Stress Corrosion Cracking in Ammonia

Tests show addition of 0.2% water to ammonia is a valid method to prevent stress corrosion cracking.

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As you may know, I participated in research conducted by the Research Committee of the Agricultural Ammonia Institute (AAI) which culminated in 1962 with the publication of a paper by A. W. Loginow and me entitled "Stress-Corrosion Cracking of Steels in Agricultural Ammonia." This paper was published in Corrosion, Vol. 18, No. 8, 1962, pp. 299t-309t.

As a result of the research studies, the Research Committee recommended that agricultural ammonia should contain 0.2% water to inhibit stress-corrosion cracking of ammonia vessels. Other recommendations were that extreme care should be 'exercised to avoid air contamination in ammonia systems and that vessels over 36 inches in diameter should be either fully stress-relieved or fabricated with heads that are hot-formed or stress-relieved. Also as a result of this research, the AAI issued, in 1961, a specification for "Inhibited Agricultural Ammonia," which required that o.2% water be added to conform with the specification. A number of companies adopted the use of this specification and, according to their reports, their experience has been satisfactory.

In January 1968, the Department of Transportation (DOT) adopted an amendment *(1)* to the Hazardous Materials Regulations requiring that MC-330 and MC-331 cargo tanks constructed of quenched and tempered steel be used only for anhydrous ammonia having a minimum water content of 0.2% by weight, or for ammonia of at least 99.995% purity. A time table was also set for internal inspection of all MC-330 and MC-331 cargo tanks made of quenched and tempered steel which had been in anhydrous ammonia or liquefied petroleum-gas service. The regulation also required that any tanks going to ammonia service be cleaned of any previous product and that tanks be purged of air before loading. (The research previously mentioned had shown that air contamination was the cause of stress-corrosion cracking of steel in ammonia.)

During the past several years the Applied Research Laboratory of U.S. Steel Corporation has conducted addtional service tests with the objective of developing additional evidence concerning the effectiveness of the water addition in preventing stress-corrosion cracking in ammonia. Now I would like to briefly review these programs and discuss the results we have obtained.

Tests in Georgia

The first series of tests was conducted with the cooperation of an ammonia distributor in Georgia. The ammonia supplied to this location was reportedly inhibited with 0.2% water. As in the previous AAI tests, we exposed cold-worked, welded and stressed tuning-fork specimens made from ASTM A517 steel and periodically examined them for the occurrence of stress-corrosion cracking. The ammonia was analyzed for water at the time of each inspection. Over a three-year exposure period, 31 specimens of 108 exposed failed in time periods ranging from 19 to 128 weeks. However, the results of 18 separate analyses for water showed that on five occasions, the ammonia in the system only contained from 0.03 to 0.06% water. On the other 13 occasions, the ammonia contained 0.11 to 0.29% water. The conclusion we draw from these tests is that the procedures used to add water to the ammonia were not effective and that, as a result, there were significant periods of time when the ammonia in the system was not inhibited.

Tests in Texas

The second series of tests was conducted with an ammonia distributor in Texas who had encountered difficulty with stress-corrosion cracking in his ammonia tanks. We informed him of the previous research showing the effectiveness of the addition of water, and cooperated with him in a test in which 0.2% water was added to the ammonia in one test tank and was not added to the ammonia in another tank. Tuning-fork specimens of A517 steel were exposed in each tank with the following results:

Table

Condition	No. of Specimens Exposed	No. of Specimens Cracked	Time to Cracking, weeks	Total Exposure Time, weeks
No Water Added	5			13
Vapor Phase	5	4	3	13
Liquid Phase	5	1	3	13
0.2% Water Added				
Vapor Phase	5	0	–	13
Liquid Phase	5	0	–	13

As can be seen in this table, specimen failures occurred in the uninhibited ammonia but they did not occur in the ammonia which was inhibited with 0.2% water.

Tests in Idaho

The next series of tests was conducted with two ammonia distributors in Idaho, both of whom received their ammonia from the same producing plant. The test plan was that all of the ammonia going to one distributor would be inhibited with water whereas the ammonia shipped to the other location would not be inhibited. The tests were again conducted with welded tuning-fork specimens of A517 steel which were exposed over a three-year period. The results were as follows:

Table

Ammonia	No. of Specimens Exposed	No. of Specimens Cracked	Time to Cracking, weeks	Total Exposure Time, weeks
Uninhibited	8	4	60	165
Inhibited	16	0	–	165
With 0.2% Water	8	0	–	122

You will note that there were no specimen failures in the inhibited ammonia whereas specimen failures did occur in the uninhibited ammonia. Water analyses were made on every incoming tank car of the inhibited ammonia and occasionally on the uninhibited ammonia shipments with the following results:

Table

Water Content in Idaho Tests
Percent by Weight

Site No. 1 Inhibited Ammonia		Site No. 2 Uninhibited Ammonia
	0.28	
	0.18	
0.17	0.17	
	0.25	
	0.19	Not Detectable
	0.21	
	0.18	0.21*
	0.22	
	0.26	
	0.22	
	0.65*	0.008

*Ammonia from Different Source

It is evident that water was always present in the inhibited ammonia. On one occasion the uninhibited ammonia at site No. 2 contained 0.21% water, but it was later established that this ammonia had been obtained from a different source.

To summarize the results of these tests, we believe that they furnish additional confirming evidence that the addition of 0.2% water to ammonia is a valid method to prevent stress-corrosion cracking.

With respect to ammonia purity, also covered by the DOT regulations, I think that there is a need to determine just how pure ammonia needs to be before it will not be capable of causing stress-corrosion cracking. The proposed research to be conducted by the Fulmer Research Institute will certainly help to answer this question. At the time that the DOT regulations were put into effect, I think it was recognized that there was a certain amount of arbitrariness in the selection of an impurity level of 50 parts per million (corresponding to 99.995% by weight ammonia purity) as being that required to prevent stress corrosion.

With respect to the types of steel that are susceptible to stress-corrosion cracking in contaminated ammonia, it is important to remember that all of the early failures which led to the AAI research program occurred in ordinary carbon steels such as ASTM A212 steel and ASME Case 1056 steel. Therefore, it is not correct to conclude that only quenched and tempered steels are susceptible to stress-corrosion cracking. In this respect, it is also of interest that most of the failures reported in Dr. Sanderson's review of European experience were observed on carbon steel vessels.

Dr. Sanderson also mentioned the studies made by Dr. Fred Radd of Continental Oil Co. These studies have led Dr. Radd to conclude that hydrogen embrittlement is a factor in stress-corrosion cracking in ammonia and the results of a number of permeation experiments are presented to support this conclusion. We disagree with Dr. Radd because, as he states in his paper, the permeation rates he measured are no higher than those which result from exposure of the steel to ordinary water and are 100 times lower than those which result from exposure to hydrogen sulfide solutions. Simply stated, exposure to "ordinary water" does not cause hydrogen embrittlement of the types of steel we are concerned with for transporting ammonia and therefore there is no basis for concluding that the extremely small rates of hydrogen permeation measured by Dr. Radd have anything to do with stress-corrosion in ammonia.

Literature Cited

1. E.A. Olsen, "New Rules for Ammonia Highway Tank Transports," Safety in Air and Ammonia Plants, Vol. II, published by AIChE.

DISCUSSION

G. SANDERSON, Fulmer Research Institute, Ltd.: I would like to thank Dr. Phelps for giving information of which I was not aware about the purity of the ammonia. I would like to confirm that the program that we are going to do should result in providing the information Dr. Phelps thinks may be required. His comments on the work by Radd I think on the whole I would agree with them. However I think that it's justifiable to use the word if, and that there is some doubt as to whether they can be just written off. Certainly I think that the changes in hydrogen pick-up rate that he observed were real effects and although the hydrogen may not be directly responsible for fracture the changes do indicate changes in surface films caused by environmental changes. This I think is true despite the fact that degassed steel was not used in the work. It has never been established that for hydrogen embrittlement failures a minimum hydrogen pick-up rate is required. The process is however time dependent. I would like to hear what the meeting has to say about this subject. Mainly because I feel that the European contingent would like more information on the situation in the States.

WILLIE CLARK, ICI, Billingham, England: You must blame me for some of this because we heard about the ammonia troubles in Denmark and had discussions with various people in England. We decided that it looked as though there was a problem that had to be gone into a bit more deeply and we asked Fulmer to take this up.

Now the situation seems very simple to me. In Denmark they don't make much ammonia; they import it. They import a lot of it, I understand, from Grace and other places. This contains 0.2% water. They have a large number of pretty large storage tanks and one or two vertical tanks. They have found a surprising amount of cracking in these, and cracks 10 millimeters deep cannot be dismissed.

A few of these cracks have been sectioned and they are stress corrosion cracks, and yet there is water there. As Dr. Phelps was saying, the water can't disappear and it's curious if the ammonia imported into Denmark was short of water. So we feel there is something wrong here and that more work needs to be done. I find it difficult to believe that ammonia in America is very different from ammonia in Europe. Of course, the plants that make it are very similar in many respects and the steels are not apparently very different.

So we have persuaded Fulmer to take up this problem and it looks as if the work will go ahead. It will go on the basis of European steels, those that the sponsors are interested in, but it would be a very desirable thing to have cooperation with people here in the States so that we also cover the points which are relevant to American practice. We hope to discuss whether there is any correlation between water content necessary for inhibition and the type of steel, whether 99.995% purity is the right answer if you are not going to have water present, and what's going to happen when ordinary constructional steels go up in strength.

There are a lot of variations possible. The QT steels have a bad name for handling ammonia and their use is restricted in certain respects. But you can get strong steels without using the QT procedure and we don't know how satisfactory they would be. It is for this reason that I think the subject needs detailed examination and the new technique available for doing stress corrosion testing should speed this up a great deal. Therefore, I very much hope that we'll have a few American people to come in with ICI and others on this program. ICI Initiated this, but we are no more than one of the European sponsors.

Q. Did anyone mention the potential cost for this study?

SANDERSON: The cost is £1,670 for the basic program which covers work on two steels selected by the sponsors. Anyone wanting a specific steel investigated can pay for that steel at the rate of £5,000.

PHELPS: I believe that it is important that I don't leave the wrong impression concerning the proposed research to be conducted at the Fulmer Research Institute. We are certainly in favor of additional research on stress-corrosion cracking of steel in ammonia and believe that the work proposed has a good chance of answering a number of important questions. The slow-strain technique which will be used is an excellent method, and we are using it in our Laboratory in research on other types of stress-corrosion cracking. This method may well turn out to be an excellent method for investigating the environmental factors which control stress corrosion in ammonia.

Q. Is the cost per participant or pro rated?

SANDERSON: £1,670 per participant. We require 12 companies to make this economically feasible for the Institute. At the moment, as I mentioned, four companies have definitely joined the programme. But there are another ten companies who will probably finally come in to the program as well.