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Compatibility of Ammonia with Candidate Dry Cooling System Materials

April 1976

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COMPATIBILITY OF AMMONIA
WITH
CANDIDATE DRY COOLING SYSTEM MATERIALS

by

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April 1976

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COMPATIBILITY OF AMMONIA WITH CANDIDATE DRY COOLING SYSTEM MATERIALS

1. INTRODUCTION

Preliminary studies conducted by the Franklin Research Institute have shown some economic advantage in the use of ammonia as an intermediate heat transfer fluid in an advanced dry cooling system concept.⁽¹⁾ Figure 1 shows a comparison of the cost of generating electricity, as a function of fuel cost, for 1000 MWe plants using the indirect dry cooling system, the steam/ammonia binary cycle, the ammonia heat rejection system, the evaporative cooling system, and the "once-through" cooling system. Of the three concepts which use dry cooling towers, both the binary cycle concept and the ammonia heat rejection concept show lower costs than the conventional dry system. Of particular significance is the fact that, for fuel costs greater than about \$0.20/10⁶ Btu, the cost of electricity is less for steam turbines using ammonia in the heat rejection system than for the binary-cycle power plants.

The initial conclusion of the work at Pacific Northwest Laboratory (PNL) concerning the use of ammonia as an intermediate fluid is that, compared with other dry cooling tower designs, potential savings may result from the lower total air-side surface area, lower cost of piping between the plant and cooling tower due to reduced duct sizes, and possibly lower material costs. Operational advantages include the ability of the system to use a conventional low back pressure steam turbine, the elimination of freezing problems, and the capability for more efficient use of augmented cooling.

Major questions which must be resolved with regard to the use of ammonia as a heat transfer fluid include the following:

- ° Will the ammonia cooling cycle enhance or degrade overall plant reliability?

- ° Will the life of the dry cooling tower and major components in contact with ammonia equal 30 years or more?

The purpose of this report is to evaluate the materials which may be used for the dry cooling tower components in an attempt to answer these questions.

Figure 1. Cost of Electricity as a Function of Fuel Cost in 1000 MWe Power Plants.(1)

2. SUMMARY AND CONCLUSIONS

Candidate materials for use in the cooling cycle of a power plant ammonia heat rejection system are aluminum, carbon steel and stainless steel. Other materials are rejected as candidates on the basis of incompatibility with ammonia (e.g., copper-base alloys) or high cost (e.g., nickel-base alloys).

Corrosion of aluminum alloys 1100 and 3003 is negligible in anhydrous ammonia. Aluminum is susceptible to impingement attack by saturated, high-velocity steam; if aluminum is used in the condenser-reboiler, the first several rows of tubes must be either constructed of stainless steel or protected with stainless steel sleeves. Leakages of ammonia into the steam condensate resulting from aluminum wastage by steam impingement could result in accelerated corrosion of the aluminum tubes from the steam condensate side, since aluminum is susceptible to corrosive attack by dilute ammonia solutions. Aluminum is also susceptible to accelerated attack in air-contaminated ammonia when it is coupled with steel. This galvanic attack is inhibited if the ammonia contains 0.2 - 0.5% water.

Carbon steel is susceptible to stress-corrosion cracking in air-contaminated ammonia; susceptibility is proportional to the yield strength of the steel. Cracking is caused by levels of oxygen and nitrogen as low as 1 - 2 ppm. Water added to a concentration of 0.1 - 0.2% is effective in inhibiting stress-corrosion cracking of susceptible steels in air-contaminated ammonia. Water added to liquid ammonia may be effective in inhibiting stress-corrosion cracking of steel in contact with the vapor phase. Stainless steels of all types are resistant to corrosion in liquid and gaseous ammonia.

Leakages of ammonia through the condenser-reboiler should not have an adverse effect on condensate chemistry. In fossil-fuel plants and pressurized-water reactors, leaks of ammonia into the condensate can be easily detected and will not cause accelerated corrosion of materials in the condensate/feedwater cycle. In boiling-water reactors, ammonia is

rapidly decomposed radiolytically; the only problem caused by an ammonia leak would be an increased volume of noncondensable gases (H_2 and N_2) in the condenser.

3. DESCRIPTION OF THE SYSTEM

A simplified schematic of the ammonia-cooled system is shown in Figure 2. Exhaust steam from the turbine is condensed on the shell-side of a condenser-reboiler; ammonia on the tube side is vaporized. The ammonia vapor is then carried to the air-cooled heat exchanger where it is condensed and returned to the condenser-reboiler. The cycle has the advantage of being essentially an isothermal process; the phase change of the ammonia maintains the heat rejection surface in the dry tower at essentially the same temperature as the ammonia side of the condenser-reboiler.

Ammonia temperature will vary with turbine backpressure, the range being about 27°C (80°F) to 66°C (150°F) and the normal operating temperature being about 46°C (115°F). Figure 3 shows the relationship between turbine backpressure and saturated steam temperature.⁽²⁾ Since the transfer of heat from the condenser to the air involves phase change of the ammonia along the saturation line, pressure in the ammonia loop will also vary with turbine backpressure. Figure 4 shows the relationship between the boiling point of ammonia and the pressure. Pressure in the ammonia loop will range between 0.95 MPa (138 psig) and 2.88 MPa (418 psig), the normal operating pressure being about 1.73 MPa (251 psig).

4. CORROSION BEHAVIOR OF CANDIDATE MATERIALS

Uhlig⁽⁴⁾ classifies the materials in Table 1 as Class A for service in compressed liquid and gaseous anhydrous ammonia. Materials in Class A are suitable for critical parts where very little dimensional change can be tolerated and whose behavior is not likely to be altered materially by turbulence, changes in oxidizing or reducing power, or other incidental conditions of exposure. Monel 400, Monel K-500, Cu-Ni alloys and copper

Figure 2. Simplified Schematic of Power Plant Ammonia Heat Rejection System.

base alloys are listed as Class C materials; that is, materials not ordinarily considered suitable. These latter materials are eliminated as candidates because of their tendency to form amino copper complexes.

Figure 3. Relationship of Turbine Backpressure to Saturated Steam Temperature. (2)

The field of candidates can be further narrowed by cost considerations. Table 2⁽⁵⁾ shows recent cost data for pertinent materials.

Nickel alloys and magnesium alloys can be eliminated as candidate materials on the basis of cost. Lead is eliminated due to strength considerations. Thus the materials which can be considered as candidates for use in the ammonia cycle are aluminum alloys, carbon steel and stainless steel, with carbon steel being by far the least expensive.

Figure 4. Dependence of Boiling Point of Ammonia on Pressure. (3)

Table 1. Materials Resistant to Corrosion in
Liquid and Gaseous Anhydrous Ammonia. (4)

- Aluminum and Aluminum-Base Alloys
- Iron and Steel
- High Silicon (>14.25%) Cast Iron
- High Nickel (>18%) Cast Iron
- Chromium Steels (4-10%)
- Stainless Steels (Martensitic, Ferritic and Austenitic)
- Nickel
- Inconel 600 (79.5% Ni, 13.0% Cr, 6.5% Fe, 0.2% Cu)
- Hastelloy B (61.0% Ni, 28% Mo, 5.5% Fe)
- Hastelloy C-276 (75.0% Ni, 16.0% Mo, 5.5% Fe, 15.5% Cr, 3.75% W)
- Ni-Cr-Cu-Mo Alloy (56-57% Ni, 23-24% Cr, 8% Cu, 4% Mo, 2% W, 1% Si or Mn)
- Hastelloy D (82.0% Ni, 9.25% Si, 3.0% Cu)
- Lead
- Silver
- Noble Metals and Tantalum
- Magnesium and Magnesium Alloys
- Carbon and Graphite

Table 2. Recent Materials Costs^{(5)*}

<u>Material</u>	<u>Cost, \$/lb</u>
Aluminum, Alloys 1100 and 3003	0.598-0.67
Aluminum, Alloy 6061	0.758
Nickel, Alloy 200	3.53-3.71
Inconel 600	3.11-3.37
Lead	0.19
Carbon Steel, hot rolled	0.11-0.12
Stainless Steel 304, 316, 321	0.52-0.93
Magnesium Alloys, wrought	2.81

* These costs do not include the cost of fabrication. All prices as of about June 1975, generally for large quantities. Materials generally in sheet form.

In the following sections the corrosion performance of each of these groups of materials in ammonia is evaluated. The data presented are from the literature, laboratories currently conducting research in ammonia corrosion, and the field experience of ammonia producers and ammonia plant designers.

4.1 Aluminum and Aluminum Alloys

4.1.1 Corrosion of Aluminum In Anhydrous Ammonia and Concentrated Ammonia Solutions

Uhlig⁽⁴⁾ states that aluminum-base alloys are highly resistant to ammonia and ammonium hydroxide. Willard and Mears⁽⁶⁾ cite an example of aluminum tubing used for handling ammonia in a water cooler for over sixteen years. No serious attack occurred anywhere on this tubing, even adjacent to welds. Cross sections were cut through five regions of the tube, and the deepest penetration found was less than 0.25 mm (0.010 in.).

Aluminum alloys 1100, 3003, 5052 and 6063 showed only mild etching after one year of exposure in liquid ammonia containing 5% H₂O at 47°C (117°F). These workers⁽⁶⁾ emphasize that ammonia has very little corrosive action on most aluminum alloys and point out that ammonia has been used in contact with aluminum at temperatures as high as 260°C (500°F). Tseitlin, et al.⁽⁷⁾, state that aluminum and its copper-free alloys are compatible with gaseous ammonia at temperatures up to 450°C (842°F).

Figure 5 shows the corrosion of aluminum alloy 1100 in 80%, 90% and 100% ammonia.⁽⁸⁾ If the blank correction of 0.01 mg/cm², which was not applied to these data, is considered, it is evident that very little corrosion occurred at ammonia concentrations of 90% to 100%.

Figure 5 also indicates that corrosion of aluminum in high-concentration ammonia solutions virtually ceases after about ten days. Figure 6⁽⁸⁾ shows that the initial corrosion rates and the total metal loss which occur as a result of this initial corrosion are negligible in anhydrous ammonia. The ratio of sample area to solution volume (A/V) appears to have no effect at ammonia concentrations greater than 30%. As will be shown later, the A/V ratio is a critical variable in dilute ammonia solutions.

Recent work at the U.S. Steel Research Laboratory confirms the conclusion of Bonewitz that corrosion of aluminum in anhydrous ammonia is negligible. In this study, aluminum alloy 3003 showed a weight gain of only 7.52 mg/dm² after one month of exposure to liquid ammonia at room temperature.⁽⁹⁾

Of concern to the use of ammonia in a dry cooling application is the production of hydrogen during the initial contact period, before the aluminum surfaces become passivated. Hydrogen is produced according to the following reaction:

This reaction is assumed because the lack of attack of aluminum in anhydrous ammonia indicates that the presence of water is necessary.

Figure 5. Corrosion of Aluminum Alloy 1100 in 80%, 90%, and 100% Ammonia. (8)

Figure 6. Total Weight Loss and Initial Corrosion Rates of Aluminum Alloy 1100 as a Function of Ammonia Concentration in Water. (8)

The presence of hydrogen in the ammonia cycle of a dry-cooled plant will decrease the cooling efficiency, and only a small rate of hydrogen generation can be tolerated. Water may be intentionally added to the ammonia at levels up to about 0.5% to inhibit stress-corrosion cracking of carbon steel components (this concept will be discussed later). Experience in gas absorption air conditioners which employ ammonia as a refrigerant indicates that a small amount of residual ammonia containing up to 40% water may remain in the evaporator.⁽⁸⁾

In the condenser-reboiler of an ammonia-cooled plant, most of the aluminum surface will be exposed to anhydrous (or nearly so) liquid or gaseous ammonia. A small area, however, may be exposed to a small amount of unevaporated solution which can have a water concentration as high as 40%. This area will corrode during an initial period of approximately ten days at a rate of about $4 \text{ mg/dm}^2/\text{day}$, creating approximately $0.1 \text{ ml/cm}^2/\text{day}$ of evolved hydrogen. Pretreatment of aluminum surfaces in the condenser-reboiler to bring about passivation, thus reducing hydrogen generation during the initial service period, may be advisable.

Manufacturers of gas absorption air conditioners handle the problem of hydrogen evolution by placing a hydrogen collection tank at a high point in the system. This tank is bled periodically to remove the hydrogen.

While the problem of hydrogen evolution due to corrosion may be somewhat more prominent with aluminum, some corrosion occurs with all materials, resulting in hydrogen evolution. Thus hydrogen collection tanks are required regardless of the material of construction.

4.1.2 Corrosion of Aluminum in Dilute Ammonia Solutions

The main mechanism for the formation of dilute ammonia solutions (<30%) in a ammonia heat rejection system is leakage of ammonia through the condenser-reboiler into the steam condensate. Among the causes of aluminum condenser-reboiler leaks is erosion on the steam/condensate side of the tubes caused by impingement of saturated, high velocity steam from the turbine. This problem has been discussed elsewhere;⁽¹⁰⁾

it can be reduced by the use of clip-on stainless steel sleeves on the first several rows of tubes or by the selective placement of stainless steel tubes in this area of the condenser-reboiler.

The effect of ammonia leakages through the condenser-reboiler on condensate and feedwater chemistry will be examined in a subsequent section. The effects of such leakages on the corrosion of the aluminum tubes will be examined in detail here.

Bonewitz⁽⁸⁾ reports that in dilute ammonia solutions (up to approximately 10%), the initial rate of attack on aluminum is controlled by liquid phase diffusion of OH^- ions to the aluminum surface and is, therefore, a function of solution pH. Figure 7 shows the initial corrosion rates of aluminum alloys 1100 and 3003 as a function of pH and ammonia concentration. Above the concentration of about 10% ammonia in water this relationship between pH and initial corrosion rate is no longer observed. Above 10% ammonia decreased initial rates of corrosion are observed.⁽⁸⁾ (See Figure 6).

It has also been shown that weight loss of aluminum per unit of surface area is a function of the ratio of sample area to solution volume for dilute ammonia solutions.⁽⁸⁾ Figure 8 illustrates this effect for aluminum alloy 1100 in 0.85% ammonia solution. This figure shows that after an initial period of about 40 to 60 hours, corrosion apparently ceases, indicating that passivation of the aluminum occurs, probably as a result of the solution near the metal surface becoming saturated with dissolved corrosion product. Table 3 shows the weight losses and bulk solution corrosion product concentrations for each sample size of aluminum alloys 1100 and 3003.⁽⁸⁾ This table shows that, except for the smallest samples, corrosion ceased when the corrosion product in the bulk 0.85% solution reached an average concentration of 538 mg Al/l for alloy 1100 and 983 mg Al/l for alloy 3003. Correspondingly, corrosion of alloy 1100 in 8.5% ammonia solution ceased when the bulk solution corrosion product concentration reached about 860 mg Al/l; the 2.2 cm² specimens, which weighed about 900 mg, were completely destroyed.

Figure 7. Initial Corrosion Rates of Aluminum Alloys 1100 and 3003 as a Function of pH Controlled by Ammonia. (8)

Figure 8. Corrosion of Aluminum Alloy 1100 Samples of Various Areas in Unrefreshed 0.85% Ammonia Solution. (8)

Table 3. Corrosion of Aluminum Alloys 1100 and 3003 in Unrefreshed 0.85% Ammonia Solution.⁽⁸⁾

Sample Size, cm ²	Weight Loss, mg/cm ²		Corrosion Product Concentration; mg/l	
	Alloy 1100	Alloy 3003	Alloy 1100	Alloy 3003
2.2	36	49	99	135
29.6	12	27	444	999
105	5	7.5	656	984
206	2	3.8	515	965

These results indicate that once a critical concentration of corrosion product at the aluminum surface is reached (the magnitude of which depends on the rate of OH⁻ ion diffusion to the surface and thus to the ammonia concentration), no further corrosion product can go into solution and corrosion ceases. However, under conditions of solution renewal, no buildup of corrosion product occurs, and corrosion is continuous.⁽⁸⁾ Other workers have found that in 10% ammonia solution corrosion is continuous in renewed solution.⁽¹¹⁾

In a dry cooling application, areas adjacent to small leaks in the aluminum condenser-reboiler will be subject to continuously refreshed solution; that is, corrosion products will be continuously swept away. This would result in continuing corrosion of the aluminum in the dilute solution formed by mixing of the ammonia and steam condensate. Thus a pin-hole leak in the condenser-reboiler caused by steam erosion could result in continuing corrosion of the aluminum tubes (alloys 1100 and 3003) at a rate of between 10 and 100 mg/cm²/day (see Figure 7). Serious ammonia leakages and condenser-reboiler tube failures would result in a short time.

The situation may be more encouraging for aluminum alloys containing magnesium, such as alloys 5052 and 6061. These alloys have been noted for their superior performance in alkaline solution due to

lower solubility of their oxide films. Bonewitz⁽⁸⁾ indicates that these alloys may be expected to perform satisfactorily in dilute ammonia solution, but further studies are required.

4.1.3 Galvanic Attack of Aluminum

In studies conducted by Alcoa⁽¹²⁾ to evaluate the compatibility of ammonia with aluminum cargo tanks, it was found that aluminum coupled with carbon steel suffers accelerated corrosion due to galvanic action between the two metals. Similar galvanic effects were observed with aluminum vs. Fe_3O_4 . The presence of air is necessary for this corrosion to proceed, and the addition of water to a concentration of 0.2 to 0.5% effectively inhibits the corrosion. As will be discussed later, water should be added at about this concentration to ammonia in contact with carbon steel to inhibit stress-corrosion cracking.

Jones and Wilde⁽⁹⁾ have developed a cadmium-saturated cadmium chloride reference electrode to measure the electrochemical potential of alloy surfaces in liquid ammonia at room temperature and elevated pressure. A galvanic series of various metals and alloys in liquid ammonia has been established using this electrode; this series is shown in Figure 9 for both uncontaminated and air-contaminated liquid ammonia. Tests conducted by these workers have shown that aluminum, when coupled to steel, acts as a sacrificial anode and cathodically protects the steel against stress-corrosion cracking in air-contaminated ammonia.⁽⁹⁾

4.1.4 Use of Aluminum in DCT Ammonia Cycles

Overall it appears that aluminum is a good choice of material for use in the condenser-reboiler of a power plant using the ammonia dry cooling cycle provided the tubes are protected from steam impingement. This conclusion is based on the susceptibility of aluminum to erosion by high-velocity saturated steam and accelerated corrosion of the aluminum tubes which would result from leakage of ammonia into the steam condensate. Aluminum is a suitable material for use in the dry cooling

Figure 9. Galvanic Series of Various Metals and Alloys in Liquid Ammonia. (9)

tower where steam erosion and corrosion in dilute ammonia solutions are not a problem. Further studies may show that the aluminum alloys containing magnesium are most suitable for use in the condenser-reboiler. If aluminum is coupled with steel, water (~0.5%) should be added to the ammonia to inhibit galvanic attack of the aluminum.

4.2 IRON-BASE ALLOYS

4.2.1 General Corrosion Behavior of Iron-Base Alloys in Liquid Ammonia

Jones and Wilde⁽⁹⁾ have shown that iron-base alloys do not experience appreciable general corrosion when exposed to liquid anhydrous ammonia over a period of several months. The general corrosion performance of various materials, including iron-base alloys, in liquid ammonia is shown in Table 4.

4.2.2 General Service Experience and Corrosion Behavior of Carbon Steel

Anhydrous ammonia has been used in commercial service for the past 60 years. Carbon steel has been the major material used for the handling and storage of anhydrous ammonia. No appreciable difficulties with steel equipment used for handling and storing ammonia have been experienced in the chemical and refrigeration industries.⁽¹³⁾ Carbon steel is used satisfactorily by the ammonia production industry in ammonia coolers, condensers, separators and associated piping.^(14,15) A summary of the design parameters of some of this equipment pertinent to dry-cooling applications is given in Appendix 7.1. Maximum allowable velocities in ammonia handling equipment are 5.1 m/sec (16.7 ft/sec) for liquid ammonia and about 33.5 m/sec (110 ft/sec) for gaseous ammonia.

In the early 1950's the practice of direct application of anhydrous ammonia to the soil as a fertilizer began. At that time a large number of steel pressure vessels were placed in service for agricultural ammonia storage, transport and application. A number of

Table 4. General Corrosion Performance of Various Materials in
Liquid Ammonia⁽⁹⁾

<u>Alloy</u> <u>Designation</u>	<u>Weight Change,* mg/dm²</u>	
	<u>One-Month Exposure</u>	<u>Eight-Month Exposure</u>
Type 304 SS	0	+3.0
Type 316 SS	0	+3.4
Type 430 SS	0	+3.8
Type 410 SS	-7.52	+0.75
Aluminum Alloy 3003	+7.52	+1.9
Aluminum Alloy 5454	+12.8	+1.12
Titanium	0	+3.0
Monel	-1.5	-3.4
Inconel 600	-1.5	+2.6
Zinc	-47.0	-21.0
Iron	-2.25	-1.5
Carbon Steel	-3.76	-0.75
Hastalloy C	-1.13	+0.75
ASTM A-517 Grade F Steel	-3.0	-0.75

* + means weight gain
- means weight loss

failures of these tanks occurred; a survey indicated that three percent of the tanks in agricultural service had failed during an average of three years service because of minor leaks from what proved to be stress-corrosion cracking.⁽¹⁶⁾

Between the mid-1950's and about 1967, the service performance of ammonia transport trucks constructed of high-strength quenched and tempered steels was excellent.⁽¹⁷⁾ In 1967, however, problems with stress-corrosion cracking began to occur in ammonia-carrying trucks made from this type of steel. This may have been due to a gradual increase in the purity of the ammonia being transported; the concentrations of impurities (water, as it will be shown later) which inhibit stress-corrosion cracking was reduced. The problem was still encountered in 1971, even after the U.S. Department of Transportation adopted more stringent rules regarding ammonia purity in an attempt to eliminate those impurities contributing to the problem.

Other incidents of failures of ammonia handling equipment have had more serious consequences. In 1968 an ammonia tank truck constructed of high-strength quenched and tempered steel ruptured in Lievin, France, killing five people.⁽¹⁸⁾ Cause of this incident was attributed to corrosion cracking aggravated by fatigue. In 1973 a pressurized-storage ammonia tank in Potchefstroom, South Africa failed, releasing a total of 38 tons of anhydrous ammonia and killing 18 people.⁽¹⁹⁾ Extensive metallurgical examination of the ruptured tank indicated that the failure was a result of brittle fracture; the vessel was not stress relieved after manufacture, and the metal had been weakened by strain aging. No evidence of stress-corrosion cracking was found.⁽¹⁹⁾

Recognizing the stress-corrosion problems which became evident soon after anhydrous ammonia came into wide-spread use as a fertilizer, the Agricultural Ammonia Institute (AAI) formed a Research Committee in 1954 to investigate the causes of failure of pressure vessels in anhydrous ammonia service.⁽¹⁶⁾ An extensive research program was begun to confirm that stress-corrosion cracking was indeed the problem and to establish

the agents in ammonia responsible for the cracking.⁽¹³⁾ The results of research by this committee and by other workers will be summarized in the following paragraphs.

4.2.3 Stress-Corrosion Cracking of Carbon Steels

The first aim of the work conducted by the AAI Research Committee was to devise and test steel specimens to establish whether stress-corrosion cracking was actually occurring. Tuning fork test specimens were devised and tested in stressed only, cold-worked and stressed, and cold-worked, welded and stressed conditions. Steels tested in this initial phase of the program are shown in Table 5⁽¹³⁾ Specimens were exposed under field conditions in 3785 liter (1000 gallon) nurse tanks and 380 to 945 liter (100 to 250 gallon) applicator tanks containing agricultural grade anhydrous ammonia. The specimens were inspected for fracture or obvious cracking about once every three months.

Table 5. Steels Tested in Initial Phase of
AAI Research Committee Program⁽¹³⁾

<u>Steel</u>	<u>Composition</u>	<u>Yield Strength ksi</u>	<u>Percent Failure</u>
ASTM A-212 Grade B	0.33% C, 0.77% Mn, 0.24% Si	51	0
ASME Case 1056	0.30% C, 1.13% Mn	48	30
ASTM A-202 Grade B	0.19% C, 1.46% Mn, 0.77% Si 0.45% Cr	57	27
ASTM A-517 Grade F	0.16% C, 0.88% Mn, 0.22% Si, 0.34% Cu, 0.84% Ni, 0.53% C, 0.48% Mo	116	74

The results of this test are shown in Table 6⁽¹³⁾ During a five-year exposure period, 82 of a total of 161 stressed tuning-fork specimens failed. As can be seen from the table, the most severely stressed specimens were those in the cold-worked, welded and stressed

Table 6 Effect of Specimen Condition and Stress Level on Stress-Corrosion Cracking of Tuning-Fork Specimens in Agricultural Ammonia⁽¹³⁾

<u>Specimen Condition</u>	<u>No. of Specimens</u>		<u>Failures, %</u>	<u>Number of Specimens Failed in Number of Weeks</u>				
	<u>Exposed</u>	<u>Failed</u>		<u>0-50</u>	<u>51-100</u>	<u>101-150</u>	<u>151-200</u>	<u>201-250</u>
Cold-worked, welded, stressed	61	37	60.6	20	2	9	1	5
Cold-worked, stressed	22	12	54.5	10	0	1	1	0
Stressed only	<u>78</u>	<u>33</u>	<u>42.5</u>	<u>14</u>	<u>9</u>	<u>3</u>	<u>4</u>	<u>3</u>
Total	161	82	50.7	44	11	13	6	8
<u>Stress Level, MPa*</u>								
780 (113,000 psi)	14	8	57.0	2	1	2	2	1
605 (88,000 psi)	12	12	100.0	11	0	0	0	1
395 (57,000 psi)	17	7	41.2	1	4	1	1	0
325 (47,000 psi)	12	0	0.0	0	0	0	0	0
205 (30,000 psi)	23	6	26.1	0	4	0	1	1

*Data obtained with stressed-only specimens

condition, in which the specimens were at a very high stress level and a heat-affected zone was present. Next most severe was the cold-worked and stressed condition, followed by the stressed-only condition.⁽¹³⁾

An important trend shown in Table 6 is that, with some discrepancies, steels with higher yield strength cracked more readily than the lower-strength steels. Failures occurred more readily in the A-517 Grade F steel, with a yield strength of 800 MPa (116,000 psi), than in the other steels with substantially lower yield strengths.⁽¹³⁾ In this test 74% of the A-517 Grade F steel specimens failed, 30% of the ASME Case 1056 steel specimens failed, and 27% of the A-202 Grade B steel specimens failed. None of the A-212 Grade B steel specimens failed, a fact that is not consistent with reported stress-corrosion failures of vessels made of this steel.⁽¹³⁾

4.2.3.1 Causes and Inhibition

Following the determination that stress-corrosion cracking was indeed the cause of the failures of pressure vessels used for handling and storing ammonia, the program sponsored by the AAI Research Committee was broadened to determine the specific ammonia contaminants which cause cracking and to identify an inhibitor that could be added to the ammonia in small amounts to prevent stress-corrosion cracking.⁽¹³⁾ In a second phase of the study, the effects of air, water and other possible contaminants were studied in refrigeration-grade ammonia.

Table 7 shows the results of an initial series of tests of A-517 Grade F and AISI 4130 steels (both of which have high yield strengths) in refrigeration-grade ammonia to which air and various amounts of water were added.⁽¹³⁾ These results suggest that air in ammonia causes stress-corrosion cracking and that water is an effective inhibitor. However, the test ammonia was not analyzed and may have contained some air; this may explain why the failure frequency in uncontaminated ammonia was about the same as it was in the ammonia contaminated with air. Further tests showed that in ammonia the combined

presence of air and carbon dioxide is necessary for the occurrence of stress-corrosion cracking.⁽¹³⁾

These studies also showed that failures of steel specimens by stress-corrosion cracking in ammonia continue to occur after long exposure periods. Figure 10 shows a plot of the cumulative cracking frequencies of tuning-fork specimens with time. These specimens were exposed in ammonia without added water at various test locations. This figure shows that the highest rate of cracking occurs during the first year, but failures occurred even after five years.⁽¹³⁾

Table 7. Effects of Air and Water Additions on Stress-Corrosion Cracking of High-Strength Steels in Refrigeration-Grade Ammonia⁽¹³⁾

<u>Additions to Ammonia</u>		<u>No. Exposed</u>	<u>Specimens* No. of Failures</u>	<u>Frequency, %</u>
<u>Air</u>	<u>Water %</u>			
No	0.0	14	3	21.4
Yes	0.0	44	10	22.8
Yes	0.10	4	0	0
Yes	0.25	4	0	0
Yes	0.50	14	0	0
Yes	1.0	14	0	0
Yes	2.0	10	0	0
Yes	4.0	10	0	0

*ASTM A-517 Grade F and AISI 4130 steel tuning-fork specimens in the cold-worked, welded and stressed condition.

Figure 10. Frequency of Stress-Corrosion Cracking of Steel in Ammonia Without Added Water. (13)

This early work resulted in several recommendations from the AAI Research Committee, with the statement that all of these recommendations should be followed if stress-corrosion cracking of ammonia vessels was to be avoided. These recommendations were as follows:⁽¹⁷⁾

(1) agricultural ammonia should contain 0.2% water as an inhibitor; (2) extreme care should be exercised to avoid air contamination in ammonia systems; and (3) vessels over 36 in. in diameter should be either fully stress-relieved or fabricated with heads that are hot-formed or stress-relieved.

In 1971, following inspections which revealed that stress-corrosion cracking of ammonia transport trucks was continuing despite the adoption of rules designed to prevent it,⁽²⁰⁾ a meeting was called by the U.S. Department of Transportation to review all aspects of stress-corrosion cracking in ammonia.⁽¹⁷⁾ At this meeting the effectiveness of water as an inhibitor of stress-corrosion cracking was questioned, and it was suggested that the problem is really one of hydrogen embrittlement.⁽²¹⁾ As a result of these questions further studies were initiated to re-evaluate the effectiveness of water as an inhibitor, investigate the hydrogen embrittlement question, and determine the actual concentration of air in ammonia which causes stress-corrosion cracking.

This more recent work has made use of a constant slow strain rate procedure to determine the influence of contamination and water additions on the stress-corrosion cracking behavior of A-517 Grade F steel. In this test a tension specimen is slowly strained (strain rate = 2×10^{-6} in/in/sec) while exposed to a liquid ammonia environment at 25°C (77°F). This test can quickly indicate the metal-environment combinations that result in stress-corrosion cracking.

In general, stress-corrosion cracking markedly reduces the ductility of the specimen and results in the formation of a number of secondary cracks in the gauge length. A non-aggressive environment, on the other hand, results in cup-cone fracture with normal ductility.⁽¹⁴⁾ Severe loss of ductility is therefore a positive indication of susceptibility

to stress-corrosion cracking. However, tests conducted at Southwest Research Institute have shown that specimens exhibiting little or no loss in ductility frequently exhibit secondary cracking, indicating their susceptibility to stress-corrosion cracking. Therefore, a high ductility is not sufficient evidence to classify a specific ammonia as a non-cracking environment; visual examination of specimen surfaces for the presence of secondary cracking is also required.

In this test, percent reduction in area (%RA) is used as a cracking index. Values of %RA markedly lower than control values are indicative of stress-corrosion cracking.

Because of the skepticism expressed regarding the effectiveness of water inhibition of stress-corrosion cracking in ammonia, a series of tests was conducted at U.S. Steel Corporation's research laboratory in which water additions were made to air-contaminated ammonia. The results are presented in Figure 11 for water additions over the range of 0.02 to 1.2 weight percent.⁽²¹⁾ These data show that the previous findings⁽¹³⁾ were correct: the addition of 0.2% water inhibits stress-corrosion cracking of high-strength steels in air-contaminated liquid ammonia. Recent studies of line-pipe steels also confirm these results.⁽²²⁾

It has been learned through recent communication with the personnel at U.S. Steel⁽²³⁾ that while no index of aggressiveness of ammonia vapor versus ammonia liquid has been established, stress-corrosion cracking of structural steels has occurred in both air-contaminated ammonia vapor and liquid ammonia. In work conducted at U.S. Steel, water added to the liquid phase has been found to be effective in inhibiting stress-corrosion cracking of structural steels in the vapor phase. However, experience is limited in this area and data is conflicting.

Work completed recently at Southwest Research Institute⁽²⁴⁾ has suggested that there may be a critical zone of potential for stress-corrosion cracking of steel in contaminated ammonia. The effect of oxygen and water on the corrosion potential and its relation to the

Figure 11. The Influence of Water Content on the Stress Corrosion Cracking Susceptibility of A517 Grade F Steel in Air Contaminated Liquid Ammonia. (21)

proposed critical zone is illustrated in Figure 12. It is postulated that stress-corrosion cracking occurs between potentials E_x and E_y on the iron oxidation curve, and raising or lowering E_{O_2/H_2O} can cause or prevent stress-corrosion cracking by moving E_{corr} into or out of the potential zone between E_x and E_y . These workers have shown that in certain ammonias with moderate concentrations of contaminants, low concentrations of water are capable of causing cracking. For example, one sample did not cause cracking but when 300 ppm water was added, severe cracking occurred. A statistical equation was developed from which it may be predicted whether a particular ammonia will cause cracking; use of the equation requires that the concentrations of O_2 , N_2 , CO_2 , CH_4 , and H_2O be known. (24)

A summary of test environments used and stress-corrosion cracking results obtained at U.S. Steel is given in Table 8. Tests conducted in air-contaminated ammonia evidenced a marked decrease in %RA along with clear evidence of secondary stress-corrosion crack formation adjacent to the main fracture face. Metallographic examination of specimens at areas close to the main fracture face revealed tight branching cracks typical of stress-corrosion cracking. (21)

Table 8. Stress-Corrosion Test Data on A-517 Grade F Steel (21)

<u>Environment</u>	<u>Ave. %RA</u>	<u>Observations</u>
Laboratory Air (Control Test)	53	Ductile cup-cone fracture
Uncontaminated Ammonia	52	Ductile cup-cone fracture
Air-Contaminated Ammonia	24	Low ductility, secondary cracks evident

The vapor phase above the various ammonia samples used in the above tests was analyzed using a gas chromatographic procedure. The

Figure 12. Schematic Polarization Curves Illustrating Effect of O_2/H_2O Equilibrium Potential on Corrosion Potential. (24)

incidence of cracking appeared to parallel the detection of both oxygen and nitrogen.⁽¹⁷⁾ Addition of only oxygen or only nitrogen to uncontaminated samples failed to produce cracking; both appear to be necessary to cause the problem. These tests also showed that carbon dioxide contamination is not essential for cracking, as was previously believed.⁽¹⁷⁾

In the work conducted at Southwest Research Institute, it was found that cracking susceptibility is a function of the concentrations of all the contaminants present. Oxygen was found to be the primary cracking agent when present in concentrations below about 300 ppm; at higher concentrations oxygen tended to produce inhibition. At concentrations below about 50 ppm, CO₂ tended to inhibit stress-corrosion cracking, while at higher concentrations it tended to cause cracking. In solutions containing water and methane, nitrogen tended to inhibit cracking, but in solutions without methane and water, nitrogen tended to cause cracking. This is consistent with the U. S. Steel test results which were obtained from ammonias containing only oxygen and nitrogen. Methane was found to act as an inhibitor at all concentrations but large quantities were required to be effective.⁽²⁴⁾

To investigate the possibility that stress-corrosion cracking of high-strength steels in liquid ammonia is due to hydrogen embrittlement, tests were conducted at U.S. Steel to establish the conditions under which hydrogen absorption takes place in air-contaminated ammonia. Hydrogen permeation was found to take place at an applied cathodic current density of 40 $\mu\text{A}/\text{cm}^2$.⁽²¹⁾ If hydrogen absorption were responsible for cracking under freely corroding conditions, then testing under conditions of known hydrogen permeation (i.e., with an applied cathodic current density of 40 $\mu\text{A}/\text{cm}^2$) should cause premature cracking.

The results of tests to determine the influence of applied current (and therefore hydrogen permeation) on the stress-corrosion cracking susceptibility of A-517 Grade F steel in air-contaminated liquid ammonia are shown in Figure 13.⁽²¹⁾ This figure shows that 40 $\mu\text{A}/\text{cm}^2$ applied cathodic current density produced no stress-corrosion cracking. At all cathodic currents, cracking was inhibited. At all anodic currents,

cracking was stimulated (except in air-contaminated ammonia containing water), leading to the conclusion that the crack propagation mechanism involves an anodic dissolution step and cannot be attributed to hydrogen embrittlement.

Figure 13. The Influence of Applied Current on the Stress Corrosion Cracking Susceptibility of A-517 Grade F Steel in Air Contaminated Liquid Ammonia. (21)

4.2.3.2 Mechanism of Cracking and Inhibition

A proposed mechanism of stress-corrosion cracking of steels in air-contaminated ammonia was presented recently by Jones.⁽²⁵⁾ This mechanism is outlined below and depicted in Figure 14.

- 1) In oxygen-contaminated ammonia an adsorbed film exists on the steel surface which maintains the potential at very noble values.
- 2) During straining after yield, breaks in the film produce film-free metal, which dissolves rapidly under the noble potential imposed by direct galvanic coupling to the filmed metal surface. In the absence of any other impurity, oxygen has a tendency to refilem the bare metal and to some degree inhibits the severity of stress-corrosion cracking, depending on the concentration and strain rate.

Figure 14. Proposed Mechanism of Stress-Corrosion Cracking of Steel in Anhydrous Ammonia Contaminated with Oxygen and Nitrogen.⁽²⁵⁾

- 3) Nitrogen dissolved in the ammonia inhibits the refilming of the bare slip steps by a process of "competitive adsorption" with the oxygen and consequently increased the severity of stress-corrosion cracking through a process of adsorption rather than through a process of electrochemical origin.⁽²⁵⁾

The mechanism of water inhibition is proposed to be rapid repassivation of bare metal formed at film rupture sites due to strain.^(23, 25)

4.2.4 Corrosion Behavior of Stainless Steel

As indicated previously, stainless steels of all types are considered to be resistant to corrosion in liquid and gaseous anhydrous ammonia.⁽⁴⁾ The International Nickel Company, Inc. (INCO) states that, of the nickel-containing alloys, the austenitic stainless steels are most frequently employed in ammonia and ammonium hydroxide. Austenitic stainless steels exhibit good resistance to all concentrations of ammonia and ammonium hydroxide up to the boiling point.⁽²⁶⁾ General Atomic recommends austenitic 304L stainless steel for the ammonia condenser tubing in a binary plant design for a gas turbine high-temperature gas reactor (HTGR).⁽²⁷⁾ In this application, stainless steel condenser tubes would be compatible with both the external pressurized ammonia and the internal circulating coolant water.

4.2.5 Use of Iron-Base Alloys in DCT Ammonia Cycles

Structural carbon steels are suitable for use in the ammonia loop components, including the condenser shell and tubes, valves, storage tanks, heater feed pumps and condensate pumps.⁽²⁷⁾ However, the following recommendations should be adhered to if stress-corrosion cracking is to be avoided:

- 1- The use of high yield strength steels should be avoided. Suitable steels for various ammonia loop components are given in Table 9.

- 2- The ammonia used in the cooling cycle should contain a minimum of 0.2% water as an inhibitor. Water additions should be made with deionized or distilled water or steam condensate. Ammonia in the cooling loop and storage tanks should be analyzed at least weekly for the prescribed water content.
- 3- Extreme care should be exercised to avoid air contamination of the ammonia system. The system should be purged to an oxygen concentration of $<0.5\%$ with an inert gas followed by ammonia vapor before being filled with anhydrous liquid ammonia.
- 4- Where practical, all components of the system should be post-weld heat treated or fabricated with steel that is hot-formed or stress-relieved.
- 5- Carbon steel components should be inspected periodically using nondestructive examination methods, particularly where components are not stress relieved or where high residual stresses are known to exist; e.g., at tube to tube sheet welds or where tubes are rolled into tube sheets.

The austenitic stainless steels are suitable for use in all ammonia loop components; however, their use may be tempered by their higher cost (see Table 2).

Table 9. Suitable Steels for Various Components in the DCT Ammonia Loop

<u>Component</u>	<u>Steel</u>	<u>Yield Strength</u>
Condenser-Reboiler and Heat Exchanger	ASTM A-179	241 MPa (35 ksi)
	ASTM A-214	241 MPa (35 ksi)
Condenser Shell and Headers	ASTM A-285 Grade C	207 MPa (30 ksi)
	ASTM A-515 Type 70	248 MPa (36 ksi)
Piping	ASTM A-53 Grade B	241 MPa (35 ksi)
	ASTM A-106 Grade B	241 MPa (35 ksi)
Flanges and Fittings	ASTM A-105	248 MPa (36 ksi)

5. EFFECT OF AMMONIA LEAKAGE ON CONTROL OF CONDENSATE CHEMISTRY

Assuming complete mixing, the added ammonia concentration in the steam condensate due to leakage from the condenser-reboiler can be approximated using the general equation

$$\text{NH}_3 \text{ in Condensate (ppm)} = \frac{\text{Leak Rate} \times 10^6}{\text{Condensate Flow Rate}}$$

Using leak rates and condensate flow rates in kg/hr, the resulting NH_3 concentrations are in mg/kg (ppm). From these values the condensate pH can be calculated from

$$\text{pH} = 11.6252 + 1/2 \log \frac{\text{ppm NH}_3}{17,000}^*$$

* Derivation of this equation is given in Appendix 7.2.

A plot of condensate pH versus ammonia leak rate is given in Figure 15 for four different condensate flow rates. Typical condensate flow rate for a 1000 MWe pressurized water reactor (PWR) is on the order of 5.5 - 6.0 million kg/hr; fossil-fuel boilers of similar size will produce a condensate flow rate of about 3.5 - 4.0 million kg/hr.⁽²⁸⁾

High pressure fossil-fuel boilers utilize all volatile treatment,⁽²⁸⁾ and since the latter part of 1974 the use of all volatile (zero solids) treatment has been specified by most PWR steam generator vendors.⁽²⁹⁾ Ammonia is used to control the pH in both cases. The recommended pH range of feedwater for both high-pressure boilers and steam generators is 9.2 - 9.5;⁽²⁷⁾ this corresponds to about 1.0 ppm ammonia. In the unlikely event of an ammonia leak into the condensate on the order of 100 kg/hr, condensate pH would increase to about 10.1-10.2 (see Figure 7). The conductivity of the condensate would increase from about 5 $\mu\text{mho/cm}$ to about 30 $\mu\text{mho/cm}$.⁽²⁸⁾ Thus the leak could be readily detected; even if it were not repaired in a matter of hours or even days no damage to carbon steel, Inconel 600 or other materials in the condensate/feedwater circuit would be expected, provided that the use of copper-base alloys in feedwater heaters was avoided.

Overloading of cation-exchange resins in condensate polishers would not be a problem since ammoniated mixed-bed demineralizers are now widely used in systems using all-volatile treatment.⁽³⁰⁾

In boiling water reactors (BWR's), ammonia can be used to suppress radiolytic oxygen production by reacting with the OH radicals produced by water radiolysis. Ammonia is being used successfully for this purpose in the CANDU-BLW pressure-tube reactor at Gentilly, Quebec.⁽³¹⁾ However, the use of ammonia to reduce oxygen concentration in the coolant of pressure-vessel BWR's of the type used in the United States is not as promising, since for 1000-MWe reactor the ammonia decomposition rate due to radiolysis is in the range of 60 to 480 kg/hr or even higher.⁽³¹⁾ This would indicate that ammonia leaks into BWR condensate would be of

Figure 15. Condensate pH as a Function of Ammonia Leak Rate at Various Condensate Flow Rates, Assuming Complete Mixing.

even less consequence than in the case of fossil-fuel boilers and PWR steam generators. The only adverse effect of an ammonia leak through the condenser-reboiler would be the increased amount of noncondensable gas production; each kg of ammonia that is decomposed radiolytically gives 2600 liters of hydrogen and nitrogen at STP.⁽³¹⁾

Overall it appears that leakage of ammonia through the condenser-reboiler into the steam condensate will not be a problem of major concern for several reasons:

- 1) The condenser-reboiler can be constructed of materials which are resistant to corrosion in ammonia, thus reducing the probability of leaks.
- 2) In fossil-fuel plants and PWR's, leaks of ammonia into the condensate can be easily detected and will not cause accelerated corrosion of materials in the condensate/feedwater cycle.
- 3) In BWR's, ammonia is rapidly decomposed radiolytically; the only problem caused by an ammonia leak would be an increased volume of noncondensable gases in the condenser.

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7. APPENDICES

7.1 Design Parameters of Industrial Equipment Handling Ammonia

7.1.1 Ammonia Condensers

	<u>Company A</u>	<u>Company B</u>
<u>Shell</u>		
Material	A-285 Grade C Carbon Steel	A-212 Grade B Carbon Steel
Thickness	-	12.70 mm (0.50 in.)
Corrosion Allowance	3.2 mm (0.125 in.)	3.2 mm (0.125 in.)
Diameter	111.8 cm (3.67 ft)	86.36 cm (2.83 ft)
Length	6.1 m (20 ft)	7.3 m (24 ft)
Design Pressure	2.1 MPa (300 psig)	1.6 MPa (230 psig)
Design Temperature	177°C (350°F)	38°C (100°F)
<u>Tube Sheets</u>		
Material	A-285 Grade C Carbon Steel	A-105 Carbon Steel
Thickness	-	13.65 cm (5.375 in.)
<u>Tubes</u>		
Material	A-214 Carbon Steel	A-179 Carbon Steel
Outside Diameter	1.9 cm (0.75 in.)	15.875 mm (0.625 in.)
Wall Thickness	2.4 mm (0.095 in.)	3.05 mm (0.120 in.)
Length	6.1 m (20 ft)	7.3 m (24 ft)
Number	1600	222
Maximum Design Pressure	Operating - 1.5 MPa (218 psig)	28.96 MPa (4200 psig)
Maximum Design Pressure	-	66°C (150°F)
Operating Temperature	102°C (215°F) - IN 39°C (102°F) - OUT	43°C (110°F) - IN 18°C (64°F) - OUT

7.1.2 Primary Ammonia Coolers (Fin-Fan)

Tubes

Company B

Material	A-210 Carbon Steel
Outside Diameter	25.4 mm (1.0 in.)
Wall Thickness	3.76 mm (0.148 in.)
Length	9.1 m (30 ft)
Number	193, 4 rows deep
Operating Pressure	25.68 MPa (3725 psig)

Fins

Material	Aluminum
Height	15.875 mm (0.625 in.)
Type	Extruded, 9 per in.
External Surface Area	5342 m ² (57,500 ft ²)

Headers

Material	A-285 Grade C Carbon Steel
Corrosion Allowance	3.175 mm (0.125 in.)

Temperature

Ammonia IN	127°C (261°F) - Vapor
Ammonia OUT	43°C (110°F) - Vapor
Air IN	38°C (100°F) - Design
Air OUT	66°C (151°F) - Design

Heat Exchange

3.87 MW (13.23 x 10⁶ BTU/hr)

7.2 Derivation of Formula Relating Solution pH to Ammonia Concentration

The equation: $\text{pH} = 11.6252 + 1/2 \log \frac{\text{ppm NH}_3}{17,000}$ is derived as follows:

Butler⁽³²⁾ gives the ionization constant of ammonia as 1.78×10^{-5} .

Thus,

$$[\text{NH}_4^+][\text{OH}^-] = (1.78 \times 10^{-5})[\text{NH}_3] \quad (1)$$

The ionization of water is governed by

$$[\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (2)$$

Thus,

$$[\text{OH}^-] = (1.00 \times 10^{-14})/[\text{H}^+] \quad (2a)$$

Balancing charges gives

$$[\text{H}^+] + [\text{NH}_4^+] = [\text{OH}^-] \quad (3)$$

Since the solution is basic, we can neglect $[\text{H}^+]$ compared to $[\text{OH}^-]$ in Equation (3), and

$$[\text{NH}_4^+] = [\text{OH}^-] \quad (3a)$$

Substituting (2a) and (3a) into (1), gives

$$\frac{(1.00 \times 10^{-14})}{[\text{H}^+]} = (1.78 \times 10^{-5})[\text{NH}_3];$$

$$[\text{H}^+]^2 = \frac{(1.00 \times 10^{-28})}{(1.78 \times 10^{-5})[\text{NH}_3]};$$

$$2 \log [\text{H}^+] = -23.25 - \log [\text{NH}_3];$$

$$\text{pH} = 11.6252 + 1/2 \log [\text{NH}_3].$$

Since

$$[\text{NH}_3] = \text{ppm NH}_3 / 17,000$$

then,

$$\text{pH} = 11.6252 + 1/2 \log \frac{\text{ppm NH}_3}{17,000}.$$

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