert kJ to kcal, divide by 4.184. Courtesy of Elliot Company.

Fig. 1. Mollier diagram for ammonia. Numbers on dashed lines represent specific volume values in m<sup>3</sup>/kg. To convert from kPa to psi, multiply by 0.145. To convert kJ to kcal, divide by 4.184. Courtesy of Elliot Company.

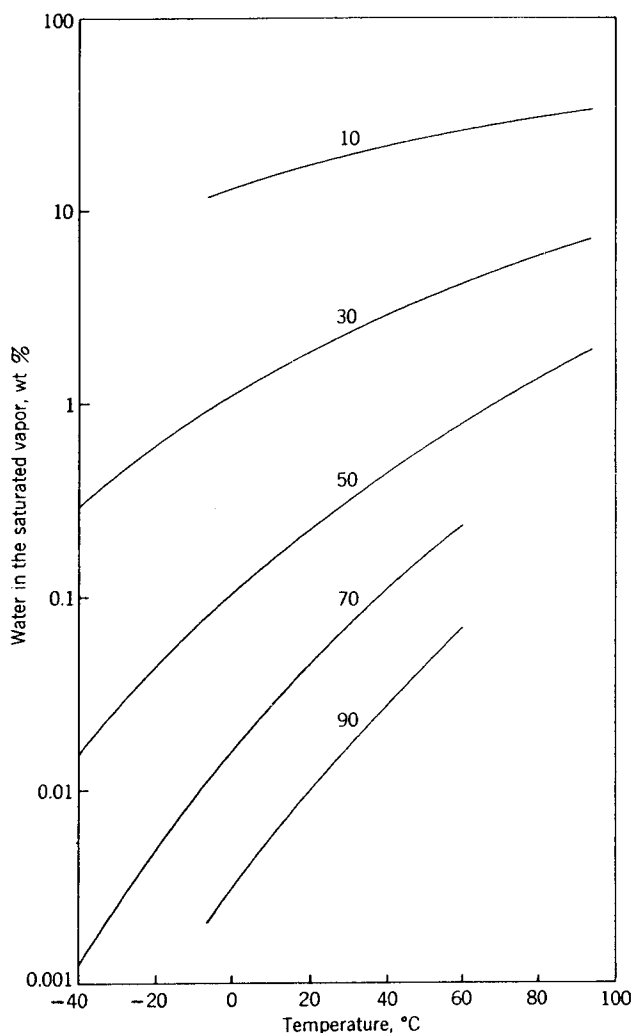
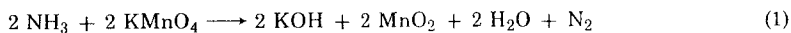
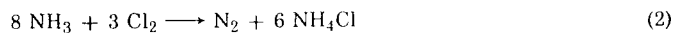


Fig. 2. Vapor-liquid equilibrium of ammonia-water system. Numbers represent the weight percent of ammonia in the liquid (1).

Ammonia reacts readily with a large variety of substances (see AMMONIUM COMPOUNDS; AMINES BY REDUCTION; AMINES). Oxidation at a high temperature is one of the more important reactions, giving nitrogen and water. Gaseous ammonia is oxidized to water and nitrogen when heated to a relatively high temperature in the presence of oxides of the less positive metals, such as cupric oxide. Powerful oxidizing agents, eg, potassium permanganate, react similarly at ordinary temperatures.



The action of chlorine on ammonia can also be regarded as an oxidation reaction.



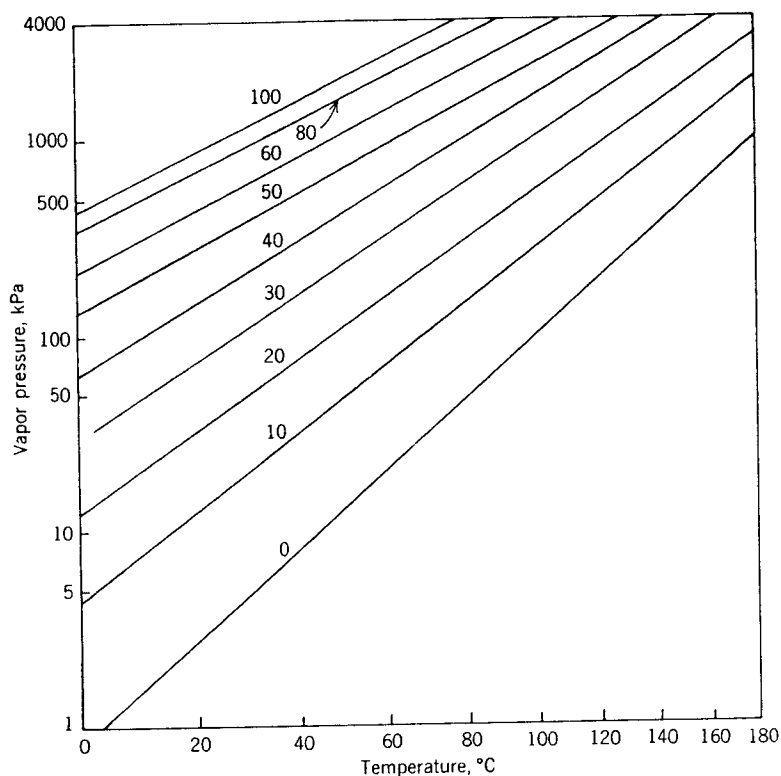
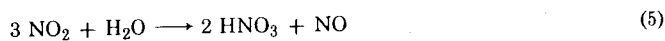
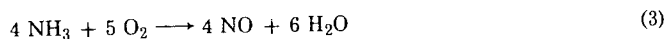


Fig. 3. Vapor pressure of aqueous ammonia solution (1). Numbers represent the weight percent of ammonia in the liquid. To convert kPa to psi, multiply by 0.145.

A major step in the production of nitric acid [7697-37-2] (qv) is the catalytic oxidation of ammonia to nitric acid and water. Very short contact times on a platinum-rhodium catalyst at temperatures above 650°C are required.



The neutralization of acids is of commercial importance. Three principal fertilizers, ammonium nitrate [6484-52-2],  $\text{NH}_4\text{NO}_3$ , ammonium sulfate [7782-20-2],  $(\text{NH}_4)_2\text{SO}_4$ , and ammonium phosphate [10361-65-6],  $(\text{NH}_4)_3\text{PO}_4$ , are made by reaction of the respective acids with ammonia.

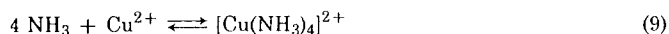
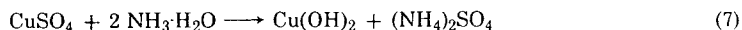
The reaction between ammonia and water is reversible.



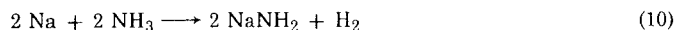
The aqueous solubility of ammonia decreases rapidly as temperature increases. The existence of undissociated ammonium hydroxide [1336-21-6],  $\text{NH}_4\text{OH}$ , in aqueous solution is doubtful although there are indications that ammonia exists in

water in the form of the hydrates  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and  $2 \text{NH}_3 \cdot \text{H}_2\text{O}$ . The ammonium ion,  $\text{NH}_4^+$ , behaves similarly to the alkali metal cations. Ammonia, a comparatively weak base, however, ionizes in water to a much lesser extent than sodium hydroxide. In a molar solution of aqueous ammonia, the concentration of the hydroxyl ion is about two-hundredths that of the hydroxyl ion concentration in a molar sodium hydroxide solution.

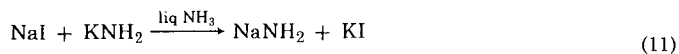
Aqueous ammonia also acts as a base precipitating metallic hydroxides from solutions of their salts, and in forming complex ions in the presence of excess ammonia. For example, using copper sulfate solution, cupric hydroxide, which is at first precipitated, redissolves in excess ammonia because of the formation of the complex tetramminecopper(II) ion.



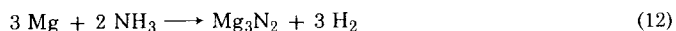
Potassium dissolves in liquid ammonia, but the conversion of a small amount of the metallic potassium to the metallic amide takes several days. By applying the same technique using sodium metal, sodium amide [7782-92-5],  $\text{NaNH}_2$ , a white solid, can be formed.



Heating metallic lithium in a stream of gaseous ammonia gives lithium amide [7782-89-0],  $\text{LiNH}_2$ , which may also be prepared from liquid ammonia and lithium in the presence of platinum black. Amides of the alkali metals can be prepared by double-decomposition reactions in liquid ammonia. For example

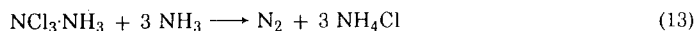


Heating ammonia with a reactive metal, such as magnesium, gives the nitride.



Magnesium reacts slowly at lower temperatures to give the amide, as do all active metals; this reaction is catalyzed by transition metal ions. Aluminum nitride [24304-00-5],  $\text{AlN}$ , barium nitride [12047-79-9],  $\text{Ba}_3\text{N}_2$ , calcium nitride [12013-82-0],  $\text{Ca}_3\text{N}_2$ , strontium nitride [12033-82-8],  $\text{Sr}_3\text{N}_2$ , and titanium nitride [25583-20-4],  $\text{TiN}$ , may be formed by heating the corresponding amides.

Halogens react with ammonia. Chlorine or bromine liberate nitrogen from excess ammonia and give the corresponding ammonium salt. Substitution probably takes place first. The resulting trihalide combines loosely with another molecule of ammonia, to give  $\text{NCl}_3 \cdot \text{NH}_3$  for example. These ammoniates are very unstable and decompose in the presence of excess ammonia to give the ammonium salt and nitrogen.



The iodine compound is more stable and separates as so-called nitrogen triiodide monoammoniate [14014-86-9],  $\text{NI}_3 \cdot \text{NH}_3$ , an insoluble brownish-black solid, which decomposes when exposed to light in the presence of ammonia. In reactions of the halogens with the respective ammonium salts, however, the action is different. Chlorine replaces hydrogen and nitrogen chloride [10025-85-1],  $\text{NCl}_3$ , separates as oily, yellow droplets capable of spontaneous explosive decomposition.



The hydrogen of the ammonium salt is not replaced by bromine and iodine. These elements combine with the salt to form perhalides.

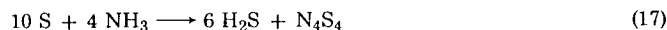


A number of perhalides are known, and one of the most stable is ammonium tetrachloroiodide [19702-43-3],  $\text{NH}_4\text{ICl}_4$ . Ammonia reacts with chlorine in dilute solution to give chloramines, a reaction important in water purification (see CHLORAMINES AND BROMAMINES). Depending upon the pH of the water, either monochloramine [10599-90-3],  $\text{NH}_2\text{Cl}$ , or dichloramine [3400-09-7],  $\text{NHCl}_2$ , is formed. In the dilutions encountered in waterworks practice, monochloramine is nearly always found, except in the case of very acidic water (see BLEACHING AGENTS; WATER).

Ammonia reacts with phosphorus vapor at red heat to give nitrogen and phosphine.



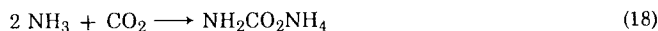
Sulfur vapor and ammonia react to give ammonium sulfide and nitrogen; sulfur and liquid anhydrous ammonia react to produce nitrogen sulfide [28950-34-7],  $\text{N}_4\text{S}_4$ .



Ammonia and carbon at red heat give ammonium cyanide [12211-52-8],  $\text{NH}_4\text{CN}$ .

Ammonia forms a great variety of addition or coordination compounds (qv), also called ammoniates, in analogy with hydrates. Thus  $\text{CaCl}_2 \cdot 6\text{NH}_3$  and  $\text{CuSO}_4 \cdot 4\text{NH}_3$  are comparable to  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$ , respectively, and, when regarded as coordination compounds, are called amines and written as complexes, eg,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ . The solubility in water of such compounds is often quite different from the solubility of the parent salts. For example, silver chloride,  $\text{AgCl}$ , is almost insoluble in water, whereas  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  is readily soluble. Thus silver chloride dissolves in aqueous ammonia. Similar reactions take place with other water insoluble silver and copper salts. Many amines can be obtained in a crystalline form, particularly those of cobalt, chromium, and platinum.

Of major industrial importance is the reaction of ammonia and carbon dioxide giving ammonium carbamate [1111-78-0],  $\text{CH}_6\text{N}_2\text{O}_2$ .



which then decomposes to urea (qv) and water



This is an example of an ammonolytic reaction in which a chemical bond is broken by the addition of ammonia. It is analogous to the hydrolysis reactions of water. An impressive number of inorganic and organic compounds undergo ammonolysis.

### Manufacture

Ammonium compounds were produced in the 1890s on a large scale as by-product ammonium sulfate [7783-20-2] from coke oven gas. Coke oven gas also provided the feedstock for the Haber-Bosch process, the first technology to synthesize ammonia directly from elemental hydrogen and nitrogen. The first commercial Haber-Bosch installation went on stream in 1913 at a Badische Anilin and Soda Fabrik (BASF) facility in Ludwigshafen-Oppau, Germany. It had a design capacity of 30 metric tons per day. The successful commercialization of this process not only produced first-of-a-kind high temperature and pressure equipment designs but also resulted in the promoted iron catalyst which is essentially still used for ammonia synthesis.

Between 1930 and 1950, the primary emphasis of ammonia process development was in the area of synthesis gas generation (3) (see FUELS, SYNTHETIC, GASEOUS FUELS). Extensive coal deposits in Europe provided the feedstock for the ammonia industry. The North American ammonia industry was based primarily on abundant supplies of low cost natural gas (see GAS, NATURAL).

Natural gas reforming at successively higher pressures resulted in lower downstream compression requirements. By the early 1960s, the expensive and cumbersome copper liquor process for final carbon oxide removal was being replaced by methanation, which permitted two-stage shift conversion with resultant low carbon monoxide leakage. The development of the second stage low temperature shift catalyst further improved the efficiency of the process by increasing the ultimate hydrogen yield from synthesis gas.

A step change in the capacity attainable from single-train plants occurred in 1963 with the commissioning of a 544 t/d unit designed by The M. W. Kellogg Company; this was followed by a similar size plant for Monsanto in Luling, Louisiana. The Monsanto plant marked the first time centrifugal compressors were used for all process services using full integration with utility systems. These innovations were the forerunner for the large scale single-train 907 and 1500 t/d plant designs which proliferated in the 1970s.

Rapid expansion resulted from engineering efforts to meet an increasing world demand for fixed nitrogen. Improvements in the energy cycle, including high pressure steam generation from waste heat, and technical advances in compressors, reformers, and converters (4,5) all led to more efficient ammonia production taking full advantage of the economy of scale provided by large tonnage single-train plants.

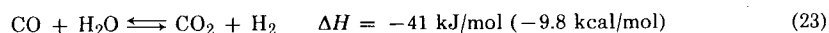


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**Synthesis Gas Preparation Processes.** Synthesis gas for ammonia production consists of hydrogen and nitrogen in about a three to one mole ratio, residual methane, argon introduced with the process air, and traces of carbon oxides. There are several processes available for synthesis gas generation and each is characterized by the specific feedstock used. A typical synthesis gas composition by volume is: hydrogen, 73.65%; nitrogen, 24.55%; methane, <1 ppm-0.8%; argon, 100 ppm-0.34%; carbon oxides, 2-10 ppm; and water vapor, 0.1 ppm.

The source of nitrogen is always air. However, hydrogen can be derived from a variety of raw materials including water, light and heavy hydrocarbons (qv) resulting from crude oil refining, coal (qv), natural gas, and sometimes a combination of these raw materials. In all cases, part of the hydrogen produced is derived from water.

Synthesis gas preparation consists of three steps: (1) feedstock conversion, (2) carbon monoxide conversion, and (3) gas purification. Table 4 gives the main processes for each of the feedstocks (qv) used. In each case, except for water electrolysis, concomitant to the reactions shown, the water-gas shift reaction occurs.



Equilibrium is achieved in steam reforming; equilibrium is approached for partial oxidation process.

**Table 4. Hydrogen Generation Raw Materials and Processes**

Raw material	Process description	Feedstock conversion reaction
natural gas	steam reforming <sup>a</sup>	$\text{C}_n\text{H}_{(2n+2)} + n \text{H}_2\text{O} \rightleftharpoons n \text{CO} + (2n + 1) \text{H}_2$
naphtha	steam reforming <sup>b</sup>	$\text{C}_n\text{H}_{(2n+2)} + n \text{H}_2\text{O} \rightleftharpoons n \text{CO} + (2n + 1) \text{H}_2$
fuel oil	partial oxidation	$\text{C}_n\text{H}_{(2n+2)} + n/2 \text{O}_2 \rightleftharpoons n \text{CO} + (n + 1) \text{H}_2$
coal	coal gasification	$\text{C} + 1/2 \text{O}_2 \rightleftharpoons \text{CO}$
water	electrolysis	$\text{H}_2\text{O} \xrightarrow{e^-} 1/2 \text{O}_2 + \text{H}_2$

<sup>a</sup>Nickel is used as catalyst.

<sup>b</sup>Promoted nickel is used as catalyst.

In the original Haber-Bosch process, the hydrogen source was coke derived from coal. In this process, shown in Figure 5, coke is first blasted with air and the heat liberated by the formation of carbon dioxide raises the coke to incandescence. The products of combustion leave the system by going to the atmosphere. Steam is added next to produce water gas containing carbon dioxide, carbon monoxide, and hydrogen. The nitrogen is usually furnished by adding a sufficient quantity of the combustion products from the blasting step to the gas stream. Dust particles and undecomposed steam are then removed by water scrubbing. A gas holder provides storage. The carbon monoxide in the gas is

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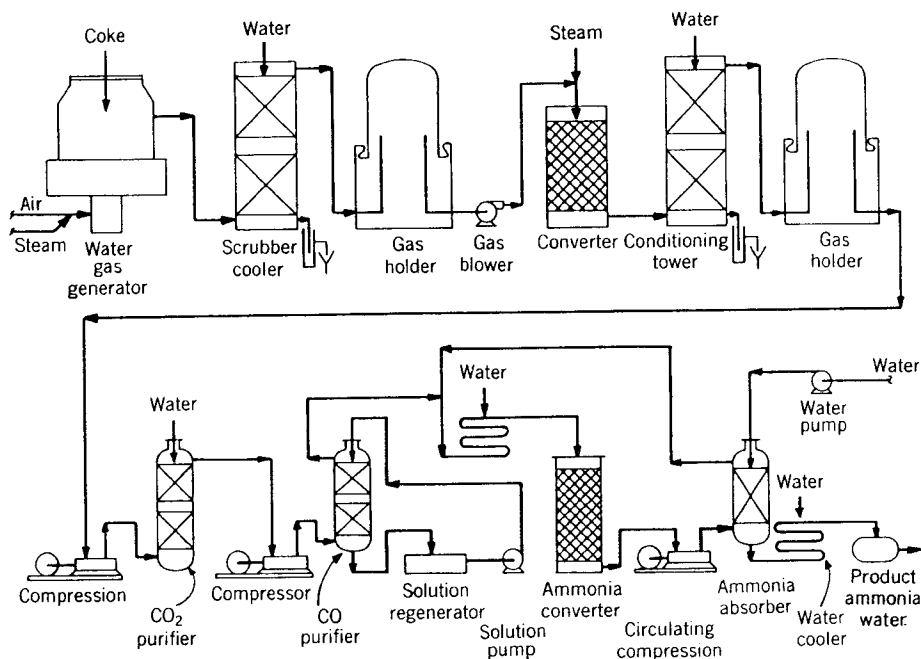


Fig. 5. Haber-Bosch process flow diagram.

converted to hydrogen and carbon dioxide by reaction with steam over a catalyst and the converted gas is stored in another gas holder, compressed, and the carbon dioxide removed by water scrubbing. The gas is then compressed and scrubbed using an ammoniacal cuprous solution to remove unconverted carbon monoxide. The resultant, relatively pure gas, consisting of three parts hydrogen to one part nitrogen, is then fed as makeup gas to the synthesis loop.

The most economic hydrocarbon feedstock is likely to be the one having the highest hydrogen to carbon ratio. From Table 4 it can be seen that, for a given amount of carbon (feed), proportionally more hydrogen is generated by steam reforming than by partial oxidation. Thus, in the manufacture of hydrogen for ammonia synthesis, partial oxidation processes require more feed, ultimately leading to larger carbon dioxide removal facilities. In addition, the raw synthesis gas generated by partial oxidation is much higher in carbon monoxide content than that coming from a steam reforming operation. This high CO content requires larger facilities, both in terms of equipment and catalyst, for shift conversion. Because more CO<sub>2</sub> removal and higher shift conversion lead to higher investment and operating costs, partial oxidation processes are normally used only for materials which cannot be handled by steam reforming such as coal or heavy hydrocarbon feeds.

Hydrogen produced by the electrolysis of water is used in special circumstances only: where electric power is plentiful, inexpensive, and light hydrocarbons are not available.

Catalytic reformer off-gases from oil refinery gasoline production have been a source of hydrogen. Several ammonia plants have been built using this off-gas which is usually about 85% hydrogen, as raw material feed. In such installations,

a liquid nitrogen wash system is used to remove the undesirable impurities in the gas feed and to provide the nitrogen required for synthesis. Because of increased demand for hydrogen in refinery hydro-treating operations, little by-product hydrogen is available and generally additional hydrogen is needed. Therefore, fewer ammonia plants using reformer off-gas have been built than in the past.

Of the raw material hydrogen sources—natural gas, coal, and petroleum fractions—natural gas is the most often employed in ammonia plants in the 1990s and steam reforming is by far the most often used process. Partial oxidation processes are utilized where steam-reformable feeds are not available or in special situations where local conditions exist to provide favorable economics. Table 5 lists the contribution of the various feedstocks to world ammonia capacity in 1983 and 1987 (31).

**Table 5. Feedstocks for World Ammonia Capacity, Annual %**

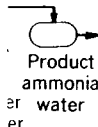
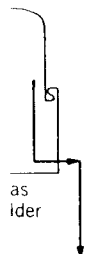
Feedstock	1983	1987
natural gas	66.4	69.8
natural gas hybrid <sup>a</sup>	7.5	5.8
naphtha, fuel oil, condensate	12.4	10.5
coke oven, refinery gas, hydrogen	4.3	3.9
coal	10.8	10.0
<i>Total</i>	<i>100.0</i>	<i>100.0</i>

<sup>a</sup>Hybrid plants are naphtha and fuel oil-based plants modified to use natural gas.

*Coal-Based Partial Oxidation Processes*

Two commercially established processes utilizing coal feeds are the Lurgi process (32) and the Koppers-Totzek process (33); the process schemes are shown in Figures 6 and 7, respectively.

In the Lurgi process, coal is gasified in a fixed bed reactor using oxygen and steam at about 2000–3000 kPa (20–30 atm). The steam and oxygen enter the gasifier through slots in a rotary grate while the coal is charged through specially designed lock hoppers and distributed evenly over the cross section of the gasifier. Ash is removed in a nonslagging operation by the rotary grate. Gasification temperatures range from about 560°C to 620°C depending on the feed characteristics. Because the gasification temperature is in the intermediate range and the operating pressure is relatively high, the methane and carbon dioxide content in the crude gas is considerably greater than for conventional reforming and partial oxidation processes. The methane and carbon dioxide contents from a typical Lurgi gasifier are 10–11% and about 28%, respectively. The crude gas from the Lurgi gasifier is treated in several processing steps including waste heat recovery, shift conversion, removal of tars, phenols, and other by-products, Rectisol (methanol wash) treatment for carbon dioxide and sulfur removal, liquid nitrogen scrubbing to produce a highly purified synthesis gas, compression, and finally ammonia synthesis. The liquid nitrogen scrubbing step removes carbon monoxide and methane which are recycled to a side stream steam reforming and shift



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streams (66,67). Purge gas recover systems can be customized to recover argon as needed.

**Energy Cycle.** The ammonia process is characterized by high process temperatures and compression power requirements. The total energy consumption consists of the process feedstock plus utility fuel requirements. Therefore, the energy efficiency of the process is logically maximized by integrating process waste heat recovery and the utility system by means of the Rankine cycle, using steam as the working medium (see POWER GENERATION).

The efficiency of the Rankine cycle itself can be increased by higher motive steam pressures and superheat temperatures, and lower surface condenser pressures in addition to rotating equipment selection. These parameters are generally optimized on the basis of materials of construction as well as equipment sizes. Typical high pressure steam system conditions are in excess of 10,350 kPa (1500 psi) and 510°C.

Efficient integration of the process with the utility system involves reducing the two principal areas of irreversibility that are inherent in the cycle: the transfer of process heat to the boiler, and the mixing of saturated boiler liquid with cooler condensate make-up. This strategy is implemented by recovering process heat at the highest possible levels into the motive steam system, and extracting cooler steam at the appropriate level after expansion in a turbine to satisfy process steam and lower level heating requirements.

Selection of the high pressure steam conditions is an economic optimization based on energy savings and equipment costs. Heat recovery into the high pressure system is usually available from the process in the secondary reformer and ammonia converter effluents, and the flue gas in the reformer convection section. Recovery is in the form of latent, superheat, or high pressure boiler feedwater sensible heat. Low level heat recovery is limited by the operating conditions of the deaerator.

A schematic of a typical ammonia plant steam system illustrating these principles is shown in Figure 21. High pressure steam is used exclusively for process drivers. The amount of extraction steam is determined by the process steam requirement for the reformer. The only other process requirement for low level heat is the CO<sub>2</sub> removal system which has been a prime area of improvement for reducing energy input. Export of additional low level heat may be available for offsite use, such as building heating, steam tracing, or desalination units where applicable.

A reasonable target for energy minimization is that process requirements dictate fuel firing, with no additional fuel being burned to raise steam. The steam available from waste heat recovery must match the power requirements of the process. Thus careful selection of the process design parameters is needed. In this case, the package or auxiliary boiler firing becomes zero, although this equipment is still included for controllability and start-up. Incremental steam capacity is also convenient for exporting motive steam to other integrated processes, such as urea.

As designs become more efficient with a corresponding reduction in steam requirements, integration with other power cycles becomes feasible. For example, the exhaust from a gas turbine process driver can be used as a source of preheated combustion air for the primary reformer, substantially increasing the efficiency of the conventional Brayton cycle (68). Additional integration options are possible

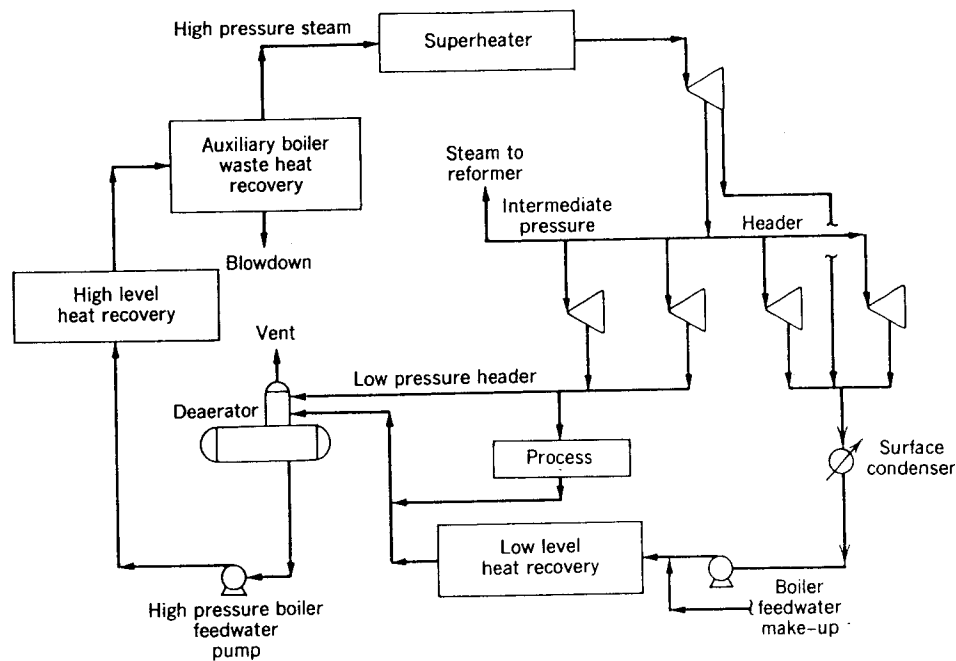


Fig. 21. Kellogg ammonia plant steam system.

using steam or electricity cogeneration (69). The result in all cases is an improvement in the overall energy cycle.

### Environmental Considerations

Ammonia production per se is relatively clean compared to other chemical process industries, and presents no unique environmental problems. Synthesis gas generation is the principal area requiring environmental controls and the nature of the controls depends on the feedstock and method of processing.

Coal feedstocks present the most serious environmental problems. Particulate emissions from the coal handling and processing facilities must be controlled (see AIR POLLUTION; EXHAUST CONTROL, INDUSTRIAL). The ash and slag solids removed from the gasification step must be disposed of in an environmentally safe manner. Some gasification produces significant amounts of other liquid by-products such as tars, phenols, and naphthas which must be recovered or incinerated (70). Some coals contain significant amounts of sulfur which must be stripped out of the raw syngas as hydrogen and carbonyl sulfides, necessitating further processing in a sulfur recovery unit (see SULFUR REMOVAL AND RECOVERY). Condensate streams from gasifiers may also contain hydrogen cyanide and metals in addition to ammonia complicating disposal further.

Partial oxidation of heavy liquid hydrocarbons requires somewhat simpler environmental controls. The principal source of particulates is carbon, or soot, formed by the high temperature of the oxidation step. The soot is scrubbed from the raw synthesis gas and either recycled back to the gasifier, or recovered as solid pelletized fuel. Sulfur and condensate treatment is similar in principle to

that required for coal gasification, although the amounts of potential pollutants generated is usually less (see COAL CONVERSION PROCESSES, GASIFICATION).

Reforming of natural gas or naphtha are the cleanest synthesis gas generation operations. Most natural gases contain sufficiently low levels of sulfur that it is possible to remove it in a simple fixed-bed adsorption system. Higher levels of sulfur are amenable to treatment in conventional solvent absorption-stripping systems for acid gas removal, such as MEA. Similarly, organic sulfur compounds in naphtha are hydrotreated over a cobalt-molybdenum catalyst and stripped as hydrogen sulfide. Residual sulfur is removed in a fixed-bed system similar to that used for natural gas before reforming.

Process condensate from reforming operations is commonly treated by steam stripping. The stripper is operated at a sufficiently high pressure to allow the overhead stripping steam to be used as part of the reformer steam requirement (71). Contaminants removed from the process condensate are reformed to extinction, so disposal to the environment is thereby avoided. This system not only reduces atmospheric emissions, but contributes to the overall efficiency of the process by recovering condensate suitable for boiler feedwater make-up because the process is a net water consumer.

Incorporation of a feed gas saturator coil in the convection section of the primary reformer allows for 100% vaporization of the process condensate. The steam is used as process steam in the reformer.

All fired equipment, whether it be a process furnace or a utility boiler, is also subject to regulation, usually in the form of sulfur and nitrous oxide limitations. These flue gases can be suitably treated by a combination of conventional control techniques including low  $\text{NO}_x$  burners, selective catalytic reduction, and flue gas scrubbing. Effluents from other utility systems, such as blowdowns from steam drums, cooling water systems and polisher regenerates, can normally be handled by neutralization and holding ponds (see AIR POLLUTION CONTROL METHODS).

Federal regulations (72) administered by the EPA establish limitations on the ammonia in aqueous effluents on a site-specific basis. The range of values is 0.05–0.1875 kg of ammonia (as nitrogen) per ton of product on a maximum daily basis; corresponding 30-day average values range from 0.025 to 0.0625 kg ammonia (as nitrogen) per ton of product. Generally, the pH of the effluent must be between 6 and 9.

### Storage, Shipping, and Handling

**Storage.** Anhydrous ammonia is ordinarily stored in refrigerated tanks at the plant site at  $-33.3^\circ\text{C}$  and atmospheric pressure. The need to store large quantities of ammonia results from the seasonal nature of the ammonia fertilizer market. Cylindrical tanks of large (27,000–50,000 t) capacities, either of single-walled or double-walled construction, have been installed in primary market areas (73). So-called double-integrity tanks have been designed having a secondary containment feature for added safety (74). Ammonia evaporating to maintain the necessary low temperatures must be vented. The vented gas is reliquefied for recycle or absorbed in water to make aqua ammonia.

Relatively small quantities of anhydrous ammonia are stored in spherical

**Transportation and Distribution Cost.** Although much ammonia serves as feedstock for other processes, the largest single use in the United States is as a direct application fertilizer without further processing. This direct application consumption is mostly in the farm belt and ammonia produced in the Gulf Coast states is shipped to terminal facilities and then distributed by retail outlets to the farmer.

Ammonia is usually transported for long distances by barge, pipeline, and rail, and for short distances by truck. Factors that govern the type of carrier used in anhydrous ammonia transportation systems are distance, location of plant site in relation to consuming area, availability of transportation equipment, and relative cost of available carriers. Typical costs (83) of pipeline, barge, and rail modes for long distance transport are \$0.0153, \$0.0161, and \$0.0215 per ton per kilometer, respectively, for distances of about 1600 km. Short distance truck transportation costs (83) are much higher. Costs are typically \$0.0365/(t·km) for distances on the order of 160 km.

Because of the nature of the industry, agricultural ammonia consumption is cyclic. During the Spring fertilizer season, about 75% of the dedicated production is sold.

To reduce storage costs involved in such a cyclic consumption pattern, there has been substantial growth in the erection of large refrigerated anhydrous ammonia storage terminals at key points within large marketing areas. Terminal cost (84) is reported to add typically about \$11.00/t.

In the United States most liquid and solid fertilizers are supplied to the farmer by retail fertilizer dealers. Because of the highly seasonal nature of the business, marketing cost can be high. In an effort to spread overhead costs over a broader base, retail dealers diversified into other farm products such as seed, pesticides, and farm equipment. In a study of 47 U.S. Midwestern retail fertilizer firms (1974 financial data) (85), using an average ammonia mark-up cost ranging from about \$47.40/t to \$91.50/t was reported for the least and most profitable firms studied, respectively. Inventory position and supply arrangements were reported to be the most significant factors in affecting profitability.

Ammonia in the world trading markets costs on the order of \$35/t to ship between the United States and Western Europe.

### Specifications and Analysis

Anhydrous and aqua ammonia are manufactured in various grades depending on use. Specifications are given in Tables 14 and 15, respectively.

**Table 14. Anhydrous Ammonia Specifications<sup>a</sup>**

Material content	Commercial or fertilizer grade	Refrigeration grade	Metallurgical grade
ammonia, min wt %	99.5	99.98	99.99
water, max ppm by wt	5000	150	33
oil, max ppm by wt	5	3	2
noncondensable gases, max mL/g		0.2	10

<sup>a</sup>Ref. 31.

**Table 15. Aqua Ammonia Specifications<sup>a</sup>**

Grade	Ammonia, wt %
<i>United States Pharmacopeia</i>	
stronger ammonia water	28-30
ammonia test solution	9.5-10.5
normal (1 N) aqua ammonia	1.7
chemically pure	28
technical, Bé° <sup>b</sup>	
26	29.4
16	10.3
18	14
20	17.75

<sup>a</sup>Refs. 87, 88.<sup>b</sup>Bé° = degree Baumé; specific gravity = 145/(145-Bé°).

Anhydrous ammonia is normally analyzed for moisture, oil, and residue. The ammonia is first evaporated from the sample and the residue tested (86). In most instances, the amount of oil and sediment in the samples are insignificant and the entire residue may be assumed to be water. For more accurate moisture determinations, the ammonia can be dissociated into nitrogen and hydrogen and the dewpoint of the dissociated gas obtained. This procedure works well where the concentration of water is in the ppm range. Where the amount of water is in the range of a few hundredths of a percent, acetic acid and methanol can be added to the residue and a Karl Fischer titration performed to an electrometrically detected end point (89-92).

Oil can be determined by extracting the residue using carbon tetrachloride and then evaporating the CCl<sub>4</sub>. Sediment such as iron is determined by dissolving in hydrochloric acid followed by colorimetric estimation. Dissolved noncondensable gases are determined by analyzing the atmosphere above the liquid ammonia.

Gas streams can be analyzed for ammonia by bubbling a measured quantity of the gas through a boric acid solution to absorb the ammonia. The solution is then titrated against sulfuric acid. This analysis is applicable only if other constituents in the gas stream do not react with boric acid.

Ammonia and ammonium ions in industrial water streams, including wastewater streams, can be determined by either of two methods (ASTM Procedure D1426). In the first, the sample is buffered to a pH of 7.4 and distilled into a solution of boric acid where the ammonia nitrogen is determined colorimetrically with Nessler reagents or titrated using standard sulfuric acid.

The other method is less accurate but more rapid and involves direct Nesslerization of the sample for colorimetric determination. Other colorimetric indicators with more sensitivity, such as indophenol, have been used in place of Nessler's reagent. Ion-selective electrodes have also found use in analysis for trace ammonia (93).

### Health and Safety

Ammonia is a strong local irritant which also has a corrosive effect on the eyes and the membranes of the pulmonary system. Vapor concentrations of 10,000 ppm



are mildly irritating to the skin, whereas 30,000 ppm may cause burns. The physiological effects from inhalation are described in Table 16. Prolonged, intentional exposure to high levels of ammonia is unlikely because its characteristic odor can be detected at levels as low as 1–5 ppm (94). The real danger occurs when escape is impossible, or the exposure victim has lost consciousness.

**Table 16. Physiological Effects of Ammonia<sup>a</sup>**

Concentration, ppm	Effects
20–50	perceptible odor
40–100	eye and respiratory system irritation
400–700	severe eye and respiratory irritation; potential for permanent damage
1,700	convulsive coughing and bronchial spasms; half hour exposure potentially fatal
5,000–10,000	death from suffocation

<sup>a</sup>Ref. 97.

Ammonia is generally not considered to pose a serious fire or explosion hazard. However, although ignition is difficult, it is not impossible as proved by an explosion resulting from a leak in an indoor ammonia refrigeration system (95). Ammonia does not produce unstable or hazardous decomposition products. However, contact with calcium, gold, mercury, silver, or chlorates may result in explosive compounds.

Current OSHA standards specify the threshold limit value (TLV) 8-h exposure to ammonia as 50 ppm (35 mg/m<sup>3</sup>). However, the ACGIH recommends a TLV of 25 ppm (96). Respiratory protection should be provided for workers exposed to ammonia. Protective clothing such as rubber aprons, boots, gloves, and goggles should be worn when handling ammonia.

### Uses

Table 17 gives a breakdown of ammonia uses in the United States for 1986. The primary use is in the fertilizer industry which also determines ammonia demand.

**Fertilizers.** The fertilizer industry constitutes the largest market for ammonia and direct application of anhydrous ammonia represents the largest single consumption. Some of the advantages (98) of anhydrous ammonia are: (1) Having 82% nitrogen, it is the most concentrated nitrogen fertilizer available. (2) It improves soil tilth, increasing the water-holding capacity, and decomposes crop residue and organic matter. (3) It is applied 150–200 mm deep or at plow depth, expanding laterally to form a band measuring about 200 mm wide. Applied in the form of a slug, or mass, this increases the efficiency for great uptake of nitrogen by crop root. It increases the number, size, and strength of crop roots resulting in deeper penetration, greater plant development, and ability to withstand periods of drought. (4) It is easy to apply; it flows under its own pressure from the applicator tank to the soil. (5) It combines with clay and organic matter to resist leaching losses. (6) It can be applied at various times, fall, winter, or spring as a

**Table 17. 1986 Markets for Ammonia in the United States<sup>a</sup>**

Use	Market, %
fertilizer	
direct application	28.7
urea	22.4
ammonium nitrate	15.8
ammonium phosphates	14.6
ammonium sulfate	3.4
nitrogen solutions and mixed fertilizers	0.6
<i>Total</i>	85.5
industrial	
commercial explosives	4.1
fibers-plastics	5.1
<i>Total</i>	9.2
other	5.3

<sup>a</sup>Ref. 31.

pre-plant, or in the summer as a sidedress application. (7) It releases other plant food elements that are present in the soil, such as potassium, phosphorus, calcium, and magnesium.

Ammonia is also the primary building block for downstream manufacturing of a wide range of fertilizer products. Table 18 gives the relative amounts of ammonia used for the manufacture of these nitrogen products.

**Table 18. Ammonia Use for Production of Nitrogen Fertilizers<sup>a</sup>**

Product	Raw material	Raw material used, (ton per ton of product)
urea	ammonia	0.58
nitric acid	ammonia	0.29
ammonium nitrate	ammonia	0.21
	nitric acid	0.77
nitrogen solutions <sup>b</sup>	urea	0.33
	ammonium nitrate	0.41
ammonium sulfate	ammonia	0.27
ammonium phosphate <sup>c</sup>	ammonia	1.29

<sup>a</sup>Ref. 31.<sup>b</sup>Based on UAN-30.<sup>c</sup>Per ton of contained nitrogen.

Ammonia and nitric acid are the two basic ingredients in the manufacture of ammonium nitrate. In addition to consuming ammonia directly, the manufacture of ammonium nitrate consumes ammonia by way of nitric acid production. The largest single use of nitric acid is that of ammonium nitrate production (see AMMONIUM COMPOUNDS). Urea (qv) is manufactured by reacting ammonia and carbon dioxide. Urea manufacturing facilities are often located close to ammonia plants.

Ammonia is consumed in the manufacture of ammonium phosphates and ammonium sulfate by reaction with phosphoric acid and sulfuric acid, respectively. The phosphates may contain ortho- and polyphosphate values. Ammonium sulfate is also a by-product from other ammonia-using industries such as caprolactam (qv) and hydrogen cyanide (see CYANIDES).

Nitrogen solutions consist of fertilizer product combinations, eg, ammonium nitrate-ammonia, urea-ammonium nitrate-ammonia, urea-ammonium nitrate, and urea-ammonia solutions. Mixed fertilizers cover a broad range and can be loosely defined as fertilizers which contain chemically mixed nitrogen, phosphorus, and potassium (N-P-K). Examples are ammonium phosphate-potash mixtures and ammonium phosphate nitrates.

**Industrial.** Nitric acid is itself the starting material for ammonium nitrate, nitroglycerin [55-63-0], trinitrotoluene [118-96-7], nitrocellulose [9004-70-0], and other nitrogen compounds used in the manufacture of explosives (see EXPLOSIVES AND PROPELLANTS). Nitric acid is made by oxidation of ammonia to nitrogen dioxide [10102-44-0] which is subsequently absorbed by water.

Ammonia is used in the fibers and plastic industry as the source of nitrogen for the production of caprolactam, the monomer for nylon 6. Oxidation of propylene with ammonia gives acrylonitrile (qv), used for the manufacture of acrylic fibers, resins, and elastomers. Hexamethylenetetramine (HMTA), produced from ammonia and formaldehyde, is used in the manufacture of phenolic thermosetting resins (see PHENOLIC RESINS). Toluene 2,4-diisocyanate (TDI), employed in the production of polyurethane foam, indirectly consumes ammonia because nitric acid is a raw material in the TDI manufacturing process (see AMINES; ISOCYANATES). Urea, which is produced from ammonia, is used in the manufacture of urea-formaldehyde synthetic resins (see AMINO RESINS). Melamine is produced by polymerization of dicyanodiamine and high pressure, high temperature pyrolysis of urea, both in the presence of ammonia (see CYANAMIDES).

Less importantly, ammonia is used: (1) As a refrigerant in both compression and absorption systems (see REFRIGERATION AND REFRIGERANTS). Ammonia's high latent heat, low vapor density, chemical stability, and low corrosion to iron parts promote its use in large industrial installations. (2) In the pulp and paper industry for the pulping of wood and as a dispersant for casein in the coating of paper (see PAPER; PULP). (3) In the metal industry for detinning of scrap metal, in the extraction of certain metals, eg, copper, nickel, molybdenum, and tungsten from their ores, in metal treating where cracked (dissociated) ammonia is used as a reducing atmosphere for the bright annealing of stainless steels, nickel and its alloys, for the reduction of metal oxides and for the nitriding of steels for case-hardening (see METAL TREATMENTS). (4) As a medium to reduce nitrogen oxides in stack gases. Both catalytic and noncatalytic systems have been developed. (5) As a modifying reagent in the flotation of phosphate ores, and as collecting reagents for the froth flotation of a wide range of minerals. (6) As a corrosion inhibitor at petroleum refineries and natural gas plants and to neutralize the acid constituents of oil, thereby protecting refinery equipment (see CORROSION AND CORROSION INHIBITORS). (7) In the rubber industry for the stabilization of natural and synthetic latex to prevent coagulation during transportation and storage (see RUBBER COMPOUNDING). (8) In the food and beverage industry as a source of

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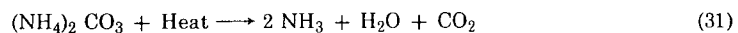
nitrogen required for the growth of yeast and microorganisms and also to control pH in yeast production; as ammoniating agent for glycyrrhizin; as an extractant for bitter principles; and as a source of nitrogen for ruminant feeding when properly combined with molasses (see FEEDS AND FEED ADDITIVES; FERMENTATION; FOODS). (9) As a curing agent in making leather, and as a slime and mold preventative in tanning liquors (see LEATHER), in the manufacture of mothproofing and other protectives agents for furs and hides. (10) In the manufacture of pharmaceuticals, such as sulfanilamide, sulfathiazole, sulfapyridine, and other sulfur drugs (see ANTIBACTERIAL AGENTS, SYNTHETIC; PHARMACEUTICALS); vitamins (qv), antimalarials, methionine and other amino acids (qv); and of dentifrices (qv), lotions, and cosmetics (qv). (11) In the manufacture of household ammonia, detergents, and cleansers. (12) In combination with chlorine to purify industrial and municipal water supplies; and as an oxygen scavenger in treating boiler feedwater. (13) In the manufacture of numerous organic and inorganic chemicals, such as cyanides, amides, aminos, nitrites, and dye intermediates. (14) As a precipitant in uranium concentrate production.

### By-product Ammonia

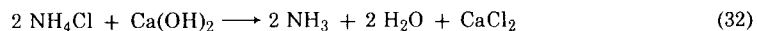
Recovering ammonia as a by-product from other processes accounted for less than 1% of the total U.S. ammonia production in 1987. The principal source of by-product ammonia is from the coking of coal. In the coking operation, about 15–20% of the nitrogen present in the coal is liberated as ammonia and is recovered from the coke oven gas as ammonium sulfate, ammonia liquor, and ammonium phosphates. The recovery product depends on the scrubbing medium employed, sulfuric acid, milk of lime, and phosphoric acid, respectively. Ammonium sulfate recovery by the so-called semidirect process, is most widely employed.

In the semidirect process, (Fig. 23) the raw coke oven gas is cooled to condense tar and ammonia liquor. The heavy layer, tar phase, is pumped to storage and the aqueous layer containing free and fixed ammonia is subsequently processed in a still operation. Free ammonia is that which is in a form which readily dissociates by heat. Fixed ammonia is in a form which requires the presence of an alkali, such as milk of lime, to effect the ammonia release.

Ammonia liquor is fed to the top of the still and heated using steam vapor which dissociates the unstable ammonium salts, eg, ammonium carbonate and ammonium sulfite.



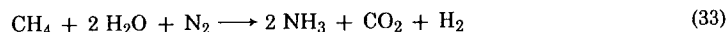
The liquor is then treated with calcium hydroxide (milk of lime) which reacts with the fixed salts, mostly ammonium chloride, to liberate ammonia. The liquor is regenerated in a steam stripping operation.



The gaseous ammonia is passed through electrostatic precipitators for particulate removal and mixed with the cooled gas stream. The combined stream

chemo-nuclear are being explored in the laboratory for fixing nitrogen as ammonia. The economic viability of these processes depends on the ability to scale-up to large capacities, to increase low yields, and to incorporate efficient energy recovery mechanisms.

A novel route to ammonia synthesis using methane, but without first producing hydrogen, has been proposed (101).



A ruthenium-based catalyst is used but low yields resulting from unexpected side reactions are still a problem. Refinement of alternative route ammonia manufacture and advances in genetic engineering, allowing a wider range of plant life to fix nitrogen *in situ*, should provide assurance for long term world food needs.

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# Ammonia

The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competence and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

*Subcommittee on Ammonia*

*Committee on Medical and Biologic  
Effects of Environmental Pollutants*

Division of Medical Sciences  
Assembly of Life Sciences  
National Research Council

1978



**University Park Press**  
Baltimore

# Preface

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In the spring of 1970, the Division of Medical Sciences, National Research Council, entered into a contract with what has since become the Environmental Protection Agency to produce reports that document the available scientific information on the effects of selected environmental pollutants on man, animals, plants, and the ecology of the environment. Since the beginning of this project, a series of reports have been prepared on a variety of pollutants. One of the substances selected for study is ammonia. A subcommittee of the Committee on Medical and Biologic Effects of Environmental Pollutants was formed to study ammonia and met for the first time in July 1975.

Ammonia is a ubiquitous substance and is known widely as a household cleaning agent and as a fertilizer. It plays an important role in the nitrogen cycle—in the life processes and in the death processes. It is both a "friendly" molecule and a hazardous one. This report has the objective of presenting a broad coverage of the available knowledge on ammonia and discusses its physical and chemical properties, the practical methods of measuring it, and the effects of its presence in the environment on man, animals, plants, materials, and the ecology of the environment. The information presented is supported by references to the scientific literature whenever possible or is based on a consensus of the members of the Subcommittee on Ammonia.

In this report, the distinction between ammonium ion ( $\text{NH}_4^+$ ) and ammonia ( $\text{NH}_3$ ) is not made, except where the distinction is specifically important. Thus, the term "ammonia" is used to describe either or both of these molecules; where quantities or concentrations are given, the term "ammonia" designates the sum of  $\text{NH}_4^+$  and  $\text{NH}_3$ .

At the first meeting of the Subcommittee on Ammonia, the chairman, a biochemist, pointed to the novelty of the notion that ammonia might be considered as an environmental pollutant. Ammonia had always been regarded by life scientists as a friendly molecule, as a food rather than a hazard, as essential to life as carbon dioxide, water, and energy. It was wondered whether that attitude would survive the thorough examination of the subject that the Subcommittee was about to undertake.

On the whole, the attitude has survived. Ammonia is an important industrial and agricultural hazard, but not a major pollutant of the environment, with the possible exception of the aspects that will be discussed shortly. We have not recommended establishment of any new environmental standards. The fundamental reason why ammonia is not itself a major pollutant is that mechanisms for taking up ammonia in nature are plentiful and effective. Ammonia is a base, and it will be readily sequestered by ubiquitous acidic substances. In addition, plants and animals have active, efficient, and rapidly operating enzyme systems to trap ammonia and to channel it into metabolic pathways.

Ammonia as a "potential pollutant" occupies an unusual, perhaps unique, niche. It may sometimes be a deleterious byproduct of current civilization, but it is also the stuff of life itself. The amount of life that the earth can support is determined by how much nitrogen, usually in the form of ammonia, can be made available. This is emphatically true of human populations. The apparent question of whether food energy (expressed as calories) or nitrogen (expressed as protein) is limiting to the nutrition of the human population is not really a question. In general, populations subject to famine eat simple diets, and the staple food determines both the caloric and the protein intake. The protein content of the

cereal or tuber determines the protein content of the diet, and the amount of plant grown is, in turn, often determined by the availability of soil nitrogen. If the crop fails, both calories and protein will become insufficient, and deprivation of one will exaggerate the effects of deprivation of the other. If the world will have more people, it must have more ammonia, not less. In recognition of this basic truth, the 1977 report, "World Food and Nutrition Study," of the National Research Council has recommended a high priority for research to improve the sources of nitrogen fertilizer, stressing particularly the need for research to increase biologic nitrogen fixation in seed and forage legumes, cereals, and other grasses.

Questions have recently been raised about possible ill effects of rapid increases in the use of fertilizer, be it synthetic ammonia or ammonia formed by biologic processes. It has been suggested that, after cycling, nitrous oxide formed by bacterial denitrification will increase and will deplete the ozone of the upper atmosphere. The Subcommittee did not come to grips with that question, but this report notes that the data are not sufficient to quantify or locate nitrous oxide formed or to assess the potential effects of increased fertilizer application on the magnitude of the process. Our response to this problem was set in part by Subcommittee boundaries and by the fact that the various valence states of nitrogen are in a dynamic relationship with each other. Should the fertilizer-ozone question be addressed by panels on ammonia, on nitrates, on "NO<sub>x</sub>," on ozone, or on what? The nitrogen atom defies administrative categorization. Perhaps the best approach is to convene a group of scientists carefully selected for appropriate expertise and instructed to deal specifically with the question of fertilizer and ozone.

However, the Subcommittee cannot ignore what it has learned of the societal context within which ammonia is made and used. This context will be highly pertinent to the question of the importance to be assigned to the fertilizer-ozone relationship. We have learned that ammonia is expensive to make, in both money and energy. In a world that is short of both, ammonia will be applied not randomly, but to areas where it can best be converted into food for human consumption. Any projection of the effect of fertilizer application on ozone must be made within the context of that assumption.

There is yet another assumption that must be taken into account: if there is much more fertilizer and much more food, there will be many more humans. These humans will compete for space and resources; within the context of the enormous problems of the increased human population that would accompany increased fertilizer use, how does one assess the importance of ozone depletion and of skin cancer that may arise from increased ultraviolet radiation? Should one wear long sleeves and a broad-brimmed hat and at the same time eat more protein and have more children? Would all societies give the same answers to those questions? These considerations may be beyond the purview of the Subcommittee on Ammonia, but we feel it our duty to call attention again to the boundless complexities of environmental interrelationships.

Finally, we call attention to suggestions that production of ammonia and fertilizer may have a directly beneficial, rather than a deleterious, effect on the atmosphere. It is now generally agreed that the provision of extra nitrogen enhances the ability of plants to absorb atmospheric carbon dioxide and fix it into photosynthetic products. If the carbon dioxide in the atmosphere is indeed increasing with the massive recent use of fossil fuels, and if increased atmospheric carbon dioxide, via a "greenhouse effect," causes an increase in the world's temperature, then perhaps the action of ammonia and ammonia-derived fertilizer in sequestering this carbon dioxide would be a useful counterbalance.

The Subcommittee has attempted to restrain itself in making recommendations, but it has made some that urge the acquisition of information of broad environmental importance and others that are in more specialized subjects or that deal with environmental problems considered less likely to represent hazards. There are many unanswered ammonia-related questions, including those raised about nitrous oxide, ozone, carbon dioxide, nitrosamine (formed from amines that generally accompany ammonia emission), and radiative climatic effects of ammonium-containing aerosols. The most important recommendation is simple and obvious: one should monitor. No amount of predictive theory can substitute for the continuous and intelligent analysis of the atmosphere for such materials as nitrous oxide, carbon dioxide, and ozone, to see whether the changes predicted by theory are actually occurring and to see whether alarm is necessary. Inappropriate complacency can be disastrous, and excessive alarm can be fearfully expensive.

hydroxide corrodes glass slowly, but this effect is insufficient to preclude recommendation for use of glass with ammonia solutions.

Most plastics resist ammonia and ammonium hydroxide corrosion. Exceptions are epoxy fiberglass, nylon, and polyvinylchloride, which deteriorate under some conditions of temperature and concentration.

## 9

### Summary

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#### CHEMICAL INTERACTIONS: TRANSFORMATIONS AND TRANSPORT MECHANISMS

Ammonia is the first inorganic nitrogen compound resulting from the degradation of plant and animal tissues and is a central and active participant in the nitrogen cycle. In the soil (and in seawater), it is oxidized to nitrate by "nitrifying" microorganisms as the energy source. The nitrate thus produced is again taken up by plants and is reduced to the level of ammonium nitrogen, which is incorporated into protein and other nitrogenous compounds, completing this portion of the nitrogen cycle.

Nitrate ion can also serve as an oxidant for other microorganisms (in the absence of available oxygen) in the metabolism of organic compounds, resulting in the production of nitrogen gas and nitrous oxide, which are released to the atmosphere. This could result in the delivery of essentially all available nitrogen to the atmosphere as nitrogen gas, were it not for the processes (largely biologic) of "nitrogen fixation," whereby the relatively inert nitrogen gas is again converted to combined nitrogen usable by plants or microorganisms. This constitutes another feature of the nitrogen cycle—operating much more slowly (because of the large nitrogen pool) than the comparatively rapid transport from soil to plant and back to soil.

The assimilation of nitrogen by plants has two principal features: the uptake of nitrate by roots and the reduction of nitrate to ammonium or amino nitrogen, which is incorporated into plant tissues. Plants can also utilize ammonia directly, but, because it is rapidly nitrified in the soil, the more common soil form is nitrate. Nitrate assimilation requires energy that is provided directly or indirectly by photosynthesis.

Nitrogen fixation also requires energy and is carried on by a limited number of microorganisms, sometimes in symbiotic association with higher plants or fungi. Nitrogen fixation need not require large amounts of energy from a thermodynamic standpoint, but in practice it does. Much of this energy is expended in splitting the nitrogen molecule.

Although it has now been shown to be possible to insert nitrogen-fixing (nif) genes into several types of organisms, the production thereby of an enzyme that is viable and functional in the organism under normal field conditions has not yet been achieved. Of the many obstacles

involved, the requirement of an anaerobic microenvironment for nitroreductase appears to be the most immediate. Thus, although the possibilities for this approach are attractive and exciting in principle, the problem is far from solved.

In plants, nitrogen is generally transported into cells in the form of nitrate from the soil: it is reduced to nitrite by the enzyme nitrate reductase. Nitrite is then reduced to the ammonia level of oxidation by a single enzyme, nitrite reductase. The ammonia formed is available for further assimilation.

Ammonia is an active metabolite, central in both the biosynthesis and the degradation of amino acids. It is fixed into organic linkage by reactions with appropriate acceptors, to form glutamic acid, glutamine, carbamyl phosphate, and, to a lesser extent, other compounds. This ammonia-derived nitrogen can enter a variety of biologic pathways; the amino nitrogen of amino acids arises from ammonia via the combined reactions of glutamic dehydrogenase plus transaminase. The equilibrium constants of the reactions catalyzed by glutamic dehydrogenase, glutamine synthetase, and carbamyl phosphate synthetase dictate that the concentration of free ammonia in animal tissues must be low, and these three enzymes are therefore of major importance in the detoxification of either exogenous or metabolically generated ammonia. Capacity to assimilate ammonia in living systems is high; glutamine synthesis and degradation are particularly rapid processes, and glutamine serves as a labile "pool" for the trapping and release of ammonia.

In amino acid degradation, ammonia is formed by the combined action of transaminases and glutamic dehydrogenase. In the various species of animals, this nitrogen is then excreted either as free ammonia (in fishes), as uric acid (in birds and reptiles), or as urea (in mammals and some other animals). Thus, ammonia is a central intermediate in both the biosynthetic and the degradative pathways of amino acids, which are the subunits of proteins.

Transport of ammonia across cellular membranes is rapid and efficient. Unionized ammonia readily traverses cell membranes, but recent evidence indicates that ammonium ions are transported by an enzyme—a sodium-potassium-dependent ATPase.

Ammonia is present in the atmosphere as a result of natural and anthropogenic emission. There is no known chemical reaction by which ammonia is produced in the atmosphere. Chemical reactions relevant to the atmospheric transformations of ammonia can be divided into four groups: aqueous-phase, heterogeneous, thermal, and photochemical reactions.

Ammonia contributes to the formation of atmospheric aerosols. It reacts with acids formed from oxides of sulfur and nitrogen. Sulfur

dioxide is further oxidized in the presence of ammonia, forming aerosols of ammonium sulfate. Aerosol formation increases substantially at high relative humidity, high ammonia concentrations, and low temperature. Although the complex reaction mechanism involved seems to be adequately described, there is considerable discrepancy in the reported sulfur dioxide oxidation rates, which range from 2 to 13%/hr.

Reaction of ammonia with soot particles results in the heterogeneous formation of particulate ammonium complexes. The atmospheric significance of this reaction in the polluted troposphere remains to be established.

Thermal reaction between ammonia and sulfur dioxide leads to the formation of the condensable products amidosulfurous acid and ammonium amidosulfite, which may undergo heteromolecular nucleation. More definitive studies conducted at atmospheric ammonia and sulfur dioxide concentrations (i.e., parts per billion) are needed to assess the possible importance of the ammonia-sulfur dioxide thermal reaction in the formation of ammonium sulfate aerosols in the troposphere. The studies of Hecklen and co-workers suggest that thermal reactions of ammonia with ozone and with nitric acid to form ammonium nitrate particles are not significant causes of ozone depletion, in that the former is at least second-order and should proceed at substantial rates only at ammonia and ozone concentrations much higher than those found in the atmosphere.

Two photochemical reactions, the photolytic dissociation of ammonia (which prevails in the stratosphere) and the reaction with the hydroxyl radical in the troposphere, are of major importance for atmospheric removal of ammonia. The latter reaction controls the half-life of ammonia, which is about 16 days in the unpolluted troposphere and certainly shorter in photochemically polluted areas. Both photolytic dissociation and reaction with hydroxyl radical produce the amino radical, whose further reactions in the atmosphere are poorly understood. Kinetic and mechanistic studies are needed to establish whether ammonia oxidation results in a significant source or sink for nitric oxide in the troposphere.

There is only limited information on the relative importance of the various reactions reviewed here in the global atmospheric ammonia budget. It has been reported that about half the atmospheric ammonia is destroyed by reaction with the hydroxyl radical, the other half being accounted for by heterogeneous removal processes, dry deposition of ammonia, and washout as particulate ammonium.

The biochemical and geochemical mechanisms of transformation of the nitrogen atom in natural waters through its various valence states have been described. Quantitative descriptions of the rates and extents

("budgets") of these processes are sparse. Thus, nitrogen budgets for natural waters based on closely spaced measurements of inputs, dynamics, and outputs are not available.

Reservoirs that impound natural waters will influence the concentration and distribution of ammonia through curtailment of mixing processes and stratification of the water column. Populations of nitrifying bacteria may be expected to increase in such environments. These processes will alter the pattern of nitrogen cycling in the previously free-flowing natural waters.

The transfer of nitrogen in the coastal wetlands is poorly understood, and little information is available. An accurate assessment of nitrogen exchanges will be required to establish the flux into the atmosphere from the nitrogen-limited coastal waters.

Models are available for geographic mapping of the seasonal variations in the concentration of dissolved ammonia or ammonium in precipitation and surface waters. The available data sets for many of the regional distribution patterns are too sparse for quantitative purposes.

#### SOURCES, CONCENTRATIONS, AND SINKS

##### Production and Use

In 1975,  $14.3 \times 10^6$  t of ammonia was produced in the United States, almost all by the fixation of atmospheric nitrogen. About 1% of the total came from the carbonization of coal. Ammonia is the source of nitrogen in fertilizer and of the chemical nitrogen added to animal feed, and it is used widely in the chemical industry.

Industrial fixation of atmospheric nitrogen began before World War I, and methods were developed for the production of nitrates from ammonia. Synthetic ammonia began to replace imported Chilean saltpeter as a nitrogen source late in the 1920s; by 1930, annual ammonia production was 177,000 t. Production capacity was significantly increased during World War II, when there was a great need for nitrates to make munitions. Ammonia from the wartime plants went into fertilizers when hostilities ceased. Since 1962, the average annual increase in ammonia production has been 8.5%, and continuing increase is expected to meet growing food requirements.

The conversion of nitrogen to ammonia requires both energy and the hydrogen atom. Natural gas is currently the feedstock and fuel in ammonia production in the United States. Significant improvements have been made in the production process, and most of the improvements have resulted in decreased energy consumption. About  $9.6 \times 10^6$  kcal of energy are required to produce a tonne of ammonia. Emission of

ammonia from the production process was also decreased by technological improvements. Total annual emission of ammonia during manufacture of the chemical is estimated to be 19,300 t.

The natural-gas shortage has resulted in a search for alternative fuels for feedstock and for process heat. Vaporized fuel oil can be used in the reformer, and this will reduce the natural-gas requirement by about one-third. A suitable alternative fuel for use as a feedstock has not been developed.

An aqueous effluent at ammonia plants results from the condensation of steam from the process gas stream. The effluent contains ammonia and methanol and must be treated to avoid water pollution. The effluent is normally treated by steam stripping, which causes ammonia and methanol to be emitted into the air. Methods should be developed to recycle and to utilize the water and ammonia waste.

About 300,000 t of ammonia are emitted per year during the production and use of fertilizers, industrial chemicals, and the nitrogen products. One of the uses—direct application of ammonia to soil as fertilizer—results in the emission of about 168,000 t/year. Techniques should be developed to minimize these losses.

##### Volatilization from Cattle Feedlots and Animal Wastes

Recent trends in livestock production in the United States have resulted in large concentrated feedlots, in contrast with the small individual farms of a few years ago. This marked increase in the confinement feeding of animals in relatively small areas has resulted in waste disposal problems and point sources of various odors and ammonia volatilization. Several workers have demonstrated that significant amounts of ammonia are volatilized from the surface of feedlots, as well as from soil surfaces on which animal waste has been applied. The atmospheric ammonia content is much higher in and around the feedlots than in other areas. The major source of the volatilized ammonia appears to be urinary urea, which is readily hydrolyzed by urease to ammonia and carbon dioxide.

The odors normally associated with feedlot areas have been shown to be due to volatile amines. Owing to the alkalinity of the soil surface in these areas, the formation of nitrosamines from these volatile amines seems highly improbable.

The ammonia that is volatilized from the feedlot and soil surfaces does not appear to be totally lost. Atmospheric ammonia has been shown to be absorbed from air by water surfaces in the vicinity of feedlots. In addition, a significant amount of the ammonia appears to be removed from the air by green plants. Atmospheric ammonia appears to enter into metabolism in the same way as ammonium ions—i.e., absorbed through roots or produced by nitrate reduction in plant cells.

### Atmospheric Sources and Concentrations

Because of their high concentrations in polluted air and their accumulation in the respirable range, particles containing ammonium and the associated anions, nitrate and sulfate, must be evaluated as a potential health hazard to human populations in urban areas. These particles can contribute significantly to the reduction of visibility. Furthermore, particulate ammonium sulfate and nitrate compounds may affect the radiative climate of the earth and are directly involved in acid rain precipitation. Despite these potentially important effects, ammonium particles have received more limited attention than other substances in air pollution research.

Although most atmospheric ammonia is produced by natural biologic processes, anthropogenic sources of ammonia—such as combustion and industrial processes, feedlot operations, production and use of fertilizers, and automobile exhaust—account for the observed substantial increase in gaseous ammonia and particulate ammonium concentrations in urban atmospheres.

Studies conducted in pollution-free areas (such as coastal, maritime, desert, and mountain sites) all indicate a background ammonia concentration of a few micrograms per cubic meter. The fact that bacterial activity is the major source of ammonia production is reflected in the temperature dependence of seasonal variation (summer > winter) and geographic variations (tropical > temperature zone) in ammonia, as well as in its vertical concentration gradient in the troposphere.

Ammonia concentrations of up to about  $300 \mu\text{g}/\text{m}^3$  have been measured in the vicinity of various types of anthropogenic sources. Ammonia in industrial and urban areas and far downwind in urban plumes often reaches concentrations 5–10 times higher than “background” values that are typical of unpolluted regions and exhibits opposite seasonal variations, with a winter maximum that reflects the increased contribution of combustion processes.

Particulate ammonium is a major constituent of tropospheric aerosols, in which it exists as ammonium nitrate, in various combinations with sulfate ions (ammonium sulfate,  $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$ , ammonium bisulfate, and possibly other intermediate combinations of these salts), and in traces of ammonium halides (ammonium chloride and ammonium bromide). Measurements conducted at unpolluted sites and vertical distribution profiles in the troposphere indicate a background ammonium concentration of about  $1 \mu\text{g}/\text{m}^3$ .

Particulate ammonium concentrations of up to about  $35 \mu\text{g}/\text{m}^3$  (24-hr averaged concentrations) have been measured in polluted areas, where most ammonium associated with nitrate and sulfate accumulates in particles smaller than  $1 \mu\text{m}$  in diameter. Sulfate- and ammonium-containing

particles account for a major fraction of the total particulate burden in the atmosphere of northern Europe and the eastern United States, whereas high ammonium nitrate concentrations are encountered in photochemically polluted atmospheres, such as in southern California.

### Plant Ammonia Fixation

Because more nitrogen is being fixed for agricultural enterprise, more ammonia may be leaking into the air. However, plant life on the land and perhaps in the oceans has a great capacity to absorb ammonia from the air. Available data show that land plants might complement their supply of nitrogen by  $10 \text{ kg}/\text{ha}\text{-year}$  through ammonia absorption at today's ambient concentrations. Unfortunately, ammonia in the form of aerosols, although known to be increasing in the terrestrial environment and recently recognized in the marine environment, has not been adequately evaluated or even distinguished from the gaseous form in many atmospheric analyses. This raises questions about sources and sinks and about the process involved.

Micrometeorologic methods of measuring ammonia gas coming and going at the earth's surface have recently been used to determine the roles of soil, plants, and animal manure as sources and sinks. More ammonia may be coming from the soil or detritus on the soil surface and being absorbed by vegetation growing above ground than previously recognized. The latter is a daytime phenomenon, inasmuch as ammonia gas is absorbed through leaf stomata that open only in daylight. These amounts are small compared with those needed for agricultural crops; however, they could be a significant source for natural ecosystems when the nitrogen available for plant growth is limited. Under these conditions, ammonia uptake from the air plays a role in damping the carbon dioxide buildup in the atmosphere through storage of more carbon in the biosphere. Wet and dry deposition of ammonium aerosols on plants could provide a pathway for plant absorption through the leaf cuticle during both day and night. Little is known about this phenomenon.

The fixation of nitrogen is probably increasing, thus leading to the leakage of more gaseous ammonia to the air, but the land plant capacity to absorb and use the nitrogen will undoubtedly prevent any significant increase in ammonia in the ambient atmosphere on a global scale. The status of ammonium aerosols is much less understood. Whether or not and how plants absorb ammonia through dry or wet deposition of aerosols is unknown.

### Oceans

Ammonia is the preferred nitrogen source for phytoplankton. Nitrogen availability frequently is the critical limiting factor in plant growth in both near-shore and open-ocean water. Organic-rich coastal sediment is



an important, but unmeasured, source of regenerated ammonia for near-shore waters.

Ammonia regeneration in the water column plays an important role in the nitrogen dynamics of the entire spectrum of marine systems. Sewage and agricultural nitrogen emission can play an important role in the nitrogen dynamics of near-shore water. Assessments of ammonia or other nitrogen input and concentrations in the coastal zone must take note, not only of the concentrations in the water, but also of the fact that organisms rapidly react to new input of nitrogen by banking it in the form of standing stocks. The population expansions are often represented by undesirable organisms capable of rapid growth.

Nitrogen exchanges between the ocean and the atmosphere are difficult to measure and are poorly understood; however, the ocean does not appear to be a significant source of either particulate or gaseous ammonia.

Atmospheric ammonia concentrations are higher over the land than over the oceans. A quantitative assessment of the global nitrogen cycle will require more accurate estimates of air-sea and sediment-water exchanges of nitrogen compounds, in addition to further work on chemical transformations within the water column.

## TOXICOLOGY

### Ammonia Toxicology in General

The intravenous or intraperitoneal toxicity of several ammonium compounds has been determined in various species, including mice, rats, chickens, and fishes. The toxic syndrome appears to be the same in all species studied and may be characterized by hyperventilation and clonic convulsions, followed by a graduate onset of coma, with death occurring during a tonic extensor convulsion. The survivors also had hyperventilation, clonic convulsions, hyperirritability, and coma for about 20–45 min; complete recovery was usually observed in 50–60 min.

Ammonium salts are more toxic at relatively alkaline, rather than relatively acid, pH. This difference appears to be due to the ability of ammonia to cross membranes more readily and thus produce the toxic effect. Hypothermia has been shown to protect animals against ammonia toxicity, whereas hyperthermia potentiates it. Hypoxia has also been shown to increase ammonia toxicity in mice. Death during ammonia toxicosis has been attributed to a direct effect of ammonia on the heart and a more generalized effect on the brain.

Comparative studies have shown that the intraperitoneal  $LD_{50}$  values for ammonium acetate are the same in mice (a ureotelic species) and chicks (a uricotelic species) but higher in selected fishes (ammonotelic species).

### Urea and Ammonia Toxicity in Ruminants

Urea is a valuable source of nonprotein nitrogen that is extensively used in ruminant nutrition. The amount of urea that can be used in the diet is limited by its toxicity. The urea toxicity syndrome is characterized by restlessness, ataxia, dyspnea, collapse, muscle spasm, tetany, and death. The toxic effects of urea in ruminants are due to ammonia toxicity. The ammonia is released by the action of bacterial urease in the rumen. When the ammonia is released too rapidly to be utilized in the synthesis of bacterial protein, it is absorbed through the ruminal epithelium; if it exceeds the detoxification capacity of the animal, it becomes toxic. Toxic signs are observed at a blood ammonia nitrogen concentration of 1 mg/100 ml; death occurs at 2 mg/100 ml.

### Ammonia Toxicity in Fishes

Several environmental factors have been shown to affect the toxicity of ammonia in fishes. The major factors are the pH and temperature of the water; these govern the concentration of unionized ammonia in solution. The unionized ammonia appears to be the toxic form of ammonia, in that relatively high concentrations of ammonium ions do not appear to be toxic. Several reports have appeared in which the water pH or temperature was not recorded; these reports are of little benefit in establishing guidelines concerning safe ammonia concentrations for various fishes. A concentration of 0.024 mg/liter has been suggested as the highest concentration of unionized ammonia that will not cause adverse effects on fishes. This value is based on sketchy data and cannot yet be considered as authoritative.

Several laboratory experiments of relatively short duration have demonstrated that the lethal concentration of ammonia for a variety of fish species is 0.2–2.0 mg/liter. Rainbow trout appear to be the most sensitive, and carp the most resistant to aqueous ammonia. The report that gave 24-hr ammonia TLM values of 0.068 mg/liter for fry and 0.097 mg/liter for adult trout seems questionable because these concentrations are about one-tenth those reported elsewhere. Sublethal exposure to ammonia has been reported to cause adverse physiologic and histopathologic effects in fishes.

Anydrous ammonia has been used experimentally in fishery management for simultaneous control of fish populations, control of submerged vegetation, and fertilization.

### Ammonia Associated with Confined Housing of Domestic Animals

A problem that has been encountered in confined housing of domestic livestock is the accumulation of atmospheric ammonia due to bacterial decomposition of animal waste and poor ventilation. In most cases, this problem can readily be avoided by proper management. Atmospheric

ammonia at 20–50 ppm has been shown to result in reduced feed consumption, reduced weight gain, airsacculitis, increased susceptibility to respiratory diseases, and a general discomfort in poultry. Higher concentrations, 60–100 ppm, were found to result in reduced egg production, tracheitis, and keratoconjunctivitis in poultry.

Atmospheric ammonia does not appear to be a problem in most commercial confined swine or cattle operations, at least in the United States. Laboratory studies have indicated that atmospheric ammonia in excess of 100 ppm will result in reduced growth rate of swine. However, this is about 10 times the concentration normally encountered in properly managed swine operations. Ammonia, with other manure gases, has been reported as the cause of reduced growth rate and death of young cattle in several confined units in Sweden and other parts of Europe. Again, this problem appears to be due to improper management.

Anhydrous ammonia has been used to exterminate wild birds and mice in farm buildings. This technique has been recommended because of its low cost, ease of application, and lack of persistent residue.

### Bats

Some species of bats that roost in caves in the southwest United States have been found to have a very high tolerance to atmospheric ammonia. The bats have apparently adapted to the high concentrations of atmospheric ammonia that result from decaying feces in the caves. Atmospheric ammonia ranged from 85 to 1,850 ppm in some of the caves. These concentrations did not appear to have any adverse physiologic effects on the bats.

### Animal Toxicology (Gaseous Ammonia)

There have been few studies of animal exposure to gaseous ammonia, and most have consisted of gross observations of animal response and mortality rate.

There appears to be species and individual susceptibility to the effects of acute exposure to toxic concentrations of ammonia. Increasing concentration or duration of exposure results in progressive injury and increasing mortality among exposed animals. Mice appear to be more sensitive than guinea pigs, which are more sensitive than rabbits, to acute toxic exposure to ammonia gas.

As much as 95% of inhaled ammonia is absorbed onto the mucous membranes of the naso-oro-pharynx. This protects the tracheobronchial tree but not the terminal airways and alveoli. The tissue of the terminal airways appears to be more sensitive to the effects of ammonia than the remainder of the tracheobronchial tree.

The subacute or chronic exposure of animals to ammonia at less than 300 ppm in inspired air does not appear to produce light micro-

scopic changes in the lung. In contrast, concentrations greater than 600 ppm resulted in a high mortality rate, with evidence of focal and diffuse interstitial pulmonary inflammation in all animals studied.

Direct exposure of the trachea to ammonia at less than 100 ppm appears to have no effect on ciliary activity. Because 95% of ammonia inhaled has been shown to be absorbed by the naso-oro-pharynx, it would require exposure to approximately 2,000 ppm to produce 100 ppm at the trachea in the intact animal—the concentration necessary to affect tracheal ciliary activity. In contrast, the inhalation of approximately 1–10% of that concentration (25–250 ppm)—i.e., approximately 1.0–12 ppm at the trachea—has been shown to increase the infection rate and severity when exposed chicks or rats were inoculated with virus or mycoplasma. Thus, the effect of ammonia on ciliary activity of the tracheobronchial tree does not appear to be a factor in the apparent increased susceptibility to infection that was noted in a few studies of such exposure to low concentrations of ammonia.

Although industrial (chronic) and accidental (acute) exposure of humans to ammonia fumes often occurs in association with exposure to other potentially toxic gases—e.g., nitrogen oxides, carbon monoxide, sulfur dioxide, and hydrogen sulfide—animal studies on the effects of such exposure are rare.

### Cerebral Effects of Ammonia Intoxication

Several possible mechanisms have been presented to explain the cerebral effects observed during ammonia intoxication. The following biochemical factors have been suggested to be responsible for the neurotoxicity of ammonia:

1. Impaired oxidative decarboxylation of pyruvic acid.
2. Slowing of electron chain generation of ATP by NADH depletion.
3. Depletion of  $\alpha$ -ketoglutarate.
4. Utilization of ATP and glutamate in glutamine formation.
5. Stimulation of membrane ATPase.
6. Decreased synthesis of acetylcholine.

In general, all these mechanisms postulate an eventual decrease in available cerebral energy, ultimately in the form of ATP, or a depletion of citric acid-cycle intermediates. The brain stem seems most susceptible to this depletion.

### Protective Agents against Ammonia Toxicity

Many compounds have been studied as possible protective agents against ammonia intoxication. The most effective compounds in mammals are substrates of the urea cycle: arginine, ornithine, and citrulline. A mixture of ornithine and aspartic acid is also very effective. These compounds,

when administered intraperitoneally 1 hr before an intraperitoneal injection of the LD<sub>50</sub> of ammonium acetate, gave total protection. The mechanism whereby these compounds exert their protective effects is postulated to be the stimulation of urea synthesis. The most effective agents are the urea-cycle intermediates.

Glycine and a mixture of glucose and glycine exert a similar protective effect against ammonia intoxication in chicks but no comparable effect in mice. These compounds exert their protective effect through increased synthesis of uric acid, the end product of nitrogen metabolism in birds.

#### HUMAN HEALTH EFFECTS

With ever-increasing industrialization and use of fertilizer, one may expect increasing exposure of the population in work areas and the community to ammonia. The acute toxic effects of ammonia are well defined and include irritation of the eyes, skin, and respiratory tract.

Liquid ammonia and solutions of ammonia are important causes of severe alkali burns of the eye. Because of its lipid solubility, ammonia penetrates the intact cornea more easily than other alkalis and therefore causes deeper damage. A pH greater than 11.5 is thought to be necessary for significant tissue destruction. Severe alkali burns cause corneal ulcerations, with a tendency toward recurrence and perforation if untreated. Complications associated with severe alkali burns include symblepharon, corneal neovascularization, secondary glaucoma, cataract, dry eye, and phthisis.

The prognosis for severe alkali burns of the eye is directly related to the amount of limbal ischemia. Irrigation with water or saline is effective treatment only if begun within 5 sec of injury; the important factor is the rapidity with which eye irrigation is begun rather than the duration of irrigation or the type of irrigant used.

The role of collagenase in stromal ulceration and the importance of the epithelium both preoperatively and postoperatively for eyes with severe alkali burns have come to be understood only in the past few years. With this understanding have come new therapeutic approaches, both medical and surgical, that promise visual rehabilitation of a substantial proportion of eyes with severe alkali burns.

Exposure to high concentrations of ammonia may result in third-degree skin burns and death from respiratory injury. Chronic eye and skin changes secondary to acute toxic exposure to ammonia are well described. Late respiratory tract sequelae are uncommon, even after nearly fatal acute pulmonary changes. However, the limited number of patients so examined and the relative insensitivity of the tests performed to detect alternations in lung function make it difficult to be certain of

the true incidence and type of chronic lung changes that follow such exposure. The results of the few studies of human inhalation of ammonia at low or moderate concentrations for 5 min to 8 hr are conflicting and suggest that brief exposure (5–30 min) to 30–560 ppm has little effect other than mild eye and upper respiratory tract irritation. Longer exposure—4–8 hr at 560 and 20 ppm, respectively—may induce metabolic changes. Certainly more such studies are warranted. The three studies that suggested a possible relationship of ammonia exposure and cancer need verification. It is apparent that environmental air standards for work areas are based on a paucity of data mostly from poorly controlled studies. The recommended TLV is an arbitrary value designed to eliminate most complaints of irritation of the eyes and upper respiratory tract. Empirically, it appears that the TLV for ammonia of 35 ppm (25 mg/m<sup>3</sup>) would result in no health hazard to workers. However, this needs verification with well-designed epidemiologic studies.

There is little information on concentrations of ammonia encountered in the workplace or on the farm. What is available suggests that such ammonia is not a problem—if the current TLVs are truly safe over a work-life exposure. Finally, there is even less information on the effects of ammonia encountered in the urban environment on the general population.

# 10

## Recommendations

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It is easy to make recommendations, particularly for research. If all recommendations of all committees were given equal priority, nothing would happen. We have therefore placed our recommendations into two categories; the more urgent of these are printed in italics. The word "urgent" is used in a special sense: italicized recommendations are those of broad current importance as well as those that deal with subjects in which there is substantial public interest. In addition, italics are used for recommendations that involve important questions or uncertainties about potential health or environmental effects. The nonitalicized recommendations are not less real, but they encompass narrower subjects, and those with primary interest in them may be groups, individuals, or agencies with objectives different from those of the Environmental Protection Agency. Other broad environmental recommendations are nonitalicized because the Subcommittee feels that although the questions raised are of interest, the environmental problems addressed are of less immediate public importance.

To illustrate: sections on the nitrogen cycle and denitrification are italicized because there is at the moment a public question of whether or not fertilizer application, followed by denitrification, leads to ozone depletion. A definitive answer cannot yet be given, so relatively high priority is attached to acquiring information on the subject. However, although studies of the inflammatory response to ammonia burns of the eye are of great importance to both patient and doctor, they are of less general public interest and are perhaps better addressed by more specialized agencies.

### NITROGEN CYCLE

*The evaluation of the interrelationship of ammonia and ammonium relative to other components and processes in the nitrogen cycle necessitates more quantitative information on a number of processes and reactions. Particular needs are:*

1. *Global figures on nitrogen fixation by all biologic and other processes in terrestrial and oceanic environments.*
2. *Estimation of the amount of ammonia produced and volatilized from tidal areas, estuaries, and marshland.*

3. *Determination of the comparative significance of nitrification and denitrification as sources of nitrous oxide on land and in the sea.*
4. *Accurate estimates of the emission, movement, and degradation of ammonia in the atmosphere.*

#### GENETIC MANIPULATION OF PLANTS FOR NITROGEN FIXATION

*Research in genetic manipulation of plants to insert nitrogen-fixing genes should continue to be pursued actively, although success is by no means ensured. In addition, the survey of existing species should continue: some strains of Rhizobium compete better in a particular soil than other strains. Understanding the basis of soil-plant interaction would improve chances for the development of more useful agricultural strains. Thousands of different species of legumes grow wild around the world. It is important that these be screened to determine their value for food and for enriching poor soils.*

#### DENITRIFICATION

*Additional information is needed regarding denitrification. This process can result, ultimately, in the production of nitrous oxide from nitrogen fertilizer. Atmospheric nitrous oxide concentrations should be monitored, and field, aquatic, and waste-disposal sources should be evaluated as nitrous oxide sources. The rates of natural processes of nitrous oxide production and destruction should be better assessed.*

#### ATMOSPHERIC TRANSFORMATIONS

Several subjects should be explored further to improve our understanding of the physical and chemical transformations of ammonia in the atmosphere. More specifically, the following studies are recommended:

1. *Kinetic and mechanistic studies of the ammonia-nitric oxide-oxygen system should be directed to establishing whether destruction of ammonia in the atmosphere represents a source of nitric oxide or a sink for nitric oxide. The rate constants for the reaction of the amino radical with oxygen and nitric oxide should be established.*
2. *To understand better the formation and fate of acid rain and of ammonia-containing particles, the dynamics of ammonia gas-to-particle conversion processes should be further investigated. This would require field measurements of aerosol and particulate concentrations and study of the thermodynamics and physics of aerosols.*

3. *The processes for the removal of ammonia from the troposphere should be better described. These processes include reactions of gaseous ammonia with receptors and washout as particular ammonium-containing materials.*
4. *Global nitrogen budgets for the troposphere should be refined to include a broad spectrum of often-neglected nitrogen compounds.*

#### WATER

The capability of monitoring ammonia in surface and ground waters in the United States is inadequate for obtaining good descriptions of ammonia concentrations in various regions. Such information should be obtained, mapped (with available computer mapping techniques), and utilized in combination with mapping of rainfall data, to show nationwide trends in ammonia concentrations.

The growth of organisms in coastal waters is nitrogen-limited. A knowledge of nitrogen budgets in wetland areas would improve our understanding of life in coastal waters.

Reservoirs can cause stratification of ammonia concentrations in surface waters. The effect of this phenomenon on plants, animals, and nitrifying bacteria should be assessed.

#### PRODUCTION AND USES OF AMMONIA

*Ammonia production requires a source of energy and of hydrogen. Natural gas can furnish both and can be both a fuel and a feedstock. The shortage of natural gas has led to studies of alternative feedstocks for ammonia production. It is recommended that priority be given to a search for potential feedstocks that will minimize pollution problems or safety hazards during ammonia production and that will permit industry to meet pollution abatement and safety standards with relatively low capital investment. Naphtha and electrolytic hydrogen are feedstocks that create environmental problems comparable with those related to natural gas. Other feedstocks should be sought. No changes in current air-pollution standards are considered necessary for emission from ammonia plants that use natural gas as a feedstock and natural gas or light fuel oil (No. 2) as fuel for the reformers.*

At modern ammonia plants, about 972 kg of water condensate is obtained per tonne of ammonia produced. The condensate contains about 1 kg of ammonia per tonne of ammonia produced. Effluent guidelines limit the amount of ammonia that can be discharged, and about 98% of the ammonia must be removed before the effluent can be discharged as a waste. With present water-treatment technology, ammonia-plant

condensate is steam-stripped, and ammonia removed from the wastewater is emitted into the air. *It may be possible to recycle the condensate in the ammonia-plant process and thereby eliminate emission of ammonia to the air. Furthermore, recycling the condensate would decrease the consumption of energy in the steam-stripping operation. It is recommended that studies be undertaken to investigate recycling of the ammonia-plant condensate in the process.*

Of all ammonia losses from production and application in industry and agriculture, the major portion occurs during the direct application of ammonia to soil. Although this process is relatively efficient (only 5% of ammonia applied is lost to air), the loss accounts for 60% of the total industrial-agricultural loss. For resource conservation, efforts should be directed toward reducing further the loss of ammonia during production, distribution, and application. The amount of total nitrogen lost in air and groundwater when nitrogen fertilizers are applied to the soil is about 8 times as much as the loss, as ammonia, during the production and distribution of fertilizers. The nitrogen losses in air and groundwater result from denitrification and leaching, respectively, of soil nitrogen. *It is recommended that major effort be directed toward development of improved nitrogen fertilizers that are less susceptible to such losses. This should be part of a continuing effort to improve agricultural practices and to decrease nitrogen losses in air and groundwater.*

#### AMMONIA VOLATILIZATION FROM ANIMAL WASTES

Methods should be developed to reduce the volatilization of ammonia from feedlot surfaces to conserve nitrogen for agricultural use. Study of the ammonia flux from feedlot areas into surface water and plant leaves would provide useful background data.

#### ATMOSPHERE

Polluted air contains particles and droplets that in turn contain nitrate and sulfate, which may constitute a health hazard to human populations in urban areas and contribute significantly to the reduction of visibility. Some of these particles contain ammonium ion, but it is not known whether the ammonium moiety lessens or heightens toxicity. Present evidence suggests that ammonia lessens toxicity. Furthermore, particulate ammonium, sulfate, and nitrate compounds may affect the radiative climate of the earth and are directly involved in acid-rain precipitation.

Ammonium-containing particles have received more limited attention than other substances in air-pollution research. Specific recommendations related to the atmospheric concentrations of ammonia are as follows:

1. An improved inventory of ammonia emission from stationary and automotive sources should be developed.
2. Methods should be developed or refined for the routine measurement of ambient ammonia at parts-per-billion concentrations. These methods should be suitable for continuous measurement of ambient ammonia as part of a limited monitoring network.
3. *Simultaneous measurements of ammonia and of particulate hydrogen (acidity), ammonium, sulfate, and nitrate content are needed to elucidate further the role of ammonia in the formation of particulate ammonium, nitrate, and sulfate and to formulate improved strategies for the control of these major inorganic pollutants.*

#### PLANT AMMONIA FIXATION

Plants may play a role in the absorption of ammonia and ammonium aerosols. Research is needed to distinguish gaseous and particulate components in the cycling of ammonia between the atmosphere and vegetation.

#### OCEANS

Ammonia is important in the nitrogen dynamics of coastal waters. Municipal sewage effluent is a major source of ammonia in these waters. The effects of municipal sewage on the nitrogen economy of coastal waters should be examined.

Ammonium fluxes across the sediment-water interface should be measured for the range of sedimentary conditions found in coastal water.

#### TOXICOLOGY AND HEALTH EFFECTS

Despite much effort, the metabolic basis of ammonia toxicity is insufficiently understood. Sound research in this area should be encouraged. The basis of hepatic coma should continue to be studied, and the functional importance of depletion of citric acid-cycle intermediates and ATP depletion should be examined. The possible role of ATPase, acetylcholine, and other neurotransmitters requires further investigation.

The treatment of urea toxicity in ruminants is not as effective as could be desired, and additional studies are needed on the causes of death due to urea feeding or rumen ammonia production.

Both short- and long-term tolerance limits for ammonia in fishes should be established, so that guidelines can be developed for safe concentrations in natural waters.

Proper ventilation and waste management can prevent the buildup of ammonia in the ambient air in confined livestock facilities. Information about proper technical construction and utilization is available and should be disseminated to livestock producers.

Bats can tolerate extremely high concentrations of atmospheric ammonia; their mechanism of tolerance should be studied in the hope that the information could be used to protect more sensitive species, including man.

Animal studies of pulmonary effects have been limited in number and sometimes inadequately controlled. Additional studies of physiologic and biochemical effects of ammonia on pulmonary ultrastructure and function would therefore be useful.

Studies of late sequelae of acute toxic inhalation of ammonia and of responses to chronic low exposure to ammonia need to be performed. Ammonia needs to be investigated as a sole pollutant and in mixtures with other pollutants, such as carbon monoxide, nitrogen oxides, sulfur dioxide, and hydrogen sulfide. Because studies of the synergistic effects of various combinations of pollutants at various concentrations could involve a large number of permutations and require a tremendous expenditure of effort and resources, these studies should be selected and designed carefully. Available empirical observations on man suggest that gaseous ammonia as encountered in air pollution adds little to the toxicity of other pollutants. Thus, it appears appropriate to suggest here, as well as for some of the recommendations to follow, that such studies be preceded by careful, well-controlled epidemiologic surveys. These will permit proper identification of the problem, if present, and of the specific combinations of pollutants that need be investigated. The following subjects warrant evaluation to determine threshold and safe limits for acute and chronic exposure to ammonia (alone or with carefully selected synergists) with respect to age:

1. Functional changes of the terminal airways, i.e., frequency-dependent compliance, closing volume, and flow rates at low lung volume.
2. Structural changes, as studied by ultrastructural techniques, scanning electron microscopy, autoradiographic techniques of cell turnover in the lung and bronchial tree, and electron microscopic tracer studies of pulmonary capillary permeability.
3. Biochemical changes *in vivo* and *in vitro*, particularly with respect to collagen and elastin metabolism; mucin production; protein, carbohydrate, and lipid (surfactant) metabolism; histamine and serotonin release; lysosomal enzyme alterations; and effects on other enzyme systems.

4. Changes in lung defenses, as manifested by changes in humoral and cell-mediated immunologic function, macrophage function, and *in vivo* and *in vitro* responses to bacterial and viral challenge.

The continued study of metabolic ammonia toxicity and of hepatic encephalopathy should be encouraged to elucidate the various intracerebral biochemical mechanisms and to assess their significance for human hepatic coma and other types of ammonia intoxication.

The initiation and perpetuation of the acute inflammatory response to ammonia burns of the eye should be studied further. Study is also needed of the various cellular interactions that result in protease degradation of the cornea and of the question of why ammonia-burned eyes are slow to epithelialize.

Monitoring of the industrial environment and workplace should continue to accumulate accurate measurements of ammonia in air and, if necessary, to refine industrial standards.

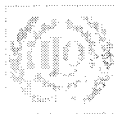
Additional well-controlled human inhalation studies should be conducted. They should last at least a few hours and should include monitoring of such metabolic and respiratory characteristics as blood urea nitrogen, urinary urea nitrogen, serum and urinary ammonia, closing volume, frequency-dependent compliance, alveolar-arterial oxygen gradient, maximal midexpiratory flow, and flow rates at low lung volumes.

*Epidemiologic studies on selected industrial-rural populations chronically exposed to accurately monitored ammonia concentration are recommended.* Other air pollutants, if present, should be identified and monitored. Detailed and accurate epidemiologic histories and tests of respiratory and metabolic characteristics are necessary, and there should be well-studied control groups. Smokers and nonsmokers should be specifically identified because the effect of cigarette smoke may obscure the effects of air pollutants. The incidence of neoplasm in the group should also be determined.

# International Chemical Safety Cards

## AMMONIUM HYDROXIDE (10%-35% solution)

ICSC: 0215



### AMMONIUM HYDROXIDE (10%-35% solution)

Aqua ammonia

Ammonium hydrate

NH<sub>4</sub>OH

Molecular mass: 35.1

CAS # 1336-21-6  
 RTECS # BQ9625000  
 ICSC # 0215  
 UN # 2672  
 EC # 007-001-01-2



TYPES OF HAZARD/ EXPOSURE	ACUTE HAZARDS/ SYMPTOMS	PREVENTION	FIRST AID/ FIRE FIGHTING
<b>FIRE</b>	Not combustible.		In case of fire in the surroundings: all extinguishing agents allowed.
<b>EXPLOSION</b>	See Notes.		In case of fire: keep drums, etc., cool by spraying with water.
<b>EXPOSURE</b>		STRICT HYGIENE!	IN ALL CASES CONSULT A DOCTOR!
<b>INHALATION</b>	Burning sensation. Cough. Laboured breathing. Shortness of breath. Sore throat.	Ventilation, local exhaust, or breathing protection. Keep containers properly closed.	Fresh air, rest. Artificial respiration if indicated. Refer for medical attention.
<b>SKIN</b>	Corrosive. Redness. Serious skin burns. Pain. Blisters.	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse skin with plenty of water or shower. Refer for medical attention.
<b>EYES</b>	Corrosive. Redness. Pain. Blurred vision. Severe deep burns.	Face shield or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
<b>INGESTION</b>	Corrosive. Abdominal cramps. Abdominal pain. Sore throat. Vomiting (further see Inhalation).	Do not eat, drink, or smoke during work.	Rinse mouth. Do NOT induce vomiting. Give plenty of water to drink. Refer for medical attention.



SPILLAGE DISPOSAL	STORAGE	PACKAGING & LABELLING
Evacuate danger area! Consult an expert in case of a large spillage! Ventilation. Cautiously neutralize spilled liquid with a dilute acid, such as dilute sulfuric acid. Wash away remainder with plenty of water. Do NOT let this chemical enter the environment (extra personal protection: complete protective clothing including self-contained breathing apparatus).	Separated from food and feedstuffs (see Chemical Dangers). Cool. Well closed. Keep in a well-ventilated room (further see Notes).	Unbreakable packaging; put breakable packaging into closed unbreakable container. C symbol R: 34-37 S: (1/2-)7-26-45 Note: B UN Hazard Class: 8 UN Packing Group: III
<b>SEE IMPORTANT INFORMATION ON BACK</b>		
<b>ICSC: 0215</b>	Prepared in the context of cooperation between the International Programme on Chemical Safety & the Commission of the European Communities © IPCS CEC 1993 No modifications to the International version have been made except to add the OSHA PELs, NIOSH RELs and IDLH values.	

# International Chemical Safety Cards

## AMMONIUM HYDROXIDE (10%-35% solution)

ICSC: 0215

<b>I M P O R T A N T  D A T A</b>	<p><b>PHYSICAL STATE; APPEARANCE:</b>                      VERY VOLATILE, COLOURLESS SOLUTION OF AMMONIA IN WATER, WITH PUNGENT ODOUR.</p> <p><b>PHYSICAL DANGERS:</b></p> <p><b>CHEMICAL DANGERS:</b>                      Reacts with many heavy metals and their salts forming explosive compounds. Attacks many metals forming flammable/explosive gas (hydrogen - see ICSC # 0001). The solution in water is a strong base, it reacts violently with acids.</p> <p><b>OCCUPATIONAL EXPOSURE LIMITS (OELs):</b>                      TLV (as TWA): 25 ppm; 17 mg/m<sup>3</sup> (for NH<sub>3</sub>); as STEL: 35 ppm; 24 mg/m<sup>3</sup> (ACGIH 1994-1995).                      TLV not established.</p>	<p><b>ROUTES OF EXPOSURE:</b>                      The substance can be absorbed into the body by inhalation of its vapour or aerosol and by ingestion.</p> <p><b>INHALATION RISK:</b>                      A harmful contamination of the air can be reached very quickly on evaporation of this substance at 20°C.</p> <p><b>EFFECTS OF SHORT-TERM EXPOSURE:</b>                      The substance is corrosive to the eyes, the skin and the respiratory tract. Corrosive on ingestion as well. Inhalation of high concentrations of vapour may cause laryngeal oedema, inflammation of the respiratory tract, and pneumonia. The effects may be delayed.</p> <p><b>EFFECTS OF LONG-TERM OR REPEATED EXPOSURE:</b>                      Lungs may be affected by repeated or prolonged exposure to the vapour or aerosol.</p>
<b>PHYSICAL PROPERTIES</b>	Boiling point: (25%) 38°C Melting point: (25%) -58°C Relative density (water = 1): (25%) 0.9	Solubility in water: miscible Vapour pressure, kPa at 20°C: (25%) 48 Relative vapour density (air = 1): 0.6-1.2
<b>ENVIRONMENTAL DATA</b>	The substance is very toxic to aquatic organisms.	



**NOTES**

Ammonia vapour is flammable and explosive under certain conditions. Be aware that ammonia gas can evolve from ammonia solution. Depending on the degree of exposure, periodic medical examination is indicated. Do NOT completely fill bottles with the substance; strong solutions may develop pressure. Release caps with care. Other UN numbers are: UN 1005 Ammonia, anhydrous liquefied or ammonia solutions, relative density of less than 0.880 at 15°C in water, with more than 50% ammonia; UN 2073 Ammonia, 35-50%. Also consult ICSC # 0414 Ammonia.

Transport Emergency Card: TEC (R)-219  
NFPA Code: H3; F1; R0

**ADDITIONAL INFORMATION****ICSC: 0215****AMMONIUM HYDROXIDE (10%-35% solution)**

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## Environmental Health Criteria 54

# AMMONIA

Published under the joint sponsorship of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization



World Health Organization  
Geneva, 1986

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The International Programme on Chemical Safety (IPCS) is a joint venture of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization. The main objective of the IPCS is to carry out and disseminate evaluations of the effects of chemicals on human health and the quality of the environment. Supporting activities include the development of epidemiological, experimental laboratory, and risk-assessment methods that could produce internationally comparable results, and the development of manpower in the field of toxicology. Other activities carried out by IPCS include the development of know-how for coping with chemical accidents, coordination of laboratory testing and epidemiological studies, and promotion of research on the mechanisms of the biological action of chemicals.

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additive hypertrophic effect of ammonium chloride and unilateral nephrectomy was observed on the remaining kidney. Increased sensitivity to ammonia toxicity was found in young rats (Benyajati & Goldstein, 1975) and in rats that had been castrated, adrenalectomized, or thymectomized (Paik et al., 1975).

8.8.2 Antagonistic effects

L-arginine and the related amino acids, ornithine and aspartic acid, substrates from urea synthesis, have been reported to exert a protective effect against acute ammonia poisoning in rats, dogs, and cats (Morris & Rogers, 1978; NRC, 1979).

High-protein diets exert an antagonistic effect on the toxicity of ammonium salts, unless liver dysfunction is present (section 7.1.2.4). In addition, an increase in toxic response has been observed with increase in age due to the adaptive response of glutaminase activity in rats to ammonia detoxication during acidosis.

8.9 Mechanisms of Toxicity

Hypotheses proposed for the mechanism of ammonia toxicity include impaired decarboxylation of pyruvic acid (McKhann & Tower, 1961), NADH depletion slowing down the generation of ATP (Worcel & Erecinska, 1962), depletion of alpha-ketoglutarate resulting in impairment of the Krebs cycle (Bessman & Bessman, 1955; Fazekas et al., 1956; Warren & Schenker, 1964); depletion of ATP due to glutamine formation by the glutamine synthetase (EC 6.3.1.2) system (Warren & Schenker, 1964; Nakazawa & Quastel, 1968), stimulation of membrane ATPase (EC 3.6.1.8) producing increased nerve cell excitability and activity (Hawkins et al., 1973), and depletion of ATP causing a decrease in cerebral acetylcholine (Braganca et al., 1953; Ulshafer, 1958).

9. EFFECTS ON MAN

9.1 Organoleptic Aspects

9.1.1 Taste

Campbell et al. (1958) determined the taste threshold concentration for ammonia in redistilled water with 21 - 22 subjects in "difference tests of the triangle type". At ammonia concentrations of 26, 52, and 105 mg/litre, the percentages of correct identifications were 61.9, 71.4, and 85.7, respectively.

Defining the threshold concentration as the level at which correct identification is 50% greater than that expected by chance, the taste threshold of ammonia was determined to be around 35 mg/litre. However, this definition of the threshold concentration seems to be somewhat arbitrary and McBride & Laing (1979) have reported significant positional bias in using the triangle test to determine taste thresholds. Furthermore, the triangle test is not intended to mimic environmental exposures in which the taste thresholds could be substantially higher. It seems reasonable to conclude only that the palatability of water is not likely to be significantly affected by total ammonia levels of  $\leq 35$  mg/litre (as  $\text{NH}_3$ ), but will be affected at higher levels.

9.1.2 Odour

Odour thresholds reported in the literature may vary according to the definition of odour response, mode of presentation of the stimulus, chemical purity of the agent used, and the number of subjects and trials in the study. The detection threshold for ammonia, defined as the concentration that produces the first detectable difference in odour over background, was reported to be 37 mg/m<sup>3</sup> (DallaValle & Dudley, 1939). This reference, though often cited, gives no information on the study design from which this number was derived.

The considerable variability in threshold data prompted work by Leonardos et al. (1969), who used a standardized procedure to determine recognition thresholds rather than detection thresholds for 53 chemicals. The odour threshold was defined as the first concentration at which all four panel members (trained odour analysts) were able to recognize the characteristic odour of the chemical. The panel tested only one chemical per day. Concentrations examined were multiples by 10 of 0.7, 1.47, and 3.3 mg/m<sup>3</sup> (1, 2.1, and 4.6 ppm). The recognition threshold for the odour of ammonia was 32.6 mg/m<sup>3</sup> (46.8 ppm).

The results of several other studies suggest that human beings can detect ammonia at much lower levels. Stephens (1971) reported 2.7 mg/m<sup>3</sup> (3.9 ppm) as the lowest concentration producing an odour response, when a contaminated air stream and a reference stream were compared by sniffing (number of subjects was not reported). A report by Saifuddinov (1966), of an olfactory threshold of 0.55 - 0.50 mg/m<sup>3</sup> for the most sensitive of 22 subjects, did not include sufficient detail to evaluate this excessively low estimate. Carpenter et al. (1948) stated that "a group of 8 persons found that the least odour they could detect on entering a room containing various concentrations" was 0.7 mg/m<sup>3</sup> (1 ppm) ammonia. Again, no other details were given.

The best estimates of the thresholds at which ammonia can be expected to be detected by taste and odour are 35 mg/litre (as NH<sub>3</sub>) and 35 mg/m<sup>3</sup>, respectively. Sensitive individuals may detect concentrations an order of magnitude lower.

## 9.2 Clinical and Controlled Human Studies

### 9.2.1 Inhalation exposure

The severe effects resulting from acute exposure to ammonia have been described in case reports of accidents involving groups of people or individuals. There are no data on actual levels of ammonia in air during such accidents, but estimates have been made (Yahagi et al., 1959; Takahashi et al., 1984; NRC, 1979).

Exposure to an ammonia concentration of 280 mg/m<sup>3</sup> (400 ppm) has been reported to produce immediate throat irritation; 1200 mg/m<sup>3</sup> (1700 ppm) to produce cough; 1700 mg/m<sup>3</sup> (2400 ppm) to be life-threatening, and 3500 - 7000 mg/m<sup>3</sup> (500 - 10 000 ppm) to cause a high mortality rate (Patty, 1963; Helmers et al., 1971).

A burning sensation in the eyes, nose, and throat, as well as respiratory distress accompanied by lachrymation, coughing, and an increase in respiratory rate are some of the irritant effects of ammonia (Caplin, 1941). Chest X-rays are generally normal in such mild cases (Watson, 1973; Close et al., 1980). More severe respiratory effects include laryngeal and pulmonary oedema and bronchopneumonia (Slot, 1938; Caplin, 1941; Levy et al., 1964; Taplin et al., 1976; Flury et al., 1983). The signs and symptoms are generally reversible, but chronic bronchitis and bronchiectasis have been reported (Slot, 1938; Sugiyama et al., 1968; Taplin et al., 1976; Close et al., 1980).

In cases with a lethal outcome, the cause of death has been severe lung damage and secondary cardiovascular effects (Slot, 1938; Mulder & van der Zalm, 1967).

There have also been some studies on volunteers exposed to ammonia under laboratory conditions. Some of these studies are summarized in Table 21.

Silverman et al. (1949) reported on 7 human volunteers exposed to a concentration of 300 mg/m<sup>3</sup> (500 ppm) ammonia for 30 min using an oral-nasal mask. All 7 experienced upper respiratory irritation, which lasted up to 24 h in 2 of the volunteers. Two subjects experienced marked lachrymation, in spite of the exposure being by oro-nasal mask. The average respiratory minute volume increased markedly compared with control values, and in the 5 subjects in which minute-by-minute expired volumes were measured, there was a marked cyclical variation in minute volume with a period of 4 - 7 min. No coughing was noted.

After exposure, respiratory minute volumes fell to levels below the pre-exposure rate, but returned to pre-exposed values within 5 min of exposure. Ammonia retention decreased progressively until an equilibrium of 24% retention (ranging from 4 to 30%) was reached at approximately 19 min (range 10 - 27 min). The indices of nitrogen metabolism (BUN, NPN, urine-urea, and urine-ammonia) remained normal. The carbon dioxide combining power did not change.

Verbeck (1977) assessed respiratory function in 16 volunteers following exposure to 35, 56, 77, and 98 mg ammonia/m<sup>3</sup> (50, 80, 110, and 140 ppm) for 0.5, 1, and 2 h. The respiratory variables of vital capacity (VC), forced expiratory volume (FEV), and forced inspiratory volume (FIV), measured before and after exposure, did not decrease by more than 10%. Subjective variables, including smell, taste, irritation of the eyes, nose, or throat, urge to cough, headache, and general discomfort were monitored every 15 min and ranked by 8 experts and 8 non-experts (students) on a scale from 0 to 5. Subjective responses were ranked higher by the non-experts. A concentration of 77 mg/m<sup>3</sup> (110 ppm) was tolerated for 2 h, but at 98 mg/m<sup>3</sup> (140 ppm), all the subjects left the chamber because the exposure was intolerable.

Respiratory responses to ammonia during exercise were examined by Cole et al. (1977). Eighteen males, aged 18 - 39 years, had 2 periods of exercise in 3 consecutive half-day sessions. Mean exposure levels were 71, 144, 106, and 235 mg/m<sup>3</sup> (101, 206, 151, and 336 ppm). Ventilation minute volume and total volume decreased, and mean respiratory frequency increased at exposure levels  $\geq 106$  mg/m<sup>3</sup> (151 ppm).

In a study by MacEwen et al. (1970), 6 volunteers were exposed to ammonia concentrations of 21 and 35 mg/m<sup>3</sup> (30 and 50 ppm) for 10 min. The irritation was rated subjectively on a scale of 0 - 4. At 35 mg/m<sup>3</sup> (50 ppm), irritation was rated as "moderate" by 4 of the volunteers, while 1 individual reported no detectable irritation. None of the volunteers



Table 21. Effects of inhaled ammonia in human volunteers

Reference	Effects and response	Duration (min)	Number Concentration (mg/m <sup>3</sup> )
Silverman et al. (1949)	Irritation of upper respiratory tract (77%); increase in minute volume; no change in blood chemistry	30	300
Verbeck (1977)	10% increase in VC, FEV <sub>1</sub> , and FIV; 98 mg/m <sup>3</sup> was not tolerated; 77 mg/m <sup>3</sup> was tolerated for 2 h	30 - 120	35 - 98
Cole et al. (1977)	no effects noted during exercise at 71 mg/m <sup>3</sup> except slight irritation; decrease in ventilation minute volume and tidal volume and increase in respiratory frequency > 106 mg/m <sup>3</sup>	8 - 11	71 - 235
MacIwen et al. (1970)	"moderate irritation" (4/5)	10	35
Industrial Biostat Laboratories (1973)	dryness of the nose (1/10) eye irritation (3/10) throat irritation (8/10) eye irritation (5/10)	5	22, 35, 50, 94
Ferguson et al. (1977)	Increase in FEV <sub>1</sub> , with increasing NH <sub>3</sub> ; adaptation to irritating effects	2 - 6 h, 5 days/week, for 6 weeks	17.5, 35, or 70+

found the irritation at 35 mg/m<sup>3</sup> (50 ppm) to be "discomforting" or "painful".

The irritation threshold for ammonia was examined in 10 human volunteers by Industrial Bio-Test Laboratories, Inc. (1973). The subjects were exposed to 4 different concentrations of 22, 35, 50, and 94 mg/m<sup>3</sup> (32, 50, 72, and 134 ppm) for 5 min. The frequency of positive findings for the 10 subjects was as follows: at 22 mg/m<sup>3</sup>, 1 subject complained of dryness of the nose; at 35 mg/m<sup>3</sup>, 2 subjects experienced dryness of the nose; at 50 mg/m<sup>3</sup>, 3 subjects had eye irritation, 2 had nasal irritation, and 3 had throat irritation; at 94 mg/m<sup>3</sup>, 5 subjects demonstrated signs of lachrymation, 5 had eye irritation, 7 had nasal irritation, 8 had throat irritation, and 1 complained of chest irritation.

A controlled study on human volunteers was conducted by Ferguson et al. (1977) to evaluate the responses to inhaled ammonia at concentrations of 17.5, 35, and 70 mg/m<sup>3</sup> (25, 50, and 100 ppm). Six adults, not acclimatized to ammonia exposure, were divided into 3 groups, which were exposed for 2 - 6 h each day, 5 days per week, for 6 weeks. One pair of subjects was exposed only to 35 mg ammonia/m<sup>3</sup> for 6-h periods throughout the test. Subjects were examined daily for irritation of the eyes, nose, or throat, and periodically for pulse rate, respiration rate, pulmonary function (forced vital capacity (FVC) and forced expiratory volume in 1 second (FEV<sub>1</sub>)), blood pressure, neurological responses, and interference in task-performance ability. A statistical analysis of the results demonstrated that the only significant change among the vital functions measured was an increase in forced expiratory volume in 1 second (FEV<sub>1</sub>) with increasing ammonia concentration. In addition, the rate of mild eye, nose, or throat irritations over the last 3 weeks of the test was significantly less than during the first 2 weeks. This indicated that an acclimatization process had occurred, with increased tolerance to the irritant effects of ammonia developing with increasing time of exposure. Overall, the ammonia exposure produced 2 incidents of mild irritation (78 observations made) at 17.5 mg/m<sup>3</sup> (25 ppm), 22 incidents (198 observations made) at 35 mg/m<sup>3</sup> (50 ppm), and 11 incidents (84 observations made) at 70 mg/m<sup>3</sup> (100 ppm). Among control subjects, 4 irritation incidents were recorded during 45 observations. When ammonia concentrations exceeded 105 mg/m<sup>3</sup> (150 ppm), all subjects experienced lachrymation accompanied by dryness of the nose and throat.

In an inhalation study, the threshold for effects on respiration, skin electric potential, and the electroencephalogram was found to be 22 mg/m<sup>3</sup> (31 ppm) (Alpatov & Mikhailov, 1963; Alpatov, 1964).

Reports from industries with ammonia exposure indicate that irritative effects have appeared over a wide range of ammonia concentrations (Elkins, 1950; Vigliani & Zurlo, 1955; Mangold, 1971). A concentration of 88 mg/m<sup>3</sup> was called "definitely irritating" (Elkins, 1950), and "barely noticeable" eye irritation was reported at 3 mg/m<sup>3</sup> (Mangold, 1971). Giguz (1968), in a study involving 140 subjects exposed to ammonia and nitrogen oxides, at concentrations not exceeding the "maximum permissible concentration" (20 mg/m<sup>3</sup>), 3 h per day during 2 - 3 years of vocational training, demonstrated increased incidences of upper respiratory tract disease, compared with those in a control group of unexposed subjects.

#### 9.2.2 Oral exposure

##### 9.2.2.1 Effects of acute oral exposure

Cases of the ingestion of large doses of ammonia have been reported. When solutions of ammonia were ingested orally, a tissue-destructive caustic effect was noted for concentrated solutions, owing to their high pH. A solution of ammonia at a concentration of 100 g/litre, for example, has a pH of 12.5.

Oesophageal burns were reported in 25 cases of accidental ammonia ingestion (Hawkins et al., 1980). One child suffered a mild burn. Four adults had mild burns limited to the mucosa and nine adults had oesophageal burns that were moderate or more severe in nature. One adult female suffered from a complication of airway obstruction from supraglottic oedema. Oesophageal stricture from the ingestion of ammonia (100 g/litre) was reported by Vancura et al. (1980) (Table 19).

A fatal outcome after ingestion of a solution containing 24 g ammonia/litre was reported by Klendshoj & Rejent (1966). Autopsy showed haemorrhagic inflammatory changes in the oesophagus, stomach, and small intestine.

There are many reports on the effects of ammonium chloride, but since acidosis is caused by the chloride, such studies have little relevance for evaluating ammonia toxicity.

There are no data on acute effects of ingestion of ammonium compounds, other than the chloride.

#### 9.2.3 Endogenous hyperammonaemia

##### 9.2.3.1 Inborn errors of metabolism

These affect the uptake of ammonia rather than its rate of production.

Congenital deficiency of carbamyl phosphate synthetase I (EC 6.3.4.1.6), and, to a lesser extent, of other enzymes of

the ornithine cycle, and several other metabolic disorders may lead to hyperammonaemia and various abnormal urinary constituents. Hyperammonaemia may be lethal in newborn infants, may cause severe symptoms in infancy, or may cause chronic remittent symptoms in older children or adults (Hsia, 1974).

Clinical features in neonates may resemble those of hepatic coma and may be precipitated by protein-rich milk feeds. In older children, episodic vomiting, neurological disorders (including seizures) or coma are precipitated by high-protein foods.

##### 9.2.3.2 Hepatic features

Varied and complex functions of the liver may fail progressively in chronic liver disease or rapidly in acute disorders. The syndromes differ in the extent to which portal blood from the intestine is shunted into the systemic venous circulation either by cirrhotic changes in hepatic vascular resistance or by surgical procedures to correct portal hypertension resulting from it.

In either case, a syndrome is recognised that comprises a spectrum of neurological features from irritability via inappropriate behaviour, tremors, hyper-reflexia and generalised muscular rigidity, to delirium, stupor, convulsions and coma.

There is disagreement regarding the extent to which this syndrome is an expression of ammonia toxicity. On the one hand, over 90% of persons with the disorder have elevated levels of ammonia in the blood or cerebrospinal fluid; the condition may be induced in those with marginal liver function by the administration of ammonium salts or an intestinal haemorrhage (which leads to intestinal ammonia production greater than that from an equivalent amount of meat) and the condition may be treated by reducing intestinal ammonia production, by the administration of antibiotics to eliminate ammonia-producing flora. On the other hand, there is an imperfect correlation between the clinical state and the blood-ammonia level and the condition may occur in the presence of normal blood-ammonia levels.

It is unlikely that the syndrome resulting from the failure of an organ as complicated as the liver should be explicable in terms of a single metabolic component, but the similarity between hepatic failure and certain expressions of congenital hyperammonaemias suggests an important role of ammonia toxicity in the pathogenesis of the syndrome.

Thus, there is both historical and theoretical evidence that most recommended exposure limits are acceptable.

10.2 Exposure Through Water and Food

Ammonia will have a toxic effect only if intake exceeds the capacity of mammals to detoxify ammonia. Unfortunately, there are no data permitting the evaluation of this capacity in healthy human beings or other terrestrial mammals. In addition, there is some evidence that the mode of intake may be a factor in the capacity of individuals to detoxify ammonia. Parenteral administration of ammonia results in patterns of metabolism and elimination that are markedly different from those seen in oral administration. Thus, the considerable body of data on the parenteral toxicity of ammonia is not of direct relevance to criteria for oral exposure. Similarly, because of the different kinetic patterns between oral and inhalation exposure to ammonia, as well as the highly irritant effects of ammonia on the lung, the available inhalation data on ammonia are not applicable to the estimation of an acceptable daily intake (ADI) for ingestion. However, it would be possible to define a clearly undesirable level of oral exposure to total ammonia (NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>) as well as a level that is clearly tolerable. The range between these 2 levels would exceed the range within which an ADI could be established.

The amount of excess ammonia (i.e., over and above the amount normally produced in the body) that can be safely ingested and assimilated is difficult to define. In short-term (28 - 90 days) studies carried out on rats and pigs, no adverse effects were reported at higher levels of ammonia intake (75 - 545 mg NH<sub>3</sub>/kg body weight per day) in the form of sulfamate, phosphate, citrate, or chloride. The effects attributed directly to elevated ammonium ion levels are acute pulmonary oedema and central nervous system (CNS) toxicity, depression of appetite due to a direct effect of the ammonium ion on the brain, and promotion of growth via the use of ammonium salts as a source of non-essential nitrogen under certain circumstances.

Some effects (such as renal growth and demineralization of bone) arising from the administration of ammonium chloride seem to be secondary effects of acidosis. (NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>) concentrations in surface waters indicate an average of < 0.18 mg/litre in most areas, and 0.5 mg/litre in waters near large metropolitan areas (Wolaver, 1972; US EPA, 1979a). Levels in ground water are usually low, since ammonia is generally immobile in soil. Ammonia is practically absent when drinking-water is chlorinated.

10. EVALUATION OF HUMAN HEALTH RISKS AND EFFECTS ON THE ENVIRONMENT

10.1 Atmospheric Exposure and Effects

10.1.1 General population exposure

Background levels of ammonia in community air are low in comparison with levels that have been established as safe in occupational settings, but there is considerable variability according to the type of land use. In general, levels in areas with intensive livestock husbandry or high rates of manure application are in the range of 100 - 200 µg/m<sup>3</sup>, levels in urban areas range from approximately 5 to 40 µg/m<sup>3</sup>, while those in rural areas, without intensive manure production or use, range up to 10 µg/m<sup>3</sup>. This is in contrast to odour thresholds of the order 10 000 µg/m<sup>3</sup>, thresholds for irritation of the order 20 000 - 50 000 µg/m<sup>3</sup>, and the estimated LC for man of 5000 - 10 000 mg/m<sup>3</sup>. The LC50 estimation for the rat was 7 600 000 µg/m<sup>3</sup>, for a 2-h exposure. In an occupational setting, workers did not voluntarily use respiratory protective devices at concentrations below about 500 000 µg/m<sup>3</sup>. General ambient atmospheric levels are therefore of no concern in respect of discomfort or acute toxicity.

Ammonia is not mutagenic and long-term studies on both laboratory and farm animals have not shown any pathological effects at levels below 35 000 µg/m<sup>3</sup>. Long-term toxic effects are unlikely, even at levels much higher than ambient levels, both generally and in the neighbourhood of ammonia-emitting systems. There is a lack of evidence regarding recent trends in global atmospheric ammonia concentrations.

10.1.1.2 Occupational exposure

Occupational problems are predominantly those of accidental exposure.

Though for certain groups in, for example, agriculture, the chemical industry, waste disposal and transport, occupational exposure levels may be very much higher than general, there is historical evidence that, even at levels significantly in excess of current occupational exposure limits, there was a low prevalence of adverse health effects.

The distribution kinetics of absorbed atmospheric ammonia suggest that the rise in blood-ammonia at a typical occupational exposure limit will be within the normal range of variation.

Ammonia is a negligible natural constituent of food, but ammonium compounds are added in small amounts (< 0.001 - 3.2%) to various foods as stabilizers, leavening agents, flavourings, or for other purposes. The daily human intake from these sources is estimated to be 18 mg as NH<sub>3</sub>.

### 10.3 Ocular and Dermal Exposure

Ammonia in aqueous solution or in contact with body fluids is alkaline and causes burns or inflammation of eyes or skin. The ocular irritation commonly experienced at atmospheric ammonia concentrations of > 20 mg/m<sup>3</sup> (MacEwen et al., 1970; Keplinger et al., 1973; Verberk, 1977) is readily reversible when exposure ceases, and may also be reduced by acclimatization (Ferguson et al., 1977).

Serious ocular damage normally occurs, only with a direct blast or splash contact with anhydrous or aqueous ammonia (Grant, 1974). Skin damage is reported to occur at concentrations of  $\approx$ 7000 mg/m<sup>3</sup> (NRC, 1979).

### 10.4 Accidental Exposure

High gaseous ammonia concentrations may be encountered locally, both in domestic and work-place environments, as a result of gaseous emissions and/or spillages of concentrated solutions, and respiratory (and skin and eye) injury may result. On a larger scale, spillage from stock or transport tanks or refrigeration plant of concentrated ammonia liquor or anhydrous ammonia would constitute a severe environmental insult and would cause serious injury to the people, animals, and plants in the vicinity. Because of its low density and short biopersistence, major spillages would be expected to disperse rapidly and not to persist in the environment.

### 10.5 Evaluation of Risks for the Environment

Environments that receive more ammonia than can be used may be acidified and nitrogen-enriched. As a consequence of these physical-chemical changes, the structure and functioning of the ecosystem will be disturbed.

Ammonia plays an important role in the metabolism of all organisms as a nutrient at low concentrations, but becomes toxic at higher concentrations. For example, microorganisms both assimilate and generate ammonia as a part of natural nutrient cycling processes. High levels of ammonia may inhibit growth or survival of microbial organisms, including, at higher levels, nitrifying organisms.

### 10.5.1 The aquatic environment

Ammonia concentrations in the aquatic environment are variable, reflecting the proximity and nature of sources (section 4).

Where there are large numbers of people and animals in relation to the volume of surface waters and drainage flow, the load of nitrogen added to surface waters from sewage and industrial effluent is the predominant source and may lead to ammonia concentrations that constitute a significant local and/or regional environmental problem.

Otherwise, ammonia deposition contributes a major input. In surface waters that are poorly buffered, poor in nutrients, and hydrologically dependent on rainfall and/or snow melt, this may result in acidification and nitrogen enrichment resulting in marked changes in plant community structure with concomitant changes in the animal population structure.

The toxic effects on aquatic organisms are attributed to non-ionized ammonia (NH<sub>3</sub>) rather than to ammonium ion levels. This is because non-ionized ammonia easily penetrates biological membranes, whereas ammonium ions require specialized transport processes.

There are similarities between the modes of the acute toxic action of ammonia in mammals and in fish: in the latter, however, environmental conditions (such as pH, ionic composition and concentration, temperature, and oxygen availability), which are more variable in water than in air, have a marked modulating effect.

Aquatic animals have a limited ability to detoxify ammonia and, therefore, the body load is dependent on ammonia concentrations in the water. Except in open oceans, exposure to environmental levels produces many chronic effects (including reduced growth, decreased survival, impaired reproduction) and may increase susceptibility to disease and also cause histopathological changes.

High levels of ammonia in aquatic systems are also toxic for plants. The detoxification of excessive ammonia places a severe strain on the carbohydrate metabolism of the plant which subsequently results in foliar injury, and growth effects, and thus may modify plant community composition.

Where the dominant species, be it fish or plant, is also sensitive to ammonia the effects on the whole ecosystem will be marked.

### 10.5.2 The terrestrial environment

The most common effect of exposure of plants to atmospheric ammonia is foliar injury. Prolonged exposure to high ambient concentrations of about 75 µg/mg, such as occur

in the vicinity of intensive livestock farms, adversely affects more susceptible species such as pine trees. The observed damage is the result of both direct and indirect effects due to, changes in soil, and secondarily, to increased susceptibility to disease and meteorological stress.

The data on ammonia toxicity for wildlife are very limited. There is no evidence that wild-life populations, in general, are at risk from ammonia, but, there may be secondary effects associated with changes in plant communities. Certain species of bats are able to withstand the very high ammonia levels found in caves where they live.

10.6 Conclusions

The major groups of organisms at risk from elevated ammonia levels are aquatic animals and terrestrial plants. There appears to be little danger for terrestrial animals, including man, except from acute accidental exposure.

10.6.1 General population

There are no data suggesting that present environmental levels of ammonia are hazardous for the general population. Only high-level accidental exposures from domestic sources and transportation and storage accidents pose an occasional acute health hazard.

10.6.2 Sub-populations at special risk

Groups likely to exhibit ammonia toxicity include those with hepatic or renal impairment, though, even in these cases, levels of exogenous ammonia are insignificant in comparison with endogenous levels, so that, in the absence of any environmental exposure, such persons would still be affected. The mechanism is different in the two cases. Hepatic impairment limits the conversion of ammonia to urea, and renal failure, by increasing urea concentrations and its intestinal secretion, leads to increased endogenous intestinal ammonia production.

There have been few studies on the chronic effects of ammonia inhalation. It can be speculated that subpopulations that have been found to be hyperreactive to other respiratory irritants (e.g., sulfur dioxide, particulates, ozone) may also be hyperreactive to ammonia. These subpopulations may include children, elderly persons with pre-existing cardiorespiratory symptoms, individuals with asthma or bronchitis, and those engaged in vigorous physical exercise (Calabrese, 1978). However, there is also some indication that previous exposure to

low levels of ammonia may cause inurement to its effects (Ferguson et al., 1977).

10.6.3 Occupational exposure

Accidental exposures are the predominant problem (section 10.1.1.3). Otherwise, occupational exposure can be controlled by the application of most current occupational exposure limits and proper industrial hygiene.

10.6.4 Farm animals

Farm animals may be at risk, because of continuous exposure under confined housing conditions resulting in high atmospheric levels of ammonia within the confinement areas; this applies particularly to cattle, swine, and poultry. Available reported data provide a range of measured exposure levels of from 2 to 1400 mg/m<sup>3</sup>. In winter months in colder climates, most of the measured concentrations exceeded the admissible upper limit of 35 mg/m<sup>3</sup> (50 ppm).

10.6.5 Environment

Environments with a low buffer capacity and poor in nutrients are susceptible to acidification and nitrogen enrichment by elevated ammonia loading; prolonged high ammonia-loading results in changes in both the structure and function of plant and animal communities. Levels of atmospheric ammonia necessary for the onset of these changes have not been established; however, changes in the structure of these communities have been observed where ammonia levels in the atmosphere were possibly up to 100 µg/m<sup>3</sup>.

Plants use ammonia as a nutrient, but high levels can be toxic. Terrestrial plants show a susceptibility to reduced growth and reduced vitality, when exposed to levels as low as 75 µg NH<sub>3</sub>/m<sup>3</sup> in the atmosphere.

Aquatic animals have a low capacity to detoxify ammonia. Acute effects on some fish have been demonstrated in laboratories at concentrations as low as 0.1 mg NH<sub>3</sub>/litre and chronic effects at concentrations as low as 0.02 mg NH<sub>3</sub>/litre. Thus, as ammonia levels in some waters are often similar to those shown to cause chronic effects in some fish, it would appear that these animals are at risk. Aquatic invertebrates are, in general, less sensitive to elevated ammonia levels in water.

Aquatic animals are at risk because of increases in ammonia concentrations in water systems, whereas some plant communities appear to be at risk from elevations in atmospheric ammonia loading.

## 11. RECOMMENDATIONS

### 11.1 Research Needs

1. Long-term monitoring of ammonia and other pollutants in water systems with different aquatic ecosystems.
2. Studies of the long-term effects of ammonia on terrestrial vegetation.
3. Studies of the global nitrogen balance to identify long-term trends.
4. Ecotoxicological studies to elucidate environmental effects.
5. Epidemiological studies in relation to ammonia exposure in order to make better hygiene recommendations.
6. Long-term experimental animal studies to establish a no-observed-adverse-effect level of exposure.
7. Studies on the role of ammonia in modifying physical and chemical conditions of soil and water systems.
8. More data are needed to assess accurately the relative contributions of various point and non-point sources of ammonia for surface waters.
9. Research into methods and their application directed towards reducing emissions from point sources.
10. Additional acute toxicity tests with salt-water fish and invertebrate species.
11. Life-cycle and early-life-stage tests with representative fresh-water and salt-water organisms from different families, with investigation of pH effects on chronic toxicity.
12. Fluctuating or intermittent exposure tests under a variety of exposure patterns on additional species.
13. Both acute and long-term tests at cold-water temperatures.
14. Studies on the effects of dissolved and suspended solids on acute and chronic toxicity.

15. More histopathological and histochemical research with fish, which would provide a rapid means of identifying and quantifying sublethal ammonia effects.
16. In fish, the relative concentration limits for both acclimatization and subsequent acute response need better definition and a more complete explanation.