

Physicochemical Behavior of Engineering Materials in Ammonia and its Derivatives (Education Example)

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Abstract

The aim of this work is to analyze how to teach physicochemical behavior of engineering materials in ammonia and its derivatives, corrosion mechanism, mitigation, preventive and monitoring measures.

Ammonia is one of the most interesting and important substances in chemical and other industries and in life, probably after water. Despite there are many books about behavior of materials in water, I have not found even a book about corrosion resistance of engineering materials to ammonia and its derivatives. This information is dispersed in different literature sources. Some data are contradictory. Usually, a scientist or an engineer should gather, describe, analyze this literary material and then deliver to audience.

Ammonia is used in liquid and gaseous states, and as a solution in water. Ammonia is one of paradoxical chemical compounds and is the source of producing of hundreds of materials, for good and bad, for people life and death: fertilizers and explosives.

Many physicochemical processes in chemical, oil and natural gas, refining, petrochemical and metallurgical industries are realized with the participation of ammonia and its derivatives under harsh conditions: from -33°C to $+1,100^{\circ}\text{C}$ and from vacuum to 80 MPa. It is important to know the behavior of engineering materials under different conditions because implementation of these technologies is associated with process safety.

Ammonia has many-faced corrosive properties. It is a corrosion inhibitor of carbon steel in aqueous solutions of electrolytes, but it is highly corrosive towards copper, zinc, nickel and their alloys. Anhydrous liquid ammonia can cause stress corrosion cracking (SCC) of vessels made of carbon steel at -33°C . Copper alloys also are susceptible to SCC in aqueous ammonia and amine solutions at ambient temperature.

Ammonia is a commonly used nitriding gas for case hardening of steel at $500-590^{\circ}\text{C}$. Furnace equipment subjected to these service conditions suffers brittle failures because of nitridation attack.

General corrosion of copper, zinc and nickel occurs in aqueous ammonium solutions with the formation of complex compounds. Fouling, under deposit, pitting corrosion occur on carbon steel and titanium surface in oil refinery equipment when ammonia is injected for corrosion control (neutralizing) and undesirable ammonium chloride and ammonium sulfide deposits are formed.

In this work, I summarize the experience of physicochemical behavior of engineering materials (mostly metals and alloys) in contact with ammonia, its aqueous solutions and derivatives under various conditions, remedies against corrosion, and corrosion monitoring methods. This knowledge is essential for teaching, education, design, maintenance, and safety process in chemical and other industries dealing with ammonia and its derivatives.

Keywords: *corrosion education, ammonia, engineering materials, mitigation, monitoring.*

Introduction

*«All substances are poisons; there is none which is not a poison.
The right dose differentiates a poison from a remedy».*

(*Von der Besucht*, Philippus Aureolus Theophrastus Bombastus von Hohenheim, 1567)
a Swiss doctor Paracelsus.

Approximately 12 elements are essential to plant growth. Of this, nitrogen is the main nutrient and is required in much larger amounts than any other element. Ammonia is the principal source of fertilizer nitrogen, and most of the ammonia production in the world is applied directly to the soil or used in the manufacture of urea and other important nitrogen-base fertilizers (ammonium nitrate, ammonium phosphate), nitric acid, acrylonitrile and other nitrogen compounds [1, 2].

Ammonia is one of the most interesting and important substances in chemical industry and in life, probably after water. Despite there are many books about behavior and resistance of materials in water, I did not find a book about chemical resistance of materials in ammonia and its derivatives. This information is dispersed in different literature sources [3-6].

Ammonia, or azane (according to IUPAC – International Union of Pure and Applied Chemistry), is a compound of nitrogen and hydrogen, NH_3 [7]. Ammonia is used in liquid and gaseous states, and soluble in water and aqueous solutions of electrolytes. Ammonia is one of paradoxical chemical compounds and is the source of producing of hundreds of materials, for good and bad, for people life and death: fertilizers and explosives, to name a few.

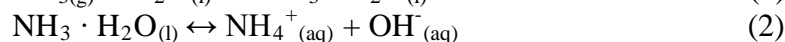
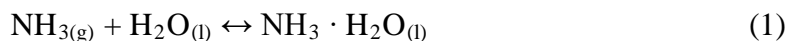
Ammonia synthesis from nitrogen and hydrogen gases is carried out at 400-500°C and 15-30 MPa [3, 8]. Ammonia is transported on highways (in tanker trucks), by railways, in pipelines, and on barges. Exposure to the general public can occur from accidents during transportation on highways and railways, during transfer between transportation vessels and storage vessels, by accidental releases at manufacturing facilities, and from farming accidents during agricultural soil application. Many physicochemical processes in chemical and other industries are realized with the participation of ammonia and its derivatives under harsh conditions: from -33°C to +1,100°C and from vacuum to 80 MPa; from very acidic to very alkali solutions. Such severe and wide conditions put forward requirements to materials suitable and resistant under these harsh conditions, because implementation of technologies with ammonia participation is associated with processes safety, namely, with possible explosions, fires, and release of hazardous substances. Safety of a plant can be improved but cannot be guaranteed [9]. Though ammonia plants exist 100 years and have well proven technology, there are failures of process equipment, and many of these are not reported in literature.

People who just begin to deal with selection of materials in contact with ammonia and its derivatives, may be confusing. In some MSDS (material safety data sheet) about ammonia, one can read that “*ammonia has alkaline properties and is corrosive*”. However, it is not indicated to which materials ammonia is corrosive. In some text books it is written that “*ammonia and ammoniacal solutions generally do not present difficult corrosion problems*”. It is necessary to indicate specific materials which are influenced and not influenced by ammonia and its derivatives and under which conditions. In my opinion, there are no corrosive or non-corrosive chemicals like there are no poisonous or non-poisonous compounds. This depend on metal and environment (chemical type, its concentration and conditions).

In this work, I analyze physicochemical resistance of engineering materials to ammonia and some of its derivatives. This knowledge is important during design, fabrication, safe operation, inspection, maintenance, and failure analysis.

Chemistry of ammonia

Ammonia (NH₃) is an alkaline gas, colorless and lighter than air. It is well soluble in water (34% at 20°C), highly corrosive to copper, zinc, nickel and some of their alloys. In solution, the following equilibria exist [8]:



The pH of a 1% aqueous solution is 11.7; 0.1N – 11.1; 0.01N – 10.6 [10]. Ammonia is extremely irritating to the skin, eyes, nose, and respiratory tract, lung, and mucous membrane tissue; causes frostbite; and suffocates victims. The permissible exposure limit of ammonia is 35 ppm for short-term exposure; 300 ppm is deemed immediately dangerous to life or health. The dangers posed by either slow or explosive ammonia releases make the safe storage and transport of anhydrous ammonia an important concern for both personal at plant facilities and the general public [3, 7, 9].

Occurrence of ammonia

Ammonia is as natural as water. Scientists believe the Earth was formed about 4.5 billion years ago, and that its early atmosphere was probably created from the gases escaping from the Earth's interior. This early atmosphere probably consisted of mostly carbon dioxide (CO₂) and water vapor (H₂O), with a smaller proportion of ammonia [11]. The ammonia concentration in the atmosphere went down because it reacted with O₂ to produce N₂ or NH₃ molecules which were broken by sunlight, leaving N₂ and H₂. Ammonia is present in small quantities in the atmosphere, being produced from the putrefaction of nitrogenous animal and vegetable matter. Ammonia is present in natural waters as a result of the breakdown of organic nitrogen (mineralisation) or by the reduction of nitrates (denitrification). Ammonia and its salts are also present in small quantities in rainwater; ammonium chloride and ammonium sulfate are found in volcanic districts; and crystals of ammonium bicarbonate have been found in Patagonian guano.

Ammonia also represents an intermediate stage in nitrogen fixation - the conversion of atmospheric N₂ to fixed nitrogen and subsequent incorporation into microbial proteins. However, this remains a relatively unimportant source of ammonia compared to mineralisation. A substantial proportion of atmospheric nitrogen deposition is in the form of ammonia, although this too is a relatively minor source [12]. Although ammonia is produced in the nitrogen cycle, anthropogenic sources are more important, notably sewage treatment effluent and run-off from agricultural land. Ammonium salts are distributed in fertile soil and seawater. Ammonium chloride and ammonium bisulfide play significant role in corrosion of oil refining equipment.

Ammonia probably played essential role in the origin of life. Using a mixture of H₂O, CH₄, NH₃, and H₂ in glass tubes, under lightning, amino acids can be formed, a necessary building blocks of living organisms [13]. In living systems, ammonia plays several important roles, serving as a source of nitrogen for plants and helping maintain acid/base balance in animals. The kidneys excrete ammonium ions (NH₄⁺) to neutralize excess acid. It is produced during the normal metabolism of amino acids and is converted to urea in the liver. Liver dysfunction may lead to toxic levels of ammonia in the blood.

Recently, ammonia was detected in the upper troposphere (between 12 and 15 km height in the area of the Asian monsoon). This suggests that the ammonia gas is responsible for the formation of aerosols - smallest particles that might contribute to cloud formation [14]. Little ammonia comes from tailpipes or smokestacks. It's mainly agricultural, from fertilizer and animal husbandry, and has a profound effect on air and water quality, and ecosystems [15]. Ammonia concentrations over agricultural centers in the USA, Europe, China and India increased during the last 15 years. Gaseous ammonia is a natural part of Earth's nitrogen cycle, but excess ammonia is harmful. In the

troposphere (the lowest, densest part of the atmosphere where all weather takes place and where people live) ammonia gas reacts with nitric and sulfuric acids to form nitrate-containing compounds that contribute to aerosol pollution that is damaging to human health. Ammonia gas can also fall back to Earth and enter lakes, streams and oceans, where it contributes to harmful algal blooms and “dead zones” with dangerously low oxygen levels. No doubt that this ammonia in the environment can influence physicochemical resistance of metallic structures.

Ammonia in chemical industry

The industrial synthesis of ammonia from nitrogen and hydrogen gases has been of greater fundamental importance to the modern world (the 20th century) than the invention of the airplane, nuclear energy, space flight, television, or Internet. The expansion of the world’s population from 1.6 billion people in 1900 to 7.6 billion in 2017 would not have been possible without the synthesis of ammonia [16].

Global output of ammonia is about 176 million tons in 2014 [7] and 80-85% of it goes into nitrogen fertilizers, of which urea is by far most important. Ammonia is one of the two most important synthetic compounds, and the ammonia industry is comprised of hundreds of mostly large plants that feed subsequent syntheses of various nitrogen fertilizer compounds, fibers, animal feed, explosives, nitriles, amines, fuel, textile, dyeing and scouring, cleaner, coolant (refrigerant for deep freezing), disinfectant, neutralizer, catalyst, producing of sodium carbonate in Solvay process, nitric acid in Ostwald process, metallurgical processes, formic gas generator (for reducing atmosphere, brazing, sintering, deoxidation, nitriding) [3, 16]. Thus, physicochemical processes with ammonia participation are carried out in metallic equipment under wide range of conditions, and design engineers should know behavior of ammonia and its derivatives in contact with metallic surface.

Resistance of metals and alloys to ammonia and its derivatives

Materials of construction of equipment where ammonia and its derivatives are used are of primary importance. The processes with the participation of ammonia are considered moderately corrosive, so large number of vessels and piping are made of carbon and low-alloy steels. However, numerous application has been found for stainless steel (SS) too [1].

The following corrosives are present in different ammonia processes: ammonia, sulfur, chlorides, carbon dioxide, hydrogen, and oxygen. Ammonia that leaks into cooling towers can be converted to nitric acid by nitrifying bacteria and pose a corrosion threat to many materials [2]. We will concentrate mainly on one corrosive species – ammonia. Much of the ammonia production processes take place at high temperatures (>400°C). At these conditions, ammonia has a potential to nitriding and formation of corrosive ammonium carbamate. Liquid ammonia (-33°C) can cause SCC of stressed carbon steels or high-strength, low-alloy steels. We will describe the resistance of carbon steel, SS, aluminum, copper and their alloys, and silver to ammonia and some of its derivatives.

Carbon steel

Experimental data about carbon steel behavior in aqueous ammonia solutions are interesting and sometimes contradictory [17-22]. Even in one paper [20], one can read that corrosion rate of carbon steel in aqueous ammonia (28-30%, pH=13-14, 27°C) defined after 24 hours can differ from 0 to 8.89 mm/year; in mixture of ammonium nitrate and ammonium hydroxide solution (67%, pH=4.5-8), corrosion rate ranged from 0.0076 to 8.89 mm/year at 27°C and was 51.18 mm/year at 74-93°C (pH=3-7) [22]. Corrosion rate of carbon steel in 0.001 M NH₄OH solution at 20°C was determined 0.038 mm/year after 5 days of immersion [23]. It was shown that 2-Mercapto-Benzothiazol (MBT)

is a good corrosion inhibitor of carbon steel in this solution: 0.01 M MBT results in efficiency 94% [22].

Corrosion rates of two types of carbon steels containing 0.06% Cr and 1.89% Cr in aqueous solution of ammonium sulfate mineral fertilizer (1-40% at 20-60°C) differ significantly [24]. In 1% (NH₄)₂SO₄ solution at 20°C, corrosion rates of two steels are 0.33 and 0.16 mm/year respectively. Nonuniform corrosion occurs on all surface of carbon steel. Corrosion rates increase twice when ammonium sulfate concentration increases from 1 to 40% and 4-7 times when temperature increases from 20 to 60°C. Electrochemical polarization curves show clear passivation in 1-40% solutions at all investigated temperatures [24].

Corrosion rate of carbon steel in aqueous solution of ammonia, ammonium nitrate and urea (pH=7-10) defined after 24 hours differed from 0 to 5.84 mm/year at 27°C [21].

In many instances, corrosion has not been severe under ambient conditions [22]. However, contaminations of ammonia by different ions can be troublesome.

Corrosion rate of carbon steel in aqueous solution of ammonia, ammonium nitrate, ammonium carbonate and urea defined after one year was 1.8 mm/year; leaks were detected in unprotected vessel; the solution became dark brown in color because of corrosion products [25]. Anodically protected vessel containing the same solutions was clean [26].

Severe internal pitting corrosion of certain carbon steel storage tanks was detected in Honolulu, Hawaii which contained 25% aqueous ammonia solution [17]. This unusual corrosion (probably because of oxygen concentration cells) was investigated by the electrochemical polarization technique. It was defined that oxygen was the major factor in the corrosion of steel by aqueous ammonia solutions. However, corrosion of carbon steel can occur in both oxygen-containing and oxygen-depleted solutions. Anodic polarization curves revealed that carbon steel in both oxygen-containing and oxygen-depleted ammonia solutions can be passive. A stable passive state was observed for carbon steel in the oxygen-containing system, but not in the oxygen-depleted system. Laboratory data for these environments indicated that both anodic and cathodic protection can be applied to control the corrosion [17].

Thus, experimental data show that corrosion rates of carbon steel in some ammonia solutions are zero or negligible. This fact can be explained by passivation under some conditions in the presence of dissolved oxygen and possible application of anodic protection [22, 27, 28].

In a packed ammonia steam stripping column, a high corrosion rate of the carbon steel Raschig rings was found [30]. When stainless steel S30400 Raschig rings were used, the corrosion rate was twice as high. This was found to be due to the use of fluorinated municipal water for steam production, the fluoride distilling over with the steam, and being concentrated in the column.

Anodic protection of carbon steel and stainless steel equipment is also applied in many ammonia fertilizer solutions in chemical industry [22, 27, 28].

Nitrogen chemical fertilizers (ammonium nitrate, urea and other ammonia combinations) can be corrosive to carbon steel. Therefore, in many cases aluminum or stainless steels are used [22].

Aluminum is often adopted in refrigeration systems and storage tanks [29].

Materials of construction for ammonia are dependent on the operating temperature. In manufacture and handling, steel and cast iron are satisfactory except for high temperatures, where stainless steels S43000 and S30400 are required [29]. It was not defined the range of high temperatures (see Nitriding below).

Stainless Steels (SS)

SS found many applications in ammonia production equipment, particularly for high and low temperatures, and to avoid iron contamination. All grades of SS are resistant to NH₄OH solutions at up to the atmospheric boiling point [2].

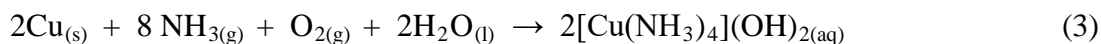
Nine types of SS are regularly used: UNS S40500, S41000, S42200, S43000, S30400, S30900, S31000, S31600, S32100 [1]. Intergranular corrosion does not appear to be a problem in ammonia production, so low carbon grades are not required. While stressed carbon steels and high-strength low-alloy steels are prone to SCC in liquid ammonia (-33°C) contaminated by dissolved oxygen (see SCC of carbon steels in liquid ammonia), SS have shown no cracking tendencies in ammonia under any conditions [1]. SS are used in the following processes [1]:

- a. Catalytic steam reforming because of resistance to oxidation, carburization, and nitriding at elevated temperatures.
- b. Ammonia synthesis because of resistance to hot nitriding gases, hydrogen attack, and excellent toughness at low temperatures.
- c. Carbon dioxide removal systems.
- d. Centrifugal turbomachinery where rotating and stationary components are subjected to erosion by high-velocity steam and corrosion by ammonium carbamate, CO and CO₂.

In general, the austenitic stainless steels are resistant to nitriding and hydrogen attack. However, nickel and its alloys exhibit the best nitriding resistance (see Nitriding). SS are used up to 816°C because they possess good high-temperature strength, ductility, and resistance to high-temperature oxidation and sulfidation. SS S30900 and S31000 are used up to 982°C [1].

Copper

Mankind's existence was related with animal husbandry and agriculture. Therefore, ammonia was always present in the environment; copper objects encountered it and corroded according to the reaction (3) to form a beautiful intensely blue copper/ammonium complex [31]:



“Season cracking”

Soldiers of the British Army in India put attention that cartridge cases of bullets made of brass were cracked after storage during the rainy monsoon season. This failure of cartridge cases was given the name of “*season cracking*” and occurred because of the presence of ammonia resulting from decomposition of organic matter containing nitrogen (horse urine, or urea, or carbamide – H₂NCONH₂), combined with the residual stress in the cold-drawn cartridge brass [32]. The ammonia reacts with the copper in the brass to form [Cu(NH₃)₄]²⁺ ions, which are soluble in water (see reaction 3). The high humidity in the air and oxygen cause these ions to dissolve and wash away, which causes cracks to form. Once the cracks start to form, the tensile stresses from cold working (residual stresses from drawing) the cartridge cases during manufacture cause the cracks to widen. Once the cracks reach a certain size, the case can suddenly fracture. Even 1 ppm of moist ammonia in the presence of oxygen can cause *cracking* of brass [29, 31]. Thus, *season cracking* can happen in any place where moist ammonia and oxygen are present: dog urine, cat urine, and common household cleaning chemicals containing ammonia. What is the solution? Not to store the cartridges in the horse stalls. Real remedy to reduce this problem is to remove the residual stress from the cartridge cases by stress-relief annealing (heat treatment at 275-350°C for 1-2 hours) them after the drawing process [33, 34].

Then stress corrosion cracking (SCC) was revealed in brass heat exchangers in the overhead of distillation columns at oil refineries (see below the Problems and solutions of ammonia use in oil refining) and in cooling water contaminated by ammonia (NH₄OH + O₂) and amines [33-35].

Ammonia SCC of thrust washers made of manganese bronze was revealed in the spillway gate at the hydroelectric dams on the Columbia River [36]. Pigeon colonies found the spillway gates to make comfortable gathering sites. The pigeon excrement provided the necessary aggressive

ammoniacal environment for the occurrence of SCC of manganese bronze thrust washers. One can choose one of the two solutions. The first solution includes a replacement for the thrust washers with a higher resistant material to SCC. Another solution is in relocation of the pigeon colony.

Polymeric materials containing or decomposing to traces of amines are a source of damage of unannealed brass. Fertilizer washing from farm land, or air over fertilized soil, has similarly caused cracking of brass [33].

Southern states of the USA farmers use ammonia as fertilizer and LPG (liquefied petroleum gas) for heating and cooking. LPG tanks have brass fittings (valves). Distributors who sell both ammonia and LPG did not clean the storage tanks and tank trucks before switching from ammonia to LPG. Residual ammonia wound up in the LPG and all the fittings cracked [29].

SCC of copper alloys can be prevented by four ways: the avoiding ammonia (containing moisture and oxygen); the removing of the residual mechanical stresses from the construction by stress-relief annealing; inhibitor treatment; painting; tin, nickel or chromium plating; and use of materials known not to crack in the specified environment [33, 34].

Zinc is not resistant to ammonia.

Aluminum and copper-free aluminum alloys

These alloys are resistant to dry gaseous ammonia from ambient to 450-500°C. Corrosion rate of EN-AW 1050 (Al 99.5) in dry NH₃ is < 0.025 mm/year at 25°C and < 0.050 mm/year at 100°C [37]. In moist gaseous ammonia, corrosion rate of aluminum and copper-free aluminum alloys is also low up to 50°C. In contrast thereto, the copper-containing aluminum alloys of the series 2xxx and 7xxx are significantly attacked in moist ammonia gas.

Water-free liquid ammonia attacks Al and copper-free Al alloys only slightly. Corrosion rate is < 0.0013 mm/year up to 95°C. For the alloy EN-AW 3003 (corresponding to AlMn) and EN-AW 5454 (corresponding to AlMg₃), corrosion rate in liquid NH₃ (with moisture <0.004 %) and 1 MPa is ~0.001 mm/year [37]. Aluminum is used for compressors, heat exchangers, evaporators and piping in the production of NH₃, and for pressure vessels for storage and transport NH₃ [2].

Silver and its alloys

These alloys are only slightly attacked by dry ammonia gas at 24°C. Uniform surface corrosion rate is < 0.05 mm/year [37]. At high temperatures silver reacts with ammonia to produce nitrides Ag₃N. In air-free aqueous ammonia solutions at 20°C, corrosion rate of silver is 0.08 mm/year. In solutions containing air, the attack is significantly higher (1.27 mm/year at 24°C) and silver cannot be utilized. Under the conditions of urea synthesis from CO₂ and NH₃, silver is resistant to attack by urea (carbamide, CO(NH₂)₂) when air is excluded [37].

Liquid ammonia

Ammonia gas condenses into a colourless liquid (“liquid ammonia” or “anhydrous ammonia”) when cooled and/or compressed.

Electrochemistry

A reference electrode has been developed to measure the electrochemical potential of alloy surfaces in liquid ammonia at room temperature and pressure 8.75 atm. [38]. The electrode consists of a pure cadmium rod in contact with a saturated solution of CdCl₂ in liquid ammonia. It has been used to establish a galvanic series in liquid ammonia to aid in engineering decisions regarding alloy

suitability for various applications. The results are similar to the galvanic series for the same metals and alloys in sea water [7, 31].

Liquid ammonia storage

Liquid ammonia is stored under the following three conditions [9, 39]:

- Cryogenic storage in large refrigerated tanks at -33°C and atmospheric pressure, often in doubled-walled flat-bottomed tanks with the capacity for hundreds or thousands of tons (10,000 to 30,000, sometimes up to 50,000) [2, 40]. Normally low temperature is maintained by the venting of ammonia gas. The vented gas is reliquefied for recycling or absorbed in water to make aqueous ammonia.
- Semi-refrigerated tanks or spheres under lowered temperature (e.g., -12°C) and increased pressure.
- Pressurized tanks at ~ 2 MPa at ambient temperatures (20 - 25°C) in spherical vessels or horizontal cylinders up to 1,700 tons [2, 41, 42].

The two main types of atmospheric tanks operating at -33°C exist [39]:

- Single wall tanks, which are tanks with one steel bottom and wall designed to contain the full liquid level of ammonia.
- Double wall tanks, which are tanks with double steel bottom and wall, each designed to contain the full liquid level of ammonia.

Tanks are designed according to the standards API 620 R or BS EN 14620-1:2006 [43, 44]. These standards have requirements for inspection of welds by radiographic and magnetic testing to ensure the good quality of the welds.

The standard type of material is low temperature certified carbon manganese steel, impact tested at or near -40°C . The susceptibility to SCC increases with increasing yield strength of the steel. Materials with a specified minimum yield strength between 290 and 360 MPa are used [39].

Ammonia is not generally corrosive to the materials selected for tank construction. The contaminants normally found are oil and water, but the quantities are normally small and the effect is positive to service life.

Carbon and low-alloy steels, stainless steels, aluminum alloys, Monel, titanium, zinc, and high nickel alloys are resistant to general corrosion in liquid ammonia during periods of 1-8 months [38]. Periodic inspection of storage tanks is very important and inspection frequency to be increased in case of older vessels. Sometimes uneven settlement of the tank foundation after long period increases the stress and results in SCC [45].

It was justified indefinite operations of an ammonia tank without the need to inspect internally for tanks having advanced safety feature [46]. A risk-based inspection (RBI) can be performed which can give the probability of failure and confidence level for ammonia storage tank can be used further for period without internal inspection. The integrity of the tank can be evaluated by a properly conducted acoustic emission (AE) test instead of an internal inspection [47]. However, AE test not always can reveal SCC [48]. Inspection performed using magnetic particle inspection discovered SCC. The SCC was found to occur mainly at the site of internal cleats and was attributed to defective welding procedures, the effect of which was aggravated by the use of high strength steel. A detailed account of the treatment of defects in this tank has been given [49].

Successful inspection of two large ammonia storage tanks which were in operation for more than fifteen years was described in [50].

Ammonia is corrosive to alloys of copper and zinc and these materials must never be used in ammonia service. Iron and steel are usually the only metals used in ammonia storage tanks, piping and fittings [41]. But under certain conditions and with few specific steels, anhydrous ammonia is liable to produce embrittlement [42].

Stress corrosion cracking (SCC) of carbon steels in liquid ammonia

Various grades of low-strength carbon steels have been in ammonia service since the 1920s. They were adequate for liquid ammonia manufacture and storage. Reciprocating compressors were used and, undoubtedly, the ammonia, which in itself was not of extraordinarily high purity, was contaminated with both oil and water. Since most ammonia was used at the point of manufacture, there was little need for over-the-road transport. Therefore, the need to construct light-weight tanks of higher strength steel suitable for road transportation did not exist [51].

Ammonia SCC in carbon steel vessels was first reported in the mid-1950s in agricultural service tanks [52]. The SCC of tanks made from carbon and low-alloy steels in liquid ammonia service has occurred since 1950 in South Africa, Finland, Denmark, Ireland, England, USA, and Lithuania [53, 54].

Causes of SCC

Ammonia SCC occurs with a brittle fracture which is a catastrophic, since the fracture can propagate at a velocity close to that of sound. The following factors influence the SCC susceptibility of carbon steel in liquid ammonia: the composition of the alloy, its metallurgical structure, heat treatment, stress level, galvanic coupling, welding practices, environmental conditions, temperature, the presence of inhibitors, and applied or residual stresses [51, 55].

The following facts were established [29, 55-59]:

1. Pure anhydrous ammonia does not cause cracking. Oxygen contamination in ammonia is the primary cause of SCC. The simultaneous presence of nitrogen contamination markedly increases susceptibility to SCC. As little as 1 ppm oxygen dissolved in liquid ammonia can cause SCC.
2. Water additions as low as 0.1 wt% and greater are effective in inhibiting SCC in ammonia contaminated with up to 200 ppm oxygen in the liquid phase. Water does not protect in the vapor phase. Hydrazine additions at the 0.025% level were also found to be effective. Addition of 0.3 wt% H₂O to anhydrous methanol-ammonia solution prevents cracking of carbon-manganese steels [58]. Nitrogen contamination increases the severity of cracking. Where water has proven effective as an inhibitor of SCC in all steel systems, it may not be adequate in a mixed metal system [59].
3. Galvanic corrosion between dissimilar metals and/or accelerated failure by SCC of stressed steel as a result of galvanic coupling may be of concern [59].
4. Post weld stress relief annealed tanks can decrease cracks in welds than tanks retaining residual stresses from welding [57].
5. Pressurized storage vessels that have a vapor zone above the liquid level may be susceptible to cracking in the vapor space, even if the liquid contains water. This cracking is caused by the condensation of ammonia without water on the walls of the vessel above the liquid level [55].
6. Ammonia SCC severity is affected by steel strength. Nickel-alloy steels and carbon-molybdenum steels are more susceptible to ammonia SCC than carbon steels [55, 60].
7. The mechanism accounting for SCC of steel in ammonia is believed to be the rupture of the corrosion-product film at sites of slip-step emergence caused by stress [56].

Mechanism

Ammonia SCC is an anodic dissolution that most often progresses via a film rupture mechanism and not a hydrogen-induced brittle fracture [29, 55]. The nature of the film has been speculated to be either an oxide corrosion product of iron or a thin nitride layer. The cracking occurs within a

specific electrochemical potential range and can be prevented via cathodic polarization. Cracks are typically filled with an oxide corrosion product [55]. The role that oxygen plays in the cracking mechanism is not clear - it may only act to change the corrosion potential to the cracking range [55].

Cracking of low-strength carbon-manganese steels in anhydrous methanol-ammonia solutions occurs at the corrosion potential only in the presence of both O₂ and CO₂; under anodic polarization O₂ is not required [58]. SCC in this system is associated with the formation of a protective film which is not an oxide and may be an iron nitride. Crack propagation is associated with an anodic process and is identical to cracking of carbon-manganese steels in anhydrous liquid ammonia [58].

Prevention of SCC of carbon steels in liquid ammonia

Prevention of ammonia SCC can be controlled by changing material and/or environment.

- a. SCC is inhibited by the addition of 0.2% water. Where water is undesirable (e.g., refrigeration) 0.025% hydrazine (oxygen scavenger) is effective [29]. A nitrogen purge to reduce oxygen concentration in a vessel is accomplished before addition of ammonia [55].
- b. Steels should possess by tensile strength <480 MPa [55, 61].
- c. Arc spray zinc coatings with 200 µm thickness protect carbon steel from SCC. The corrosion rate of zinc sprayed film is ~10 µm/y in liquid ammonia, and the blisters of zinc film are observed after ~3 years, but the preventive effect had been kept. If the thickness of sprayed zinc film on the steel is <200 µm, the cracks can be detected from on top of the film by the magnetic particle inspection [62].

Stress corrosion cracking has been detected in some liquid ammonia storage tanks operating at -33°C and in some ammonia pressure spherical tanks operating at ambient temperatures. The presence of water inhibits the formation and growth of SCC. In the USA it is customary to make sure that liquid ammonia contains at least 0.2% weight of water to inhibit SCC [63]. This phenomenon raises the question of whether SCC could also occur in carbon steel liquid ammonia pipelines. The USA and EU operators of liquid ammonia pipelines confirm that SCC is not an issue in this service [63].

Probability of cracking

The probability of ammonia SCC is the highest for carbon and low-alloy steel vessels that meet one or more of the following criteria [55]. The vessels:

- a. Contain anhydrous ammonia with oxygen content greater than 1 ppm or the vessel is frequently exposed to air internally.
- b. Cyclic pressure operation.
- c. Use of higher-strength steels (tensile strength >480 MPa), especially if not stress relieved.

Inspection

The occurrence of SCC in ammonia storage tanks/spheres has created a considerable problem in the maintenance of such storages. The procedures for isolation, emptying, purging and entry, bringing back on stream, inspection and repair are given in [64, 65].

In Europe, there are approximately 50 refrigerated ammonia storage tanks in operation [39]. Guidelines for the inspection of atmospheric, refrigerated ammonia storage tanks are described in [39]. The guidance uses a risk-based inspection (RBI) approach requiring the evaluation of the probability and consequences of failure for each individual tank. RBI approach optimizes the

inspection program between the need for knowledge about the condition of the tank and the negative effects of opening the tank for inspection which could increase the potential for SCC.

- a. Wet fluorescent magnetic particle inspection (WFMT) with an AC (alternating current) yoke on a properly prepared surface is recommended for detecting ammonia SCC [66].
- b. Ultrasonic examination of anhydrous ammonia tanks is used for determination of location, size, and orientation of cracks and other flaws [57]. However, this method is limited in sensitivity [55].
- c. Acoustic emission testing also is used in conjunction with ultrasonic examination.

The frequency of inspection may vary according to the service conditions of the particular vessel. A vessel with a high probability of cracking or one with a history of cracking should be inspected more frequently than a vessel with a low probability of cracking [55].

Failures of equipment containing ammonia

Ammonia is produced in significant quantities, which need to be transferred or transported to the user plants such as nitric acid, ammonium nitrate, urea, other chemical and petrochemical plants, and agricultural farms. Much of this transfer between sites as well as within integrated complexes takes place by pipelines, trucks, or nurse tanks. In a considerable number of cases these pipelines are close to public roads or other areas of population, and there have been several accidents with such pipelines, trucks, and nurse tanks. Therefore, safety related to these pipelines, trucks, and nurse tanks is particularly important. A few accidents are described below.

In 1973 at Potchefstroom, South Africa, an ammonia tank suffered brittle fracture which resulted in the release of 38 tons of anhydrous ammonia into the atmosphere. Eighteen people died and an unknown number were injured [67, 68]. A visible cloud extended about 300 m wide and about 450 m downwind; all deaths occurred within 200 m of the release point [59]. It appears to be the worst accident involving ammonia. There was no overpressure or over temperature of the tank contents and no other triggering event was determined. The fracture occurred in a dished end which was fabricated in carbon steel and which had not been stress relieved after manufacture. Stress-relieving does not overcome fully the damage done by progressive cold-forming of a dished end. This is particularly so where seam welds have had to be made in the dished end. Subsequent tests were conducted and found the minimum transition temperatures 20°C for the fragment and 115°C for the remaining part of the dished end. Thus, the metal was below its transition temperature under normal operating conditions.

In the Houston accident in 1976, the crash of a tanker truck released 19 tons of pressurized anhydrous ammonia. The chemical cloud extended 1,500 m downwind and was 550 m wide. Six people died; five of those died from inhaling ammonia. Another 178 sought medical attention; 78 of those were hospitalized with serious injuries. The fatalities and disabling injuries occurred within about 70 m of the accident [69].

Nurse tanks are welded steel pressure vessels used to transport anhydrous ammonia fertilizer from vendor sites to farm fields. There are hundreds of thousands of ammonia nurse tanks in use worldwide; some have been in service for more than 60 years. The steels used to manufacture nurse tanks are all low-carbon steels according to the standards ASTM A285, ASTM A455, and ASTM A516 Grade 70 [70]. In a 2012 incident near Casey, Iowa, USA, a nurse tank rapidly vented its entire contents from a fracture initiated at a crack on a leg weld. A nearby worker escaped injury by running to his truck and driving upwind away from the expanding ammonia cloud, which destroyed more than a hectare of corn plants. The failure analysis of leg welds showed that fatigue cracks occurred rather than SCC [70]. More than 9% of 532 nurse tanks examined by side-angle ultrasound contained indications near the leg welds. There are 200,000 nurse tanks in use in the USA. This means that 18,000 tanks have leg-weld fatigue cracks. Nurse tanks are the only large,

pressurized packages for ammonia that do not contain manways; thus, their interior walls cannot be inspected for flaws with magnetic particle or fluorescent dye penetrant methods. It was recommended that side-angle ultrasound be considered for use in periodic nurse tank inspections [70].

There is a guidance for the inspection and leak detection in liquid ammonia pipelines [63]. The guidance focuses on pipelines transporting cold (close to the atmospheric boiling temperature of -33°C) or warm liquid ammonia.

Incidents with pipelines transported liquid ammonia

The European Gas Pipeline Incident Data Group (EGIG) [71] provides statistical information on 1123 incidents with EU liquid ammonia gas pipelines for the period 1970-2004 (Table 1).

Table 1. Pipeline (NH_3 liquid) incidents in Europe (1970-2004) [71]

<i>Cause of incident</i>	<i>% of all incidents</i>	<i>Notes for the cause of incident</i>
External interference	49.8	Digging, piling, ground works, bulldozer, excavator, plough
Construction defects/Materials failure	16.7	
Corrosion	15.1	
Ground movement	7.1	Dyke break, erosion, flood, landslide, mining
Hot-tap made by error	4.6	
Unknown	6.7	Design error, lightning, maintenance

Causes of incidents were overpressure, external corrosion, maintenance work, fatigue cracking, seam failure and an unforeseen freeze-thaw cycle. Moreover, two of the failures were the result of malicious acts. These two failures made clear that liquid ammonia pipelines (tanks and other facilities for transport) could potentially be subject to terrorist attack.

It was suggested the installation of an alarm cable, situated about half a metre above the pipeline [40]. If that cable is hit by a digging tool, it can transmit a warning signal to the control centre of the pipeline even before the tool hits the pipeline.

Nitriding (Nitridation)

Many of the operations in NH_3 production take place at high temperatures. In ammonia production, the following corrosion phenomena can occur: nitriding, hydrogen attack, temper embrittlement, metal dusting, hydrogen sulfide corrosion, and SCC [2, 41]. Nitriding will be described here. Ammonia at high temperatures and pressures may dissociate into hydrogen and nitrogen atoms. Ammonia dissociation is catalyzed by iron. The nascent nitrogen atoms have a high affinity to Fe, Mo, Cr, W, Al, Ti, Nb, Ta, Zr, Si, and reacts to form a very hard, brittle ceramic materials nitrides: Fe_4N , Fe_3N , Fe_2N , CrN , Cr_2N , MoN , MoN_2 , AlN , TiN , Ti_2N , Si_3N_4 , etc. [72].

Nitriding as a constructive process of surface hardening heat treatment (named also *case hardening*) was developed in the early 1900s. The solubility limit of nitrogen in iron is temperature dependent, and at 450°C the iron-base alloys can absorb up to 6.1% of nitrogen atoms [73]. We can compare this with maximum solubility of carbon in iron of 6.67% with iron carbide (Fe_3C) formation. When nitrogen in the alloy exceeds its solubility limit, nitrides (Fe_4N , Fe_3N – needle-like particles) precipitate out in the matrix and at grain boundaries [74]. As a result, the alloy becomes very strong and can become brittle. Ammonia is a commonly used nitriding gas for case hardening of steels, usually performed at $500\text{-}590^{\circ}\text{C}$ [2, 72]. We should differ between nitriding as a beneficial

phenomenon *case hardening* for improving wear resistance of alloys and as a harmful phenomenon resulting in brittle failures. Nitriding begins above 316°C and becomes severe above 482°C [74]. Above 410°C, preferential grain boundary nitriding may lead to microcracking and embrittlement. A loss of high temperature creep strength, ambient temperature mechanical properties (specifically toughness/ductility), weldability and corrosion resistance may result. For these reasons, steels are restricted to use at $T < 300^{\circ}\text{C}$ in NH_3 service [2]. Furnace equipment (pipes, grid supports) repeatedly subjected to service conditions at $T > 300^{\circ}\text{C}$, often suffer brittle failures as a result of nitridation attack. For Fe, Ni, and Co, only iron forms nitrides. Alloys with Ni (or Ni + Co) in excess of ~60% showed the most resistance to nitridation [72]. Austenitic SS S34700 containing ~13% Ni also can be used [2].

Problems and solutions of ammonia use in oil refineries

Ammonia was the first neutralizer and probably still the most commonly used in the overhead systems at crude distillation columns at oil refineries [31, 35, 75]. It was readily available, cheap and provided acceptable protection of the overhead condensers, air coolers, and heat exchangers. Ammonia was adapted as concentrated aqueous solution (25 wt%) or compressed gas. The use of ammonia, especially gaseous ammonia, sometimes has the problems to control the feed rate because of possible pressure changes on the unit. Another drawback of using ammonia as a neutralizer is that it nearly does not protect the area where water begins to condense. Ammonia behaves like a typical gas and is not well soluble in hot water (~100°C) and so does not enter the water when it first condenses. Opposite, hydrogen chloride is strongly attracted to the hot water and can significantly diminish the pH in such areas. However, in systems with low amounts of acid (good and sufficient desalter of crude oil) and large amounts of water present ammonia can be used successfully. Ammonia is not recommended in overhead with high concentrations of chlorides because of formation of NH_4Cl solid salt which deposits on metals' surface. This salt is very hygroscopic and hydrolyses with formation of acid underneath:



Values of pH decrease to ~1 and severe localized corrosion can occur (Figure 1).



Figure 1. *Under deposit corrosion*: corrosion pits formed under NH_4Cl acidic salt deposits on carbon steel surface (four months) [31].

These ammonium chloride corrosive deposits are removed by water washing [31, 35]. Ammonium chloride salt is completely soluble in water and insoluble in naphtha. Ammonia easily increases the pH of condensed water from 1-2 to 5.5-6.5. If too much ammonia is injected in the presence of H_2S , bisulfide (HS^-) ions are formed and bisulfide corrosion can occur [75]. It is not recommended using copper alloys in the overhead because of possible attack by ammonia. Some authors write that when Admiralty brass bundles are opened to the atmosphere for cleaning, residual ammonia in deposits can cause SCC of the tubes [35]. My personal experience with the use of heat exchangers made from Admiralty brass C44300 tube bundles in the overhead of distillation columns at the oil refinery during 22 years showed that no bundle suffered from ammonia or amine SCC. However, they were sometimes attacked by hydrogen sulfide [31, 75]. Brass condenser tubes

do not crack in boiler feed water containing ammonia, because the concentration of oxygen is extremely low [33]. Similar explanation can be applied to the brass heat exchangers in the overhead of distillation column because the reduced atmosphere exists in the overhead.

Beneficial use of corrosion by ammonia and its compounds

While aqueous ammonia solution is detrimental to Cu, Zn and Ni, it has been used for many centuries to restore consciousness (as 10% NH₄OH aqueous solution) – to revive fainting people. In everyday life, ammonia is used in dyeing fabrics, removing stains from clothes and cleaning dishes, furniture, sanitary ware, jewelry, as well as washing glass, crystal, and mirrors [76].

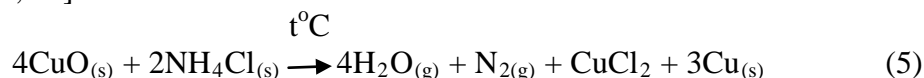
Ammonia vapor oxidizes brass to a green-brown patina. This is very close in appearance to a natural, aged patina. The antique brass patina should be protected with a coating of wax or lacquer.

Using cleaning solutions that contain ammonia, even in small amounts, to clean or polish brass components of clocks and watches could damage the very objects you are seeking to preserve.

The tendency of copper to react with ammonia was exploited in making rayon (manufactured fiber made from regenerated cellulose fiber), and the deep blue (azure) colour of the aqueous solution of cupric hydroxide in ammonia is known as Schweizer's reagent [36]. This reagent is used in production of cellulose materials such as rayon and cellophane, because wood pulp, cotton fiber, and other natural cellulose sources are soluble in the solution. Dissolved cellulose precipitates when the solution is acidified.

Ammonium bisulfite is a liquid scavenger and is used to remove dissolved oxygen from oilfield waters [77].

When ammonium chloride (NH₄Cl) deposits are deleterious and cause severe under deposit corrosion in oil refineries (see Fig. 1), the same solid salt NH₄Cl is used as a flux in preparing metals to be tin coated, galvanized and soldering metals for removal oxide film from their surface (equation 5) [7, 10]:



Similar reactions occur with participation of oxides of other metals. It is commonly used to clean the soldering iron in the soldering of stained-glass windows. The same NH₄Cl is used in "dry" galvanic cells (Leclanché cell or battery) [10].

Conclusions

1. Ammonia (NH₃) is one of paradoxical chemical compounds and is the source of producing of hundreds of materials, for good and bad, for people life and death: e.g., fertilizers and explosives.
2. Corrosion data about carbon steel behavior in ammonia aqueous solutions are contradictory because small changes in content of components (dissolved oxygen, other impurities), temperature, and contact time can significantly influence corrosion rate of steels.
3. Ammonia and ammonium hydroxide (NH₄OH) are not particularly corrosive in themselves (except Cu, Zn, Ni), but corrosion problems can arise with some materials when contaminants are present. Usually oxygen (air) contamination causes general and localized corrosion, and specifically SCC of stressed carbon or high-strength, low-alloy steels at -33°C.
4. Carbon steel is passivated in ammonia aqueous solutions under certain conditions in the presence of dissolved oxygen. Anodic and cathodic protection can be applied in these solutions.

5. Nitriding (high-temperature corrosion) of certain alloys can occur in hot dissociated NH_3 . In this case, high-nickel (or Ni + Co) alloys (>60%) should be used.
6. As everything in nature, ammonia and its compounds can be useful in our being.

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