

Stress Corrosion of Steels Anhydrous Ammonia

The results of the research program discussed here will be used to prepare recommendations for a code to ensure the safe handling of ammonia in steel vessels.

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Liquid ammonia is being stored and transported in ever increasing quantities throughout the world. Because of its physiological effects, accidents involving ammonia are usually serious if not fatal, even when it is released in only moderate quantities as a result of plant failures. This was illustrated by recent cases in America (1) and France (2).

Following the discovery of a stress corrosion phenomenon in steel-ammonia systems, work by Phelps and Loginow (3) indicated that oxygen and carbon dioxide contaminants were responsible for promoting failures, and that the addition of approximately 0.20% water would inhibit attack. Further laboratory work by Radd and Oertle (4) has revealed that the influence of water may not be as reliable and predictable as was first thought and that oxygen may, in fact, be beneficial.

During the past 2 yr., cracks have been detected in steel storage tanks in Denmark, Finland, and Ireland. Most of these cracks were associated with welds, but a few were present in parent plate, and in some cases have been shown to be stress corrosion cracks. In the case of the Danish tanks it is known beyond all reasonable doubt that many of the cracks had initiated by stress corrosion. The ammonia handled by the Danish tanks and spheres contained 0.2% water on delivery.

In view of the conflicting information from the laboratory tests and the reports of in-service stress corrosion cracking, it now appears that the available information on the stress corrosion of steel in anhydrous ammonia is insufficient to allow prediction of completely safe handling conditions. Such information is required to prevent further accidents arising from the failure of storage spheres or transportation tanks. If such accidents do occur with serious consequences, the resulting government legislation could seriously disrupt the ammonia industry. Therefore, it is in the interests of all companies involved in the manufacture, marketing, transportation, and use of anhydrous ammonia, to establish the conditions under

which steel vessels may be used to contain liquid ammonia and its attendant vapor.

In-service information on stress corrosion

Following the rapid expansion of the ammonia industry in America, a large number of pressure vessels were put into service for storing and handling ammonia. A survey of data available prior to 1956 indicated that few problems had been previously experienced. A fatal accident did, however, occur and this prompted a program of re-tests which showed that 3% of containers were failing within an average of 3 yr. service. Investigation (1) of these defective containers revealed that all were built to specification (ASME Codes U-69 or W.52) and had not been stress relieved. The ammonia handled in these tanks probably contained air and water. Failures were observed in all steels commonly used at that time (e.g., ASTM A.285 and A.212).

The heads of vessels were either deep drawn or cold formed and there was no predominance of failures in one particular alloy, although some heats of a steel were more susceptible than others. It was established that the majority of failures were caused by stress corrosion cracking (S.C.C.) of the cold formed heads. Stress relieving of cold formed heads and complete vessels was, therefore, recommended.

In 1968 (2) a welded road tanker manufactured from medium high strength T1 steel fractured along, or near, a weld associated with an internal baffle and external support brackets. At the time the tanker was loaded with approximately 19 tons of liquid ammonia of unspecified composition. The failure was due to stress corrosion cracking.

During 1969-70 several storage tanks in Denmark have been thoroughly examined by a magnetic particle inspection technique and found to be cracked (3). In some cases, several hundred cracks were detected. None of the tanks had been stress relieved and the majority of cracks

Table 1. Test specimens.

ASTM No.	Y.S._2 MNm	U.T.S._2 MNm	Welding Electrode
A-212B	353	573	E6015
A-285	255	406	E6010
Case 1056	331	544	E7016
A-202B	393	642	E7016
'T-1' Steel	800	863	E12015
AISI 4130	818	926	E12015

were associated with welds, although in some cases the parent metal outside heat affected zones had also cracked. There was evidence that some cracks had grown from weld defects, but it seems certain that stress corrosion had also initiated cracks in non-defective regions. The tanks were either constructed from SiMnAl carbon steels having yield strengths of 324 - 335 MNm⁻² (21- to 23 tonf/in²), or ASTM A.285 Grade C steel with a 200 MNm⁻² (13 tonf/in.²) yield strength. C-Mn or C-½Mo welding electrodes were used for welding and in the latter case there was evidence that welding defects were more frequent. The ammonia handled by some of these tanks and spheres has contained 0.2% water on delivery and a further addition of 0.2% is now made. The interior had not been contaminated with oil.

More recently, as a direct result of the Danish experience, a storage sphere belonging to Nitrogen Eirann Teoranta was inspected and found to contain several hundred cracks (4). The vessel was manufactured in 1965 from FB50 fine grained steel which was not stress relieved, and was used to contain ammonia whose average water content was about 0.1%. Magnetic particle examination was made of most circumferential weld seams, which were made up from six passes and the overall weld as about 6 mm. proud of the parent metal. In one seam, hundreds of cracks were detected, all confined to the weld metal and mainly occurring across the individual weld caps. In a number of areas, the cracks were running in all directions, and in some cases had joined together to form larger cracks. Average depth of these cracks was about 0.25 mm and the length varied from 3- to 4 mm. in most cases, to 15 mm. in isolated cases. In one area, a group of five cracks, about 0.5 mm. deep and 3- to 4 mm. in length, were running at right angles to the weld and about 14 mm. away from it. Cracking was also detected in two other weld seams. All the cracks were readily removed by grinding without the need for re-welding. Cracks have been detected in storage tanks in Finland, but no details are available at this time.

Information from laboratory investigation

Only two detailed investigations (5, 6) of the influence of liquid ammonia are available in the open literature. The first (5) was carried out following the re-testing of transporter tanks referred to previously, and consisted of

exposing specimens under stress in contaminated liquid ammonia. The materials studied are shown in Table 1.

Besides testing alloys from several heats, cold worked and welded samples were studied to simulate the possible service conditions of each steel.

Tuning-fork specimens of 'T-1' and ASTM 212 were exposed in nurse and applicator tanks and inspected periodically. Eighteen of 30 samples of 'T-1' steel failed in 10 weeks, whereas the ASTM 212 steel was unaffected. Further, longer term tests on 161 specimens of all the alloys in an ammonia distributing plant showed a failure rate of 50.7% overall in approximately 5 yr. All steels except ASTM 212 showed some failures, which is not consistent with service experience since vessels made from this steel have fractured.

Because the above tests were under service conditions the composition of the ammonia was unknown and, in addition, was changing during the tests. Consequently, the influence of variations in composition were determined by laboratory tests. Although the effects of ethyl mercaptan, sodium cyanide, sodium chloride, and copper sulphate were studied briefly, the main program was concerned with water, air, and carbon dioxide additions to various grades of ammonia, only one of which was analyzed (70 ppm H₂O 1.6 ppm oil). In the majority of tests where failures occurred the steels were either 'T-1' or AISI 4130 steels, although some failures of Case 1056 and ASTM A202 did occur in ammonia containing air and carbon dioxide. A summary of the tests carried out and results obtained are given in Table 2.

Bearing in mind that the composition of the liquid ammonia was not known in detail in most cases, and that the number of specimens tested was small, the above tests indicate:

1. The higher strength alloys, 'T-1', AISI 4130, and the spring steel, are more susceptible.
2. The addition of water retards stress corrosion and, in fact, 0.25% may eliminate failure in less susceptible alloys.
3. Failures do occur in ammonia contaminated with air containing carbon dioxide.
4. Pure ammonia probably does not cause stress corrosion.

The second investigation (6) was primarily concerned with the electro-chemistry of steel-ammonia reactions as affected by contaminants such as air, CO₂, and H₂O. On the basis that such reactions could be similar to aqueous reactions which result in hydrogen pick-up by steels, an experimental technique was devised to monitor (by an ion pump) the hydrogen permeating a hollow, sealed tube of mild steel in liquid or gaseous ammonia. The effect of additions of O₂, H₂O, and CO₂ are shown in Table 3.

These results show that the majority of hydrogen pick-up occurs in the vapor phase and that it is promoted by:

1. Addition of H₂O when oxygen is absent.
 2. Addition of CO₂ with or without water present.
- Water only retards hydrogen pick-up if oxygen is

Table 2
Summary of tests involving the exposure of specimens under stress
in contaminated liquid ammonia, and their results.

No.	Additions to Ammonia			Specimens		
	Air	Water %	CO ₂	No. Exposed	No. Failed	Frequency %
1	No	No	—	14	3	21.4
2	Yes	No	—	44	10	22.8
3	Yes	0.1	—	4	0	0
4	Yes	0.25	—	4	0	0
5	Yes	0.5	—	14	0	0
6	Yes	1.0	—	14	0	0
7	Yes	2.0	—	10	0	0
8	Yes	4.0	—	10	0	0
9	No	No	—	43	7	16.3
10	Yes	No	—	43	1	2.3
11	Yes	0.25	—	43	0	0
12	Yes	0.25	0.1%	54	1	1.85
13	Yes	—	0.1%	54	54	100
14	Yes	—	0.002%	16	5	31.2
15	Yes	—	0.1%	16	9	56.2
16	Yes	0.25	0.1%	16	0	0

Notes:

1. Tests 12 to 16 were carried out in refrigerant grade ammonia.
70 ppm H₂O, 1.6 ppm oil.
2. Tests 1 to 8 were carried out on site, composition of ammonia not specified.
3. Air additions were only CO₂-free in tests 12 to 16.
4. Ammonium carbonate added to give appropriate CO₂ levels in tests 14 to 16, and AISI 4130 was not tested.
5. The failed specimens were either 'T-1' or AISI 4130 except in tests 12 and 13 where a spring steel was used throughout, and in tests 14 and 15 when the failures included 1 of Case 1056, and 1 of Case 1056 and 2 of ASTM A202, respectively.

present, whereas oxygen is inhibitive even in the absence of water.

In liquid ammonia, the rate of hydrogen pick-up is low, but can be increased by cathodic polarisation, or eliminated by anodic polarisation. The effect of anodic polarisation is sufficiently beneficial to ensure that subsequent exposure to gaseous ammonia does not result in hydrogen pick-up. Similarly, additions of O₂ and H₂O not only decrease pick-up, but delay its onset when the environment is changed to one in which hydrogen contamination normally occurs. The beneficial influence of O₂ and H₂O in the presence of CO₂ is, however, time dependent, and subsequent additions appear to be necessary to give continuous inhibition. Additions of ammonia containing CO₂ to systems previously conditioned with ammonia + H₂O + O₂ results in breakdown of the inhibition established by pre-conditioning. The above effects can be explained in terms of the formation and breakdown of

protective films which, if artificially produced, may offer a means of combating stress corrosion. The authors also investigated the effect of hydrogen, ammonium nitrate, and sodium chloride, all of which increased hydrogen pick-up. The most marked effect was produced by ammonium nitrate.

Tests on stressed high strength steel clips confirmed that failures could be produced in the aggressive environments defined by the hydrogen probe work, but no tests were conducted on low strength alloys.

The problem

As indicated by the existing state of knowledge from laboratory investigations and in-service behavior, some general, and many detailed aspects of stress corrosion of steels in ammonia require further investigation before absolutely safe handling conditions can be defined. In particular, quantitative answers are required to the

Table 3
The electro-chemistry of steel-ammonia reactions
as affected by O₂, CO₂, and H₂O.

No.	Ammonia Composition	Position of Test Tube in Ammonia	Potential of tube	Ion Pump Current (μ a)*	Remarks
1	As Received	Partially Immersed	Natural	0.40	Background Level 0.13 μ a.
2	As Received	Gaseous Phase	Natural	0.58 Max. After 20 hr.	Background Level 0.007 μ a.
3	As Received	Partially Immersed	8 Volts Cathodic	4.0 Max. After 20 hr.	Background Level \sim 0.20 μ a. Gradual Build-up in pick-up and 8 hr. Decay Period
4	As Received	Almost Totally Immersed	8 Volts Anodic	0.11	Pick-up Within Background Range. After Removal of Anodic Potential the Pick-up Rate Did Not Increase.
5	Ammonia and Dry Air	Gaseous Phase	—	\sim 0.07	Dropped From 0.16 μ a.
6	Ammonia and 1 ml. H ₂ O Containing Some Air	Gaseous Phase	—	\sim 0.07	Dropped From 0.50 μ a.
7	Ammonia and Dry CO ₂	Gaseous Phase	—	> 1.4	Rose From 0.63 μ a. Water Still Present.
8	As in 7 + Dry O ₂	Gaseous Phase	—	\sim 0.15	Dropped From > 1.4 μ a.
9	Ammonia H ₂ O (O ₂ free)	Gaseous Phase	—	\sim 0.36	Rose From 0.24 μ a in Pure Gaseous Ammonia.
10	Ammonia + H ₂ and Dry CO ₂ + H ₂ O (O ₂ free)	Gaseous	—	16.0	Rose From \sim 0.4 μ a When the H ₂ O was Added.

*1 microampere (μ a) is approximately equivalent to 5.5×10^{-9} cc. of hydrogen cm.²/sec.

Table 4
Set of selected environmental conditions

Water	Carbon Dioxide	Oil Coated	Oxygen	Temperature
5,000	20	Yes	0.10x*	20
500	40	Yes	0.20x	35
150	60	No	0.10x	20
800	70	No	0.55x	-30
600	50	No	0.95x	-10
800	80	Yes	0.00x	-10
9,000	70	No	0.35x	-10
300	30	Yes	0.70x	-10
500	60	Yes	0.45x	-30
20	20	Yes	0.55x	-10
600	80	Yes	0.25x	20
50	10	No	0.55x	35
1,200	40	Yes	0.10x	5
20	100	Yes	0.45x	-10
50	50	Yes	0.30x	-30
20	40	No	0.35x	-10
20	30	Yes	0.10x	-30
5,000	20	Yes	0.60x	5
20	40	No	0.35x	-30
800	40	Yes	0.60x	-10
50	50	No	0.80x	20
3,000	70	No	0.50x	-10
200	70	No	0.80x	20
200	10	No	0.95x	20
20	50	No	0.70x	-10
150	40	Yes	0.95x	-10
800	20	No	0.30x	5
7,000	60	Yes	0.70x	20
2,500	60	No	0.80x	35
20	100	Yes	0.10x	35
600	90	Yes	0.35x	-10
2,000	90	Yes	0.15x	-10
400	40	No	0.80x	20
50	80	No	0.50x	20
300	60	No	0.00x	20
100	30	No	0.30x	35
1,200	60	Yes	0.75x	20
100	60	No	0.80x	20
150	40	No	0.75x	35
9,000	70	Yes	0.45x	20
50	50	Yes	0.35x	20
2,000	80	Yes	0.95x	20
300	50	Yes	0.45x	5
400	60	Yes	0.30x	-10
100	40	No	0.90x	5
200	40	No	0.75x	5
600	30	No	0.20x	20
20	20	No	0.35x	-10
800	30	No	0.70x	-10
200	40	Yes	0.05x	-30

*Maximum concentration of oxygen

following questions:

1. For a given ammonia composition, is the vapor more aggressive than the liquid?
2. Are oxygen and water both necessary to inhibit stress corrosion, and if so, in what relative amounts? If not, what is the effect of oxygen and what level of water is required to inhibit stress corrosion under all conditions?
3. What is the critical level of CO₂ which promotes stress corrosion cracking, and how is this influenced by different oxygen and water contents?
4. Does oil act as an inhibitor?
5. Is a stress relieving treatment sufficient to prevent failure in welded structures?
6. What are the relative susceptibilities of welds formed from different welding electrodes?
7. What effect do metallurgical variations in the condition of any one steel have on susceptibility?

The solution

A major research program has just commenced at the Fulmer Research Institute (7) aimed at defining the conditions under which steel vessels may be used to contain liquid ammonia and its attendant vapor. So far, this project is being supported by a consortium of 13 European companies.

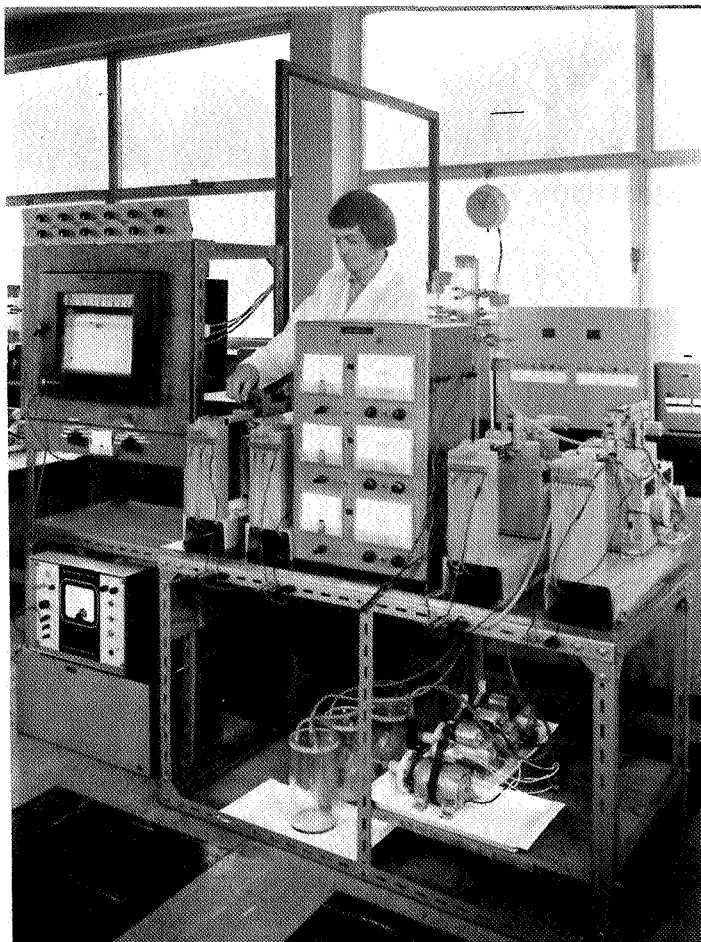


Figure 1. Equipment designed and constructed at Fulmer Research Institute for corrosion fatigue testing under sinusoidal, impulse or square wave loading.

The complexity of the experimental variables make it imperative that a careful experimental design be used as a basis for a detailed statistical analysis of the results. Normally, experimental designs are chosen to be efficient in extracting the direct effects of factors and their first order interactions. This is not sufficiently flexible for the present problem, so the following design has been chosen. Initially the range of each experimental variable which is to be investigated has been specified, and then a random value within the range has been assigned to each experimental trial. This gives a set of experimental points scattered at random in the ranges which are to be investigated, the advantage of which is that since no commitment to any particular model is implied in the design, alternative regression analysis models may be tried. The ranges of experimental variables to be investigated are:

- 20 < X₁ < 10,000 ppm water (X₁ is the experimental concentration)
- 10 < X₂ < 100 ppm CO₂ (X₂ " " " ")
- 0 < X₃ < 50 ppm oil (X₃ " " " ")
- 30°C < X₄ < +35°C temperature (X₄ is the experimental temperature)
- A < X₅ < B ppm O₂ (X₅ is the experimental concentration)

In the case of oxygen, the minimum content A to be investigated corresponds to that present in the stock ammonia, and the maximum content B is to be 1 volume air to 1 volume ammonia.

The selected environmental conditions are shown in Table 4, from which it will be noted that because water is believed to have a substantial inhibiting effect below 2,500 ppm, the density of points below that value is greater than at higher water contents.

For each set of conditions the stress corrosion susceptibility will be assessed using a constant strain rate test as used extensively by Parkins (8, 9) and Scully (10, 11). Initially, tests will be carried out at four different strain rates in the range 10⁻⁵ to 10⁻⁷ sec.⁻¹ in both liquid and gaseous ammonia, and the elongation at failure will be measured and used as the criteria of stress corrosion cracking. The results will be analyzed using initially discriminant analysis to determine the conditions within which stress corrosion occurs. The points will then be fitted to an equation of the form:

$$e = e_0 + \sum a_i x_i + at + \sum b_i x_i^2 + \sum c_i x_i x_j + v \sum d_i x_i t_i = J \quad (1)$$

plus terms of higher order, the most significant being selected by stepwise and multiple regression techniques.

The results will be a relationship which can be used to predict the minimum elongation of the steel under known conditions of temperature and contamination. Once the range of aggressive ammonia compositions has been determined, the influence of metallurgical variables such as stress relieving, weld metal composition, and cold deformation will be investigated.

Although the constant strain rate test is very useful for

the initial experiments because of its speed, simplicity and sensitivity, it does not accurately represent the situation in which cracks (e.g., welding defects) pre-exist in a structure.

Consequently, it does not represent the most dangerous case which might arise in practice, and for this reason the final experimental stage of the program will involve the use of fracture toughness approach. Compact tensile specimens (CTS) will be pre-cracked by fatiguing and then fracture toughness tests will be conducted in air and aggressive environments. This will define critical crack lengths and the rate of crack propagation under the different environmental conditions. These results will be directly applicable to in-service behavior of the steels.

Finally, the results will be used to prepare recommendations for a code of practice designed to ensure the safe handling of ammonia in steel vessels. #

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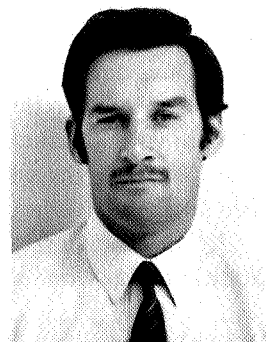
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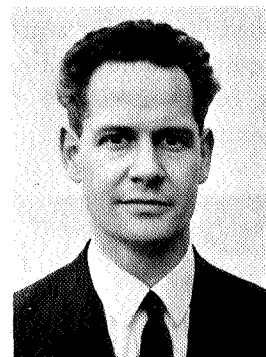
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