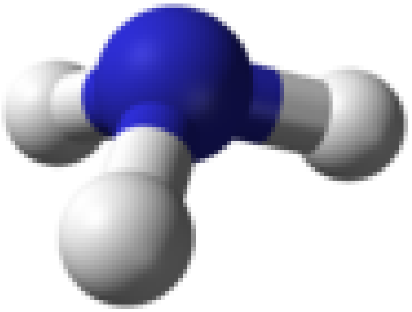
Physicochemical Resistance of Engineering Materials in Ammonia and its Derivatives



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

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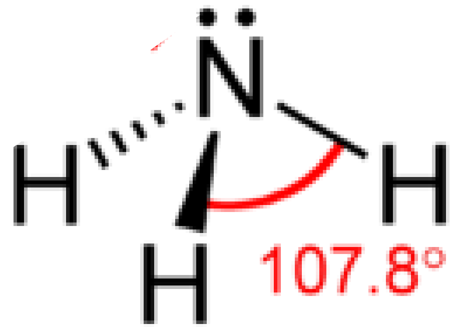
Ammonia Use

Fertilizers, Urea, Explosives, Nitriles, Amines, Fuel, Textile, Dying and Scouring, Cleaner, Coolant, Disinfectant, Neutralizer, Catalyst, Solvay process, Ostwald process, Metallurgical process, Formic gas generator (for reducing atmosphere, brazing, sintering, deoxidation, nitrization).



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

$T = -34^oC$ to $+1{,}100^oC$

P = Vacuum to 800 bar

Physicochemical Resistance of Engineering Materials in Ammonia and its Derivatives ?

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.

Turbine-driven centrifugal compression trains (SS)

Buckets or shrouds on rotors	***Martensitic***	***SS 403 (11.5-13.0% Cr)*** ***< 0.15% C***
Hard surface weld overlay for seating surfaces; Turbines and compressors	***Martensitic***	***SS 410 (11.5-13.5% Cr)*** ***< 0.15% C***
Stationary components	***Ferritic***	***SS 405 (11.5-14.5% Cr)*** ***< 0.08% C***

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.

Process	Conditions	Equipment	Material
$NH_{3(g)} \xrightarrow{\text{Pt/Rh catalyst}} NO_{(g)} \rightarrow NO_{2(g)}$	650 °C 10–13 atm.	Mixer, burner	Inconel 600 >72% Ni; 14-17% Cr; 6-10% Fe
$NO_{2(g)} \rightarrow HNO_{3(aq)}$ 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)

70-90% HNO_3

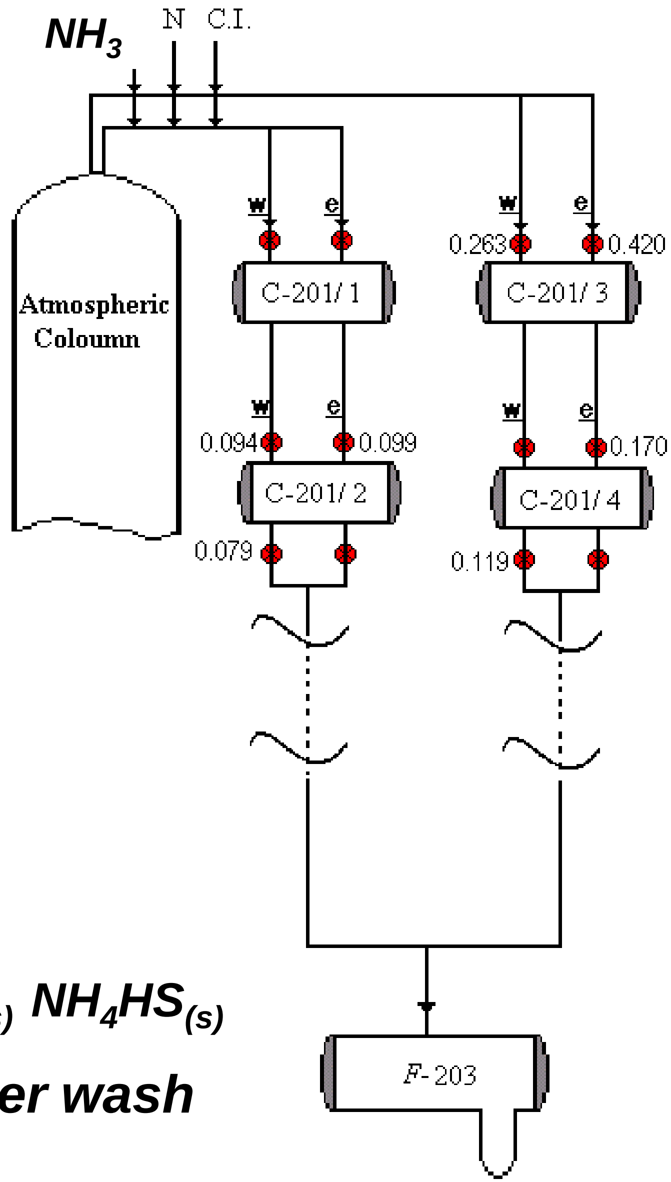
5% silicon grade UNS S32615 (austenitic SS): 19-22% Ni; 16.5-19.5% Cr; 46.4-57.9% Fe; 4.5-6.0% Si; 1.5-2.5% Cu; 0.3-1.5% Mo)

Shipment and storage (>90% HNO_3)

Aluminum alloys

Oil Refinery - Crude Unit Overhead

$H_2O_{(g)}$
$HCl_{(g)}$
$H_2S_{(g)}$
HC



Organic N-containing compounds break down at high temperature and form NH_3 – may combine with HCl, H_2S to form corrosive compounds (NH_4Cl, NH_4HS).

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

Hydrotreater Effluents

FCCU

Notes :

- Corrosion Probe (mm/yr)

N - Neutralizer

C.I. - Corrosion Inhibitor

w - west

e - east

Fouling: $NH_4Cl_{(s)}$ $NH_4HS_{(s)}$

Solution: Water wash

Under deposit corrosion

Carbon steel,
4 months
Deep shallow pits

$$NH_4Cl_{(s)} + H_2O_{(l)} \rightarrow HCl_{(aq)} + NH_4OH_{(aq)}$$

pH ~ 1

$$NH_{3(g)} + H_2O_{(g)}$$

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 (NH_4Cl)

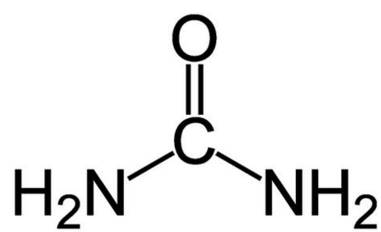
Ti – 0.9 mm | Thickness of tubes | C.S. – 2.336 mm

Ammonia has “two corrosive faces”

Protective ← NH_3 → ***Agressive***

for iron

The Iron Pillar of Delhi



Urea

$$\xrightarrow[\textit{enzyme urease}]{\textit{Soil bacteria}} NH_{3(g)}$$

Ammonia and Ammonium Hydroxide

$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$1.0\ M\ NH_4OH_{(aq)}$ pH = 11.6
$0.1\ M\ NH_4OH_{(aq)}$ pH = 11.1
$0.01\ M\ NH_4OH_{(aq)}$ pH = 10.6

Ammonia itself is noncorrosive to CS (except for SCC in the anhydrous state), but can become corrosive by contamination with H_2O, O_2, CO_2.

Al and its alloys

Al and copper-free Al alloys are resistant to dry $NH_{3(g)}$ up to 500°C.

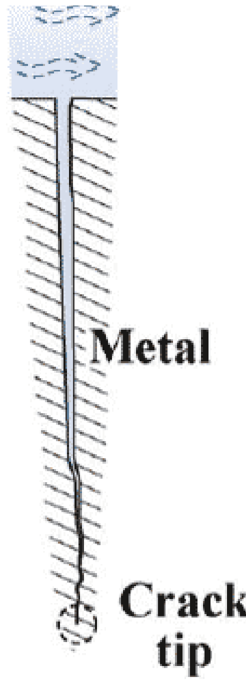
Corrosion Rate (CR) of Al 1050 (99.95%) in dry $NH_{3(g)}$ is <0.025 mm/year at 25°C and <0.050 mm/year at 100°C.

In moist $NH_{3(g)}$, CR of Al and Cu-free Al alloys is also low up to 50°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.

$H_2O + NH_3$



Although Cu and its alloys are not corroded by dry $NH_{3(g)}$, they are rapidly attacked by moist NH_3 and NH_4OH. Corrosion is caused by the formation of complex soluble copper ammonia compounds.

Cu-Zn

Cartridge before and after "season cracking"

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

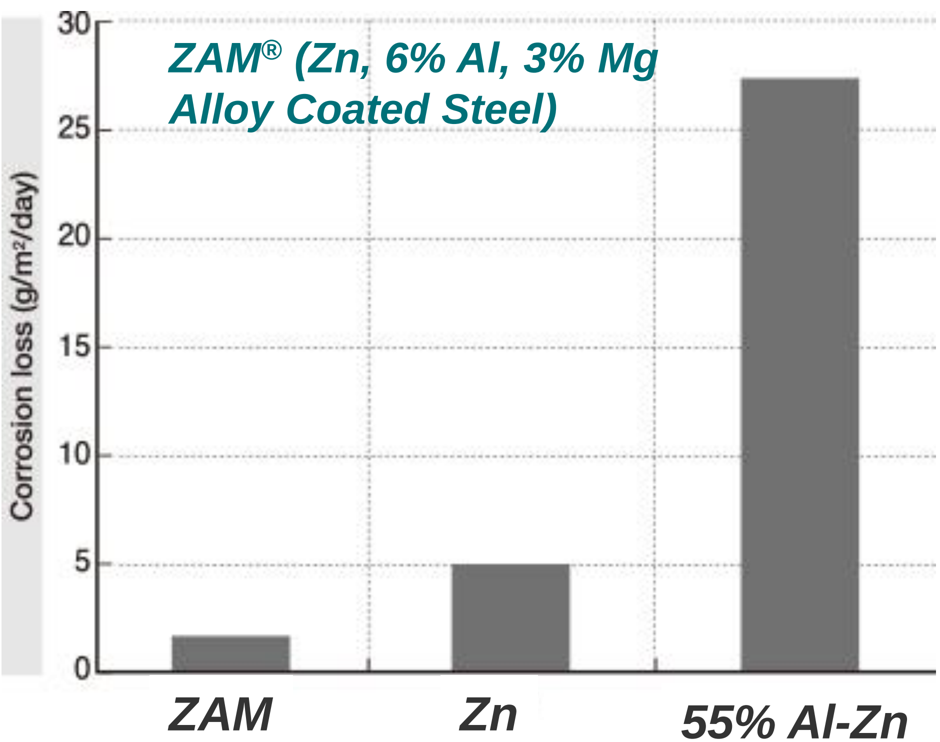
1 ppm NH_3 causes SCC of brass!

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 <u>ammonia</u> 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

Metals and Alloys in Liquid Ammonia (-34^{o}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 NH_3.

D. A. JONES, B. E. WILDE, Corrosion Performance of Some Metals and Alloys in Liquid Ammonia, CORROSION, 1977;33(2):46-50.

Water-free liquid NH_3 attacks Al and copper-free Al alloys slightly. Corrosion rate is <0.0013 mm/year up to 95^{o}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.

Stress Corrosion Cracking of Steel in Liquid Ammonia (-34°C)

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.

T.J. Dawson, "Behavior of Welded Pressure Vessels in Agricultural Ammonia Service," Welding Journal, 1956, Vol. 35, p. 568.

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) NH_3 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 NH_3 tank.

(6) Water additions above 0.1 wt% are effective in inhibiting SCC in NH_3 contaminated with up to 200 ppm O_2 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!

NACE Publication 5A192 (Revision 2017), "Integrity of Equipment in Anhydrous Ammonia Storage and Handling" (1992 – 2004 – 2017 - Reaffirmed)

ANSI K 61.1-99, "Safety Requirements for the Storage and Handling of Anhydrous Ammonia," New York, ANSI, 1999.

Health and Safety Booklet HS/G 30, "Storage of Anhydrous Ammonia Under Pressure in the United Kingdom—Spherical and Cylindrical Vessels," London, U.K., 1986.

Vessel Design

1. Steels - tensile strength < 480 MPa.

2. Fabrication defects can act as sites for initiation of 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^{o}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 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).*

A modern nitriding furnace

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

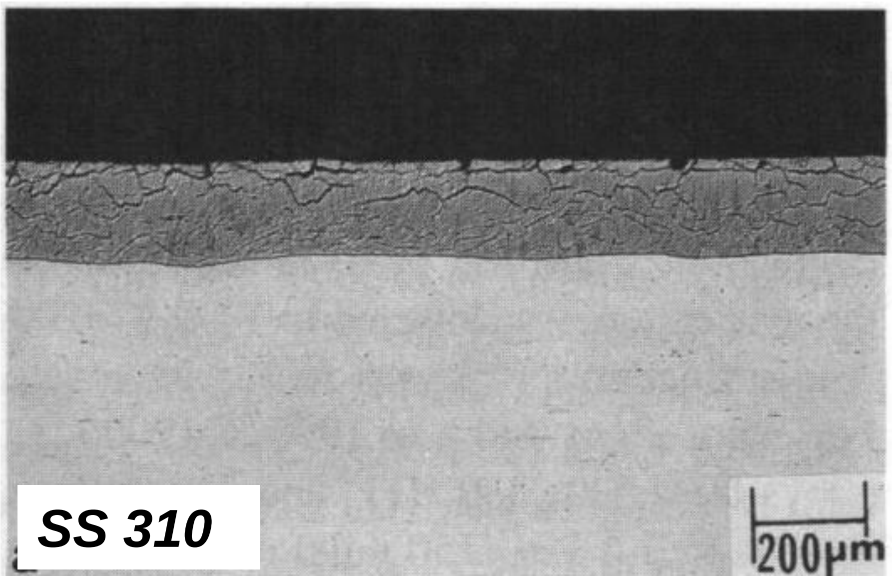
Typical application: gears, crankshafts, camshafts, cam followers, valve parts, extruder screws, die-casting tools, forging dies, extrusion dies, firearm components, injectors, plastic-mold tools.

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

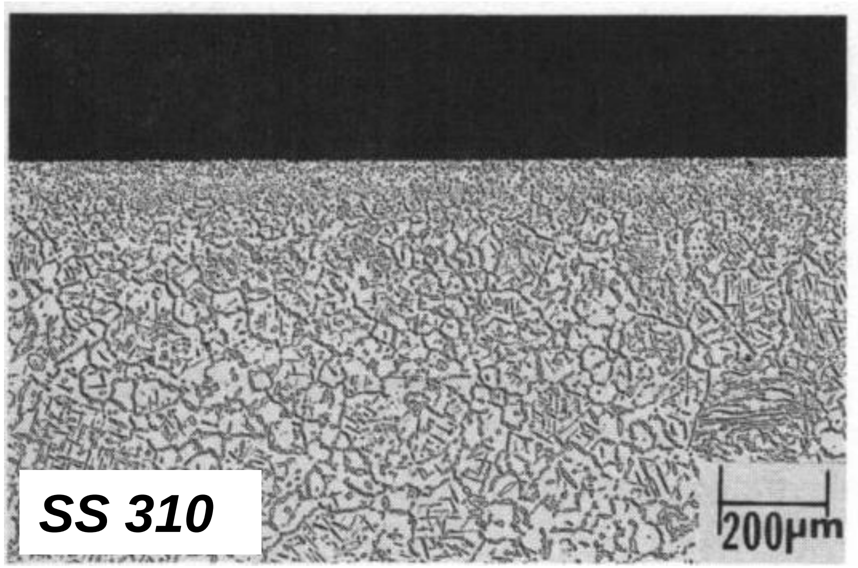
The alloy absorbs nitrogen from the environment. When dissolved nitrogen in the alloy exceeds its solubility limit, nitrides may be formed and then precipitate out in the matrix as well as at grain boundaries. As a result, the alloy can become embrittled.

500-1100^{o}C

650^{o}C   Surface nitride layer



1090^{o}C   Internal nitrides, mostly CrN, Cr_2N, and/or $(Fe, Cr)_2N$.

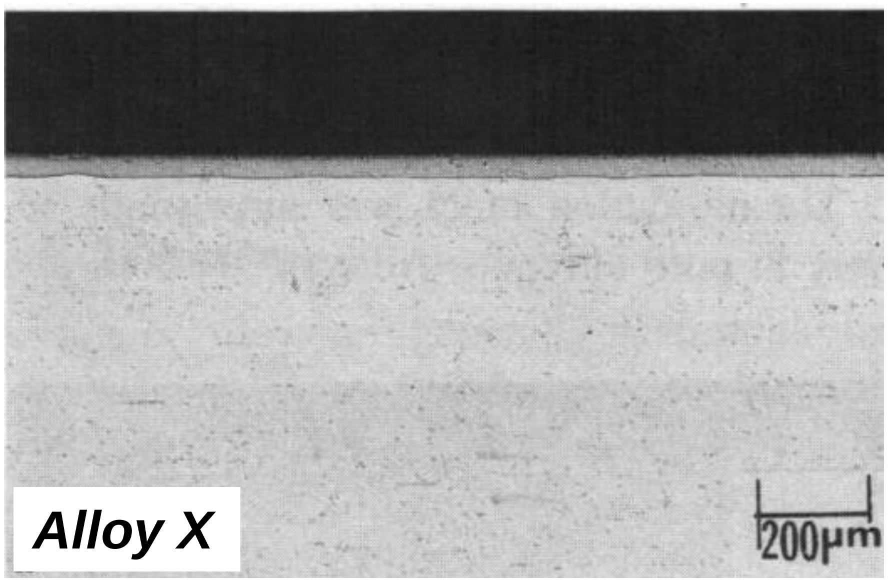


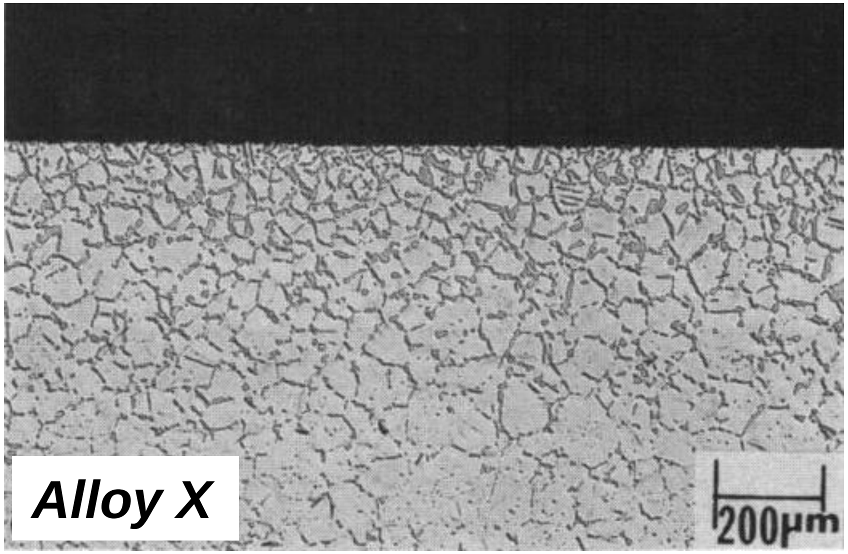
SS 310: (24-26%)Cr; (19-22%)Ni

Morphology of nitrides formed in ammonia at 650^{o}C and 1090^{o}C for 168 h

650^{o}C Surface nitride layer

1090^{o}C Internal nitrides, mostly CrN, Cr_2N, and/or $(Fe, Cr)_2N$.





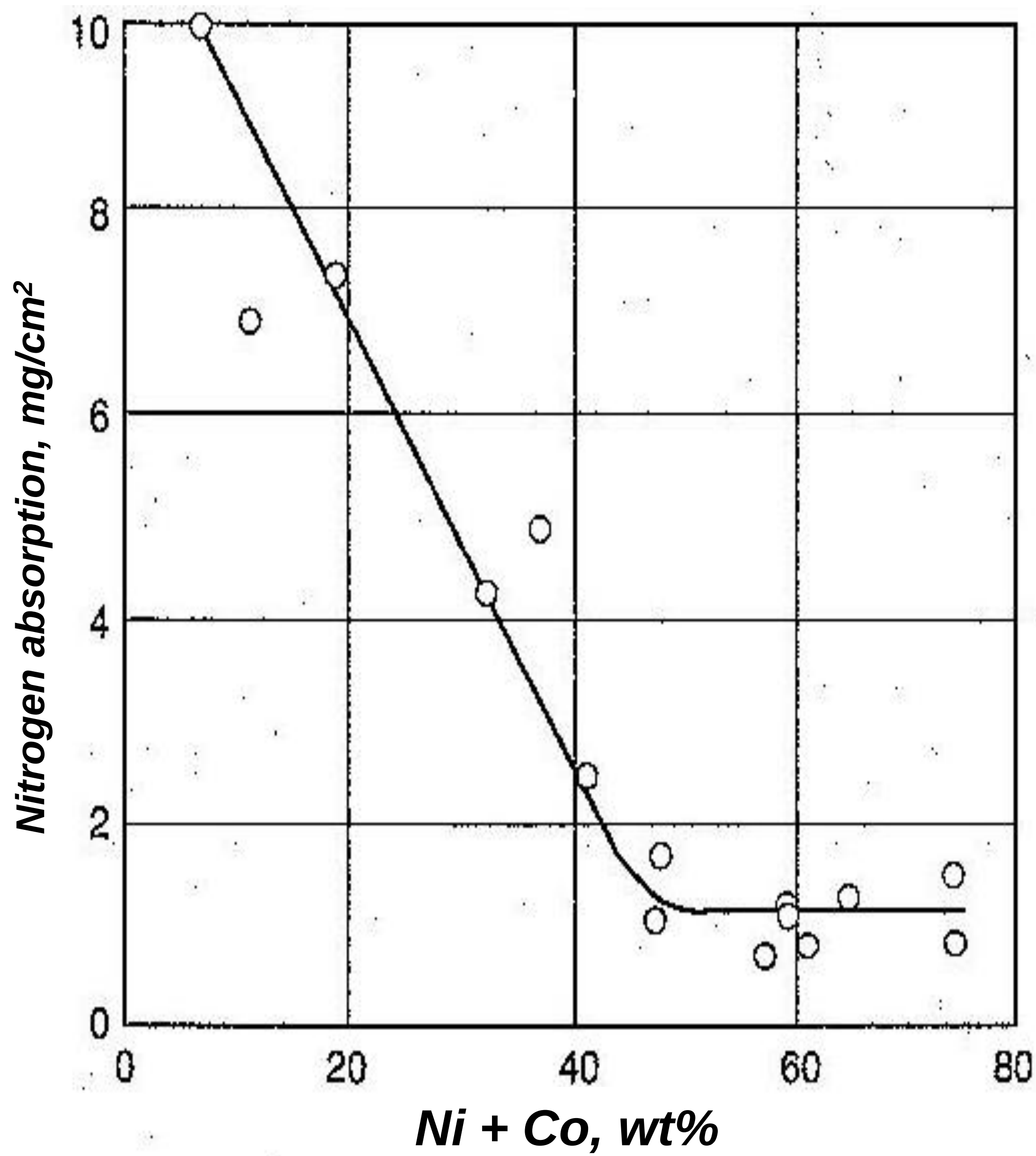
Alloy X: (43-53)Ni; (20-23)Cr; (17-20)Fe; (8-10)Mo; 1.5Co; 0.6W

Morphology of nitrides formed in ammonia at 650^{o}C and 1090^{o}C for 168 h

The resistance of SS to nitriding depends on alloy composition, ammonia concentration, and T.

Effect of Ni + Co content in Fe-, Ni-, and Co-base alloys on nitriding resistance at 650°C for 168 h in NH_3

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.



Corrosion Rates of SS in ammonia converter and plant

Material	Ni Content, %	Corrosion Rate, mm/year	
		Ammonia Converter[a]	Ammonia Plant Line[b]
446	-	0.03	4.11
304	9	0.01	2.49
316 (2.23 Mo)	13	0.01	>13
309	14	0.006	2.38
330 (0.47 Si)	34	0.0015	-
330 (1.00 Si)	36	0.0005	-

[a] 5-6% NH_3, 1,215 days at 490-550°C

[b] 99.1% NH_3, 64 days at 500°C

J.J. Moran, J.R. Mihalisin, E.N. Skinner, Corrosion, 1961, Vol. 17, p.191t.

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

Alloy	Nitrogen Absorption, mg/cm^2	Depth of Nitrided Layer, μm
188	1.2	15
230	0.7	30
600	0.8	33
X	1.7	38
310	7.4	152
304	9.8	213

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 170ºC and 6 bar. Thermal insulation would have to be on outer surface of injection pipe and bend.

7 days

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

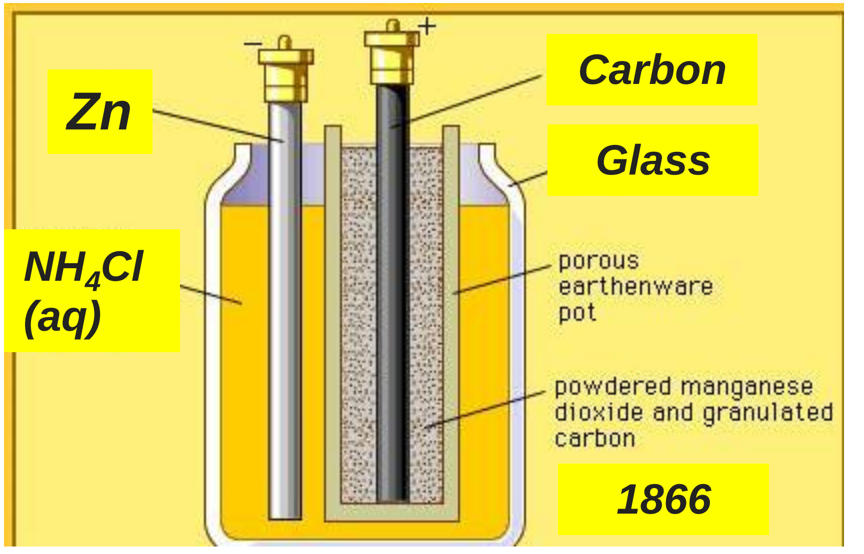
Failure phenomenon: Erosion and cavitation

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

2. To keep thermal insulation undamaged and carry out its periodical inspection.

Constructive (Beneficial) Corrosion

Sal ammoniac (NH_4Cl) 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.

At cathode: $2NH_4^+ + 2MnO_2 + 2e^- \rightarrow 2MnO(OH) + 2NH_3$

At anode: $Zn \rightarrow Zn^{2+} + 2e^-$

It is commonly used to clean the soldering iron in the soldering of stained-glass windows.

Ammonium hydrogen fluoride

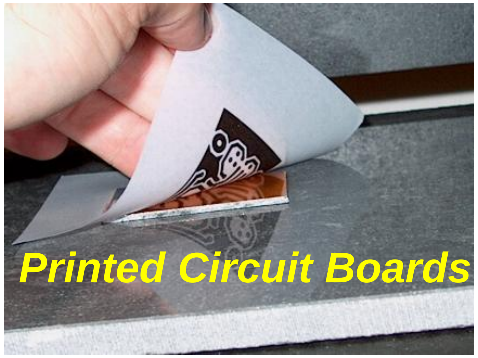
Acids, alkalis, some salts ($NH_4F \cdot HF$) are harmful to human health and the environment.

$$SiO_2 + 4\ NH_4 \cdot HF_2 \rightarrow SiF_4 + 4\ NH_4F\ \ + 2\ H_2O$$

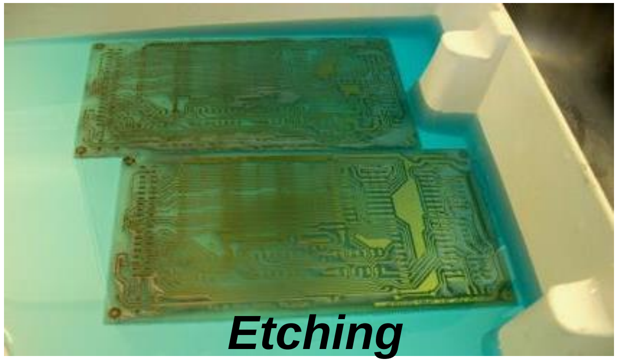
Ammonium bifluoride is a component of some etchants. It attacks silica component of glass.

Ammonium peroxydisulfate $(NH_4)_2S_2O_8$

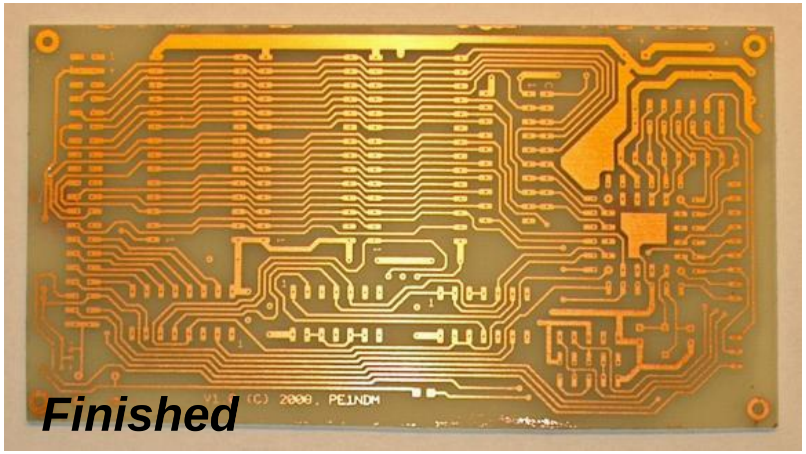
It is a strong oxidizer that is used in etching



Place layout with toner side on copper of the PCB

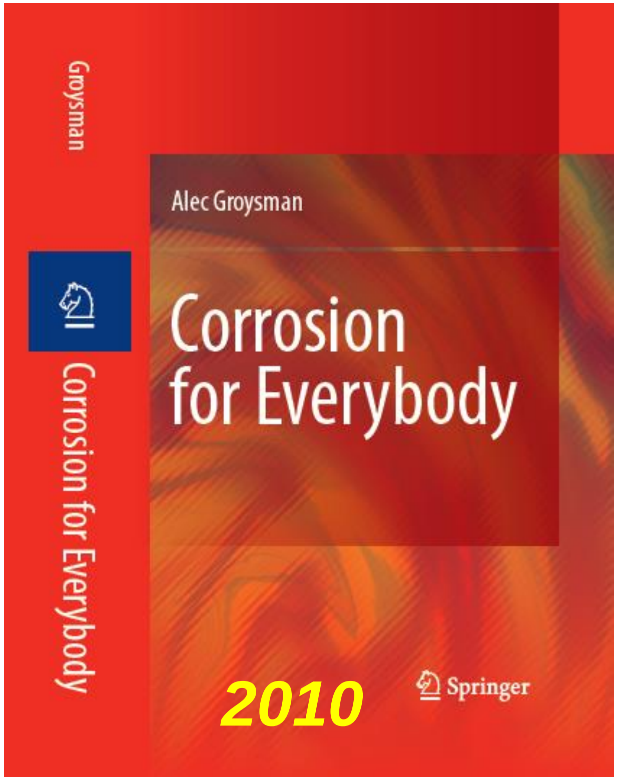


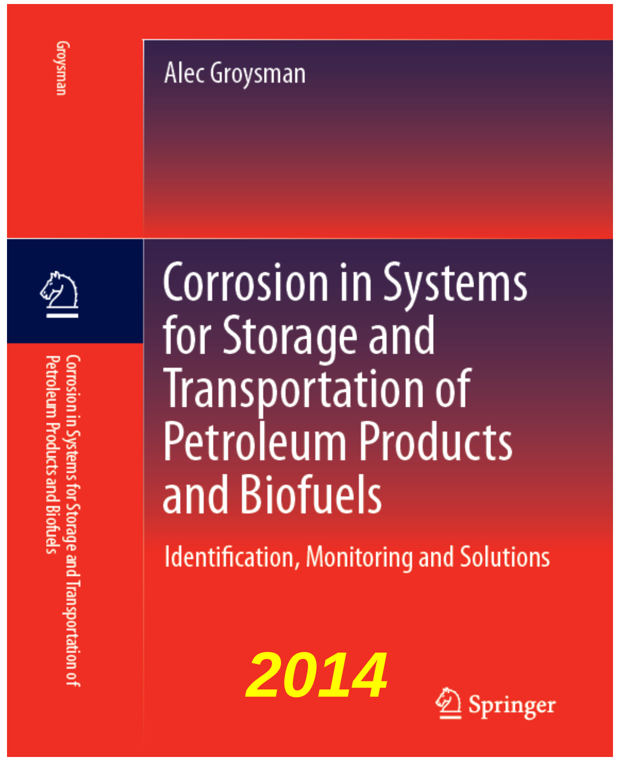
The etchant reacts with the unprotected metal essentially corroding it away fairly quickly.



Brass patina - fuming with ammonia and salt

How to antique Brass with ammonia ?


Groysman
Corrosion for Everybody
Alec Groysman
Corrosion
for Everybody
2010
Springer


Groysman
Corrosion in Systems for Storage and Transportation of Petroleum Products and Biofuels
Alec Groysman
Corrosion in Systems
for Storage and
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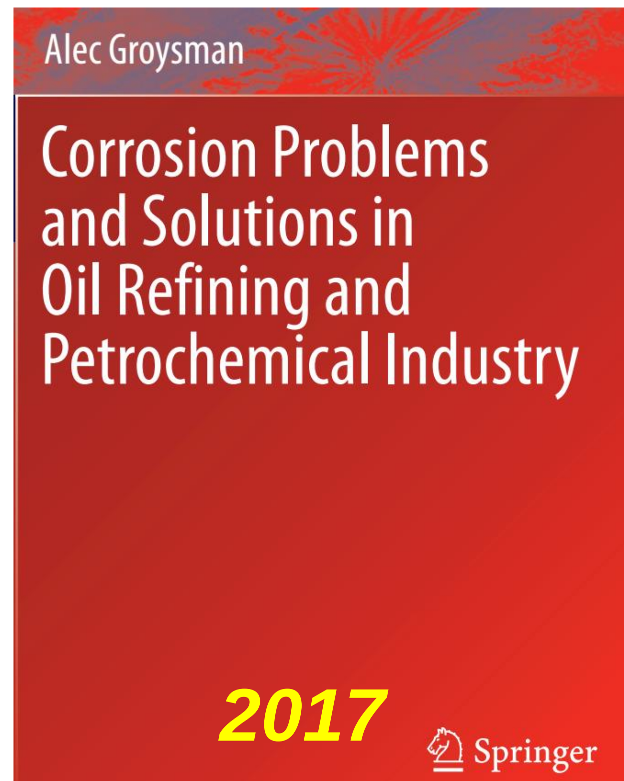
Petroleum Products
and Biofuels
Identification, Monitoring and Solutions
2014
Springer


Alec Groysman
Corrosion Problems
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Petrochemical Industry
2017
Springer