Physicochemical Resistance of Engineering Materials in Ammonia and its Derivatives

Alec Groysman

Technion (The Israel Institute of Technology), Haifa, Israel
The Israeli Society of Chemical Engineers & Chemists, Tel Aviv, Israel
E-mail: alecgroysman@gmail.com
Website: www.alecgroysman.com

“New and Old in the Ammonia World” 2017 Conference

15-16 November 2017, Technion, Haifa, Israel
Ammonia Use


$T = -34^\circ C$ to $+1,100^\circ C$  \hspace{1cm} $P =$ Vacuum to 800 bar

Physicochemical Resistance of Engineering Materials in Ammonia and its Derivatives?

Ammonia is one of paradoxical chemical compounds, which is used for people life and death.
Ammonia Synthesis

\[ N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \]

Steel reactor for production of ammonia, the Haber process.

Stainless Steels (SS) withstand ammonia.

Converters – SS clad: 2.5Cr-1Mo steel (to resist atomic H) with a SS 304L or SS 347 cladding and internals.

Karlsruhe Institute of Technology, Germany, 1921
**Turbine-driven centrifugal compression trains (SS)**

<table>
<thead>
<tr>
<th>Component</th>
<th>Material Type</th>
<th>Material Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buckets or shrouds on rotors</td>
<td>Martensitic</td>
<td>SS 403 (11.5-13.0% Cr) &lt; 0.15% C</td>
</tr>
<tr>
<td>Hard surface weld overlay</td>
<td>Martensitic</td>
<td>SS 410 (11.5-13.5% Cr) &lt; 0.15% C</td>
</tr>
<tr>
<td>for seating surfaces;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbines and compressors</td>
<td>Ferritic</td>
<td>SS 405 (11.5-14.5% Cr) &lt; 0.08% C</td>
</tr>
<tr>
<td>Stationary components</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Turbine-driven centrifugal compression trains (SS)

Heat exchangers (cooling water)
- Superferritics; SS 6-Mo (254SMO; AL-6XN)

On-stream instruments, valves
- Austenitic SS 304 (18Cr-8Ni)
- SS 316 (18Cr-8Ni-2Mo)

Valve stems subjected to heavy loading
- Inconel X-750 (Nickel alloy); 15Cr-26Ni-1.25Mo-2.15Ti
**Nitric Acid (HNO\(_3\))**  

**Ostwald process**

HNO\(_3\) - powerful oxidizer. SS of various kinds are workhorse materials for its manufacture and handling.

<table>
<thead>
<tr>
<th>Process</th>
<th>Conditions</th>
<th>Equipment</th>
<th>Material</th>
</tr>
</thead>
</table>
| \(\text{NH}_3(g) \rightarrow \text{NO}(g) \rightarrow \text{NO}_2(g)\) | 650 °C  
10–13 atm. | Mixer,  
burner | Inconel 600  
>72% Ni; 14-17% Cr; 6-10% Fe |
| \(\text{NO}_2(g) \rightarrow \text{HNO}_3(aq)\) | 60% | Downstream  
apparatus | SS 304L, 321; 347  
(low-carbon and stabilized grades against intergranular corrosion) |
Nitric Acid Grade – very low C, Si, P (resistant to intergranular attack).

Mo-bearing grades are oxidized

At higher T and conc. (>60% HNO_3)
Resistant to HNO_3 and intergranular attack.

SS 310L; Incoloy 800 (30-35% Ni; 19-23% Cr; >39.5% Fe);
Sandvik 2RE10 (austenitic SS: 24.5% Cr; 20% Ni; <0.015% C; <0.020% P; <0.005% S)

5% silicon grade UNS S32615 (austenitic SS):
19-22% Ni; 16.5-19.5% Cr; 46.4-57.9% Fe;
4.5-6.0% Si; 1.5-2.5% Cu; 0.3-1.5% Mo

70-90% HNO_3

Shipment and storage (>90% HNO_3) 

Aluminum alloys
\[
\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)
\]

**Oil Refinery - Crude Unit Overhead**

**Organic N-containing compounds** break down at high temperature and form \(\text{NH}_3\) – may combine with \(\text{HCl}, \text{H}_2\text{S}\) to form corrosive compounds (\(\text{NH}_4\text{Cl}, \text{NH}_4\text{HS}\)).

**Fouling:** \(\text{NH}_4\text{Cl}(s), \text{NH}_4\text{HS}(s)\)

**Solution:** Water wash

**Notes:**
- Corrosion Probe (mm/yr)
- N - Neutralizer
- C.I. - Corrosion Inhibitor
- w - west
- e - east
Under deposit corrosion

\[ \text{NH}_4\text{Cl}_\text{(s)} + \text{H}_2\text{O}_\text{(l)} \rightarrow \text{HCl}_\text{(aq)} + \text{NH}_4\text{OH}_\text{(aq)} \]
\[ \text{pH} \sim 1 \]

\[ \text{NH}_3\text{(g)} + \text{H}_2\text{O}_\text{(g)} \]

Can we control corrosion phenomenon?

Washing!
Ti alloys (ASTM B338)

Gr. 7 (+0.15% Pd)

Gr. 12 (0.3% Mo + 0.8% Ni)

Resistant to crevice under deposit corrosion \((\text{NH}_4\text{Cl})\)

\(\text{Ti} – 0.9 \text{ mm}\) Thickness of tubes \(\text{C.S.} – 2.336 \text{ mm}\)

Distillation column Overhead
Ammonia has “two corrosive faces”

Protective

for iron

Agressive

NH₃

for copper

The Iron Pillar of Delhi

1600 years!

Urea

NH₃(g)

Soil bacteria

enzyme urease
Ammonia and Ammonium Hydroxide

\[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

1.0 M \(\text{NH}_4\text{OH}_{(aq)}\) \(\text{pH} = 11.6\)

0.1 M \(\text{NH}_4\text{OH}_{(aq)}\) \(\text{pH} = 11.1\)

0.01 M \(\text{NH}_4\text{OH}_{(aq)}\) \(\text{pH} = 10.6\)

Ammonia itself is noncorrosive to CS (except for SCC in the anhydrous state), but can become corrosive by contamination with \(\text{H}_2\text{O}, \text{O}_2, \text{CO}_2\).

Al and its alloys

Al and copper-free Al alloys are resistant to dry \(\text{NH}_3(g)\) up to 500\(^\circ\)C.

Corrosion Rate (CR) of Al 1050 (99.95%) in dry \(\text{NH}_3(g)\) is <0.025 mm/year at 25\(^\circ\)C and <0.050 mm/year at 100\(^\circ\)C.

In moist \(\text{NH}_3(g)\), CR of Al and Cu-free Al alloys is also low up to 50\(^\circ\)C.

In contrast thereto, the copper-containing Al alloys of the series 2xxx (Cu) and 7xxx (Zn-Mg-Cu) are significantly attacked in moist ammonia gas.
General corrosion of Cu, Zn, Ni occurs in ammonium solutions with the formation of complex compounds.

Although Cu and its alloys are not corroded by dry NH$_3$(g), they are rapidly attacked by moist NH$_3$ and NH$_4$OH. Corrosion is caused by the formation of complex soluble copper ammonia compounds.

Ammonia in the presence of moisture and air may cause SCC ("season cracking") of Cu alloys.

1 ppm NH$_3$ causes SCC of brass!

The problem was solved by annealing the brass cases after forming so as to relieve the residual stresses.
Hot-dip Zinc-Aluminum-Magnesium (ZAM) alloy coated steel sheet

ZAM® shows better resistance to ammonia than hot-dip zinc-coated and hot-dip 55% aluminum-zinc alloy coated steel sheet

Corrosion weight loss of coated steel sheets in ammonia water

Buildings and Equipment in Agriculture

ZAM® (Zn, 6% Al, 3% Mg Alloy Coated Steel)
Metals and Alloys in Liquid Ammonia (-34° C)

Carbon and low alloy steels, SS, Al alloys, Monel, Ti, Zn, and Ni alloys.

Weight loss: Periods of 1 and 8 months in an autoclave

Most metals and their alloys (general corrosion) – resistant to liquid NH₃.

Water-free liquid NH$_3$ attacks Al and copper-free Al alloys slightly. Corrosion rate is <0.0013 mm/year up to 95°C. For the Al 3003 (AlMn) and Al 5454 (AlMg), corrosion rate in liquid NH$_3$ (with moisture <0.004 %) and 10 bar is ~0.001 mm/year.

[Corrosion Handbook, DECHEMA, Germany, 2008]

Liquid ammonia can attack rubber and certain plastics.
Liquid Ammonia is stored under three conditions:
1. Cryogenic storage: -34°C, 1 atm. (large tanks).
2. Containing the ammonia under 21 atm. at 25°C.
3. Semirefrigerated storage: $T\downarrow$ and $P\uparrow$

CS, alloy steel, and high-strength, quenched and tempered steel, under applied or residual stress and especially when cold formed and/or welded without subsequent thermal stress relief, are subject to failure by SCC in air-contaminated dry liquid NH$_3$. 
Ammonia SCC in carbon steel vessels was first reported in the mid-1950s in agricultural service tanks.


In most cases, the developing cracks have been detected by inspection before leakage or rupture.

However, there have been a few catastrophic failures:
- France, 1968, a tanker ruptured, killing 5 people.
- South Africa, 1973, large tank failed, 22 fatalities.
- Dakar, Senegal, 1992, tank rupture, 129 deaths, 1,150 injured.
Facts (1980s):

(1) Oxygen contamination in ammonia is the primary cause of SCC. As little as 1 ppm oxygen in liquid phase will cause SCC.

(2) NH₃ SCC is accelerated by:
- Cold work;
- Welding;
- Applied stresses;
- The use of higher-strength steels (tensile strength > 480 MPa).

(3) Ni-alloy steels and carbon-Mo steels are more susceptible to ammonia SCC than CS.

(4) Pure anhydrous ammonia does not cause cracking.

(5) There is a problem area with vapor phase of NH₃ tank.

(6) Water additions above 0.1 wt% are effective in inhibiting SCC in NH₃ contaminated with up to 200 ppm O₂ in the liquid phase. (Philosophy)
Mechanism

NH$_3$ SCC is an anodic dissolution that progresses via a film rupture.

The nature of the film: an iron oxide or a thin nitride layer.

Cracks are filled with an oxide corrosion product.

The cracking occurs within a specific electrochemical potential range.

The role that O$_2$ plays in the cracking mechanism is not clear — it may only act to change the corrosion potential to the cracking range.

When ammonia SCC does occur, cracks progress at a relatively slow rate compared to other SCC phenomena.

Cracking strongly depends on the strain rate applied to the material. Cyclic variations of stress may result in much more severe cracking than would occur in steady-state operation.
Prevention

Practical Operating Guidance:
Design, Fabrication, Operation, Inspection, Maintenance!


Vessel Design

1. Steels - tensile strength < 480 MPa.

2. Fabrication defects can act as sites for initiation of \( \text{NH}_3 \) SCC because of stress concentration. Shot peening has been suggested as a technique for stress modification, but no practical experience has been reported.

3. Postweld heat treatment (thermal stress relief) at 595\(^\circ\)C.

4. The hardness of welds < 225 HB.

Cathodic Protection by Zinc Spray

To flame spray zinc onto susceptible areas, such as welds.

Cracking cannot be prevented by conventional cathodic protection (galvanic or impressed current) because of the high resistivity of dry \( \text{NH}_3 \).
Ammonia Purity

1. Maintaining sufficient purity of the anhydrous NH$_3$, particularly with respect to oxygen content (< 1 ppm). A commissioning procedure to reduce oxygen in a vessel via a nitrogen purge before addition of NH$_3$.

2. Addition 0.2% (mass) water as an inhibitor only in liquid phase. Water is not an inhibitor, when is added after SCC is detected.

Maintenance

To control cyclic pressure operation.
Inspection Techniques

Wet Fluorescent Magnetic Particle inspection.

Detection of small cracks has not always been successful using visual, dye penetrant, or radiographic techniques. Ultrasonic examination has detected some cracks, but is limited in sensitivity.

Acoustic emission in conjunction with ultrasonic examination.

Any tank that has not been so inspected and has been in service longer than 2 years should be inspected at the first opportunity.

This is one of the reasons of stopping of exploitation of carbon steel ammonia storage tank in Haifa, Israel in 2017.
Nitriding (Nitridation)

Nitriding is a heat treating that diffuses N into the surface of a metal to create a case-hardened surface. Low-carbon, low-alloy steels, medium and high-carbon steels, Ti, Al, Mo (1913-1924).

In 2015, nitriding was used to generate unique duplex microstructure (martensite-austenite, austenite-ferrite) – enhanced mechanical properties.

Typical application: gears, crankshafts, camshafts, cam followers, valve parts, extruder screws, die-casting tools, forging dies, extrusion dies, firearm components, injectors, plastic-mold tools.

Ammonia is a commonly used nitriding gas for case hardening of steel at 500-590°C. Furnace equipment subjected to these service conditions suffer brittle failures because of nitridation attack.
The alloy absorbs nitrogen from the environment. When dissolved nitrogen in the alloy exceeds its solubility limit, nitrides may be formed and then precipitate out in the matrix as well as at grain boundaries. As a result, the alloy can become embrittled.

**500-1100°C**

650°C  **Surface nitride layer**

1090°C  **Internal nitrides, mostly CrN, Cr₂N, and/or (Fe, Cr)₂N.**

SS 310: (24-26%)Cr; (19-22%)Ni

Morphology of nitrides formed in ammonia at 650°C and 1090°C for 168 h
Alloy X: (43-53)Ni; (20-23)Cr; (17-20)Fe; (8-10)Mo; 1.5Co; 0.6W

650°C Surface nitride layer

1090°C Internal nitrides, mostly CrN, Cr₂N, and/or (Fe, Cr)₂N.

Morphology of nitrides formed in ammonia at 650°C and 1090°C for 168 h

The resistance of SS to nitriding depends on alloy composition, ammonia concentration, and T.
Most metals form nitrides, except Ni and Co. Therefore, Fe-base alloys are generally more susceptible to nitriding attack than Ni- and Co-base alloys. Ni is the most effective alloying element in improving nitriding resistance. Alloys with at least 50% Ni or Ni + Co are most suitable.
<table>
<thead>
<tr>
<th>Material</th>
<th>Ni Content, %</th>
<th>Corrosion Rate, mm/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ammonia Converter&lt;sub&gt;a&lt;/sub&gt;</td>
</tr>
<tr>
<td>446</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>304</td>
<td>9</td>
<td>0.01</td>
</tr>
<tr>
<td>316 (2.23 Mo)</td>
<td>13</td>
<td>0.01</td>
</tr>
<tr>
<td>309</td>
<td>14</td>
<td>0.006</td>
</tr>
<tr>
<td>330 (0.47 Si)</td>
<td>34</td>
<td>0.0015</td>
</tr>
<tr>
<td>330 (1.00 Si)</td>
<td>36</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

<sup>a</sup>5-6% NH<sub>3</sub>, 1,215 days at 490-550°C  
<sup>b</sup>99.1% NH<sub>3</sub>, 64 days at 500°C

Nitriding resistance of various alloys in ammonia
650°C; 168 hours

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nitrogen Absorption, mg/cm²</th>
<th>Depth of Nitrided Layer, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>188</td>
<td>1.2</td>
<td>15</td>
</tr>
<tr>
<td>230</td>
<td>0.7</td>
<td>30</td>
</tr>
<tr>
<td>600</td>
<td>0.8</td>
<td>33</td>
</tr>
<tr>
<td>X</td>
<td>1.7</td>
<td>38</td>
</tr>
<tr>
<td>310</td>
<td>7.4</td>
<td>152</td>
</tr>
<tr>
<td>304</td>
<td>9.8</td>
<td>213</td>
</tr>
</tbody>
</table>

*Alloy Haynes 188: 39Co; 22Ni; 22Cr; 14W; 3Fe; 0.04La*
*Alloy 230: 55.5Ni; 22Cr; 14W; 3Co; 3Fe; 2Mo; 0.3Al; 0.03 La*
*Alloy X (N06002): (43-53)Ni; (20-23)Cr; (17-20)Fe; (8-10)Mo; 1.5Co; 0.6W*
Corrosion of connection (T) of the urea solution injection pipe and bend into the furnace

The system is intended for neutralization NO$_x$ polluted the atmosphere. Aqueous urea solution was injected into fuel gases containing NO$_x$ at 170°C and 6 bar. Thermal insulation would have to be on outer surface of injection pipe and bend.

Carbon steel. Diameter of the pipe - 60 mm; wall thickness - 6 mm.

Failure phenomenon: Erosion and cavitation

Solutions: 1. To replace carbon steel “T” with SS 316L.

2. To keep thermal insulation undamaged and carry out its periodical inspection.
Sal ammoniac (NH$_4$Cl) was the electrolyte in Leclanché cells, a forerunner of the dry battery; a carbon rod and a zinc rod or cylinder formed the electrodes.

Use: telegraphy, signaling, electric bell work, early years of the telephone.

\[
\begin{align*}
\text{At cathode:} & \quad 2\text{NH}_4^+ + 2\text{MnO}_2 + 2e^- \rightarrow 2\text{MnO(OH)} + 2\text{NH}_3 \\
\text{At anode:} & \quad \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \\
\end{align*}
\]

It is commonly used to clean the soldering iron in the soldering of stained-glass windows.
Acids, alkalis, some salts ($NH_4F \cdot HF$) are harmful to human health and the environment.

$SiO_2 + 4 NH_4 \cdot HF_2 \rightarrow SiF_4 + 4 NH_4 F + 2 H_2O$

Ammonium bifluoride is a component of some etchants. It attacks silica component of glass.
Ammonium peroxodisulfate \((\text{NH}_4)_2\text{S}_2\text{O}_8\)

It is a strong oxidizer that is used in etching

The etchant reacts with the unprotected metal essentially corroding it away fairly quickly.
Brass patina - fuming with ammonia and salt

How to antique Brass with ammonia?