Stress Corrosion Cracking in Ammonia Storage

Survey of spherical storage tanks shows the strong influence of service conditions on this type of corrosion, and emphasizes the need for further studies.

H. Arup,
Danish Corrosion Centre ATV,
Glostrup, Denmark

Stress corrosion cracking (SCC) of steel tanks for liquid ammonia has been a serious problem on both sides of the Atlantic; and in spite of the research efforts made in several countries, part of the problem and a number of unanswered questions remain.

Early work in the United States was concerned with cracks in road tank trucks, and when the investigation by Phelps and Loginow was reported in 1962, many were led to believe that SCC in liquid NH_3 only occurred in quenched and tempered steels and that it could be prevented altogether by inhibition with 0.2% water.

European experience with cracking in ammonia service is very different. With one notable exception, a tragic failure in France of a road tank made of quenched and tempered steel not approved for this application, all incidences of cracking recorded in the late 1960s and early 1970s have been in storage tanks made of normalized, fine-grain steel. Denmark has had a lion's share of these cases, and it may be of interest to give a brief review of the situation in that country.

The use of liquid ammonia as a direct fertilizer is widespread in Denmark, where 40% of the nitrogen in fertilizers is supplied as liquid ammonia. This corresponds to appr. 170,000 ton/yr. of ammonia; and most of this is distributed during three to four weeks in spring. The distributors, A/S Ammonia, have storage facilities for 110,000 tons, of which 80,000 is atmospheric (- 33°C) and 30,000 tons is in pressurized tanks, mostly spheres (15 in number) with a design pressure of 8 atm. corresponding to a maximum temperature of 17°C. Another 10,000 small tanks are used in distribution and local storage.

The first case of cracking was in 1964 in a 230-cu.m. bullet-shaped tank. A crack adjacent to a repair weld had penetrated the tank wall. Since then, the authorities have demanded regular magnetic particle inspections of all the pressurized tanks, and in every one of them some cracks were found. Inhibition with 0.2% water used since 1969 has not completely prevented the formation of new cracks. This point will be commented upon later.

The cracking experienced in these tanks raised a number of questions, which could not be answered by the 1962 paper of Phelps and Loginow. We also learned in 1971 that U.S. Steel had not continued or resumed their work on this problem, and we then prepared to start research of our own. Before this was started in 1972, a multisponsored project was proposed by Fulmer Research Institute in England, and as our sponsor was willing to support both projects, we were able to plan our research to be supplementary to the Fulmer work, especially with respect to the use of electrochemical methods.

It is not the purpose here to discuss the results of that research, which is available elsewhere (*1*) and which is in good agreement with the concurrent work by U.S. Steel. But it may be relevant to note the following conclusions, which become the basis of later surveys and subsequent research:

1. Cracking could be promoted in the normalized steel as well as in the quenched and tempered steels in air-contaminated liquid ammonia.
2. Cracking was associated with a passive condition of the steel, which could be a function of the composition of the ammonia (air contamination) or imposed by potentiostatic control. Cathodic protection prevented cracking, even if hydrogen was evolved on the specimen.
3. Addition of 0.2% water effectively prevented cracking at any potential and did not change the natural corrosion potential very much. Later research may lead to a modification of that statement. The development of a corrosion monitor, based on potential measurements already tried in one of the large spherical tanks, was therefore put on the shelf. The same applied to the possible use of oxygen scavengers such as hydrazine, which would be of no interest from an economic point of view, where water could be used as inhibitor.

The frequency of cracking in Danish tanks—including stress-relieved tanks and tanks for water-inhibited ammonia—raised widespread interest and was difficult to explain, when the problem was discussed in international groups, such as the group of companies sponsoring research at Fulmer.

We were aware that the frequent magnetic particle inspections demanded in Danish tanks inevitably led to high oxygen levels in the ammonia during long periods, because the tanks could only be purged with ammonia. This was indirectly confirmed when cracks were found in tanks in other Scandinavian countries during a second and rather close inspection one to two years after a first inspection, where no cracks had been found.

Survey covers 49 returns from 10 countries

With the encouragement of Imperial Chemical Industries Ltd., and with the co-sponsorship of A/S Ammonia, a survey was then carried out among European owners of large ammonia spheres. It was hoped the survey would make it possible to correlate reported cases of SCC with a) service conditions, b) composition of the ammonia, c) type of steel and welding procedures, and d) inspection practice.

Questionnaires were sent to tank owners and institutions in 14 countries. The present summary is based on 49 returns from 10 countries. It seems that answers have been received most readily from countries where SCC has been observed; countries with no records of SCC may have felt less obliged to contribute to the inquiry. In the U.S., no approaches were made to individual companies, but we were informed that no cracking had been reported in storage tanks, but also that no tanks had been subjected to magnetic particle examination.

Many tank owners were unable to supply the information wanted, especially regarding the composition of the ammonia, and this limits the number of conclusions to be drawn. Most of the detailed information can be found in the report (*2*), but some of the conclusions considered particularly interesting or significant are mentioned below.

The main results of the survey were as follows: a) total number of tanks, 49 in 10 countries; b) number of tanks with cracks; 28 in 7 countries (among these were all 15 Danish tanks); and c) number of tanks without cracks; 21 in 4 countries.

With the exception of the UK tanks and one two-year-old Irish tank, cracks have been found in every tank subjected to magnetic particle inspection.

Service conditions seemed to exert an important influence. The relation found between the temperature of the ammonia and the cracking history of the tanks is given in Table 1.

Tanks for cool storage are cooled by drawing vapor from the tank. The vapor is compressed, condensed and returned to the tank. In this process, noncondensible gases including oxygen are removed.

It was believed that the flushing procedures before filling a tank would have an important influence. In all cases, some kind of flushing is used before filling a tank with liquid NH_3, but no distinction can be made between the use of nitrogen vs. ammonia vapor for this purpose. However, all the cracked Danish tanks have rather poor facilities for flushing, and are flushed with ammonia vapor only.

Surprisingly few tank owners have been able to report on the typical composition of their ammonia. Again, the 15 UK tanks form a notable exception. They are all regularly analyzed, and the content of oxygen in the ammonia is normally below 1 ppm. Other analyses reported are in the following ranges: oxygen, 1-10 ppm.; nitrogen, 10-20 ppm.; carbon dioxide, 0-15 ppm; and water, 0-0.3%.

Table 1. Relation between ammonia temperature and tank corrosion history

Storage temperature	Tanks without cracks	Tanks with cracks
Below −15°C	8	0
Between −15°C and 0°C	8	2
Between 0°C and +15°C	0	6*
Ambient	3**	20

*These six tanks are from Norway and Finland, where the ambient temperature is often quite low.

**These three tanks have not been magnetic particle inspected.

The small number of replies does not allow any further conclusions. As already mentioned, the use of water inhibition in Danish tanks since 1969 has not completely prevented SCC, but cracks are now found more frequently in the upper part of the tanks.

It is not possible, on the basis of the survey, to draw conclusions concerning the susceptibility towards SCC of different types of steel. The most common steels mentioned in the forms are ferritic-pearlitic fine grain steels with tensile strength from 37 to 50 kp/sq.mm. and SCC is reported in the entire range.

Vapor above the liquid ammonia a factor

When the results of the survey are discussed, one of the unanswered questions is: Why has it not been possible to prevent cracking in Danish tanks by the use of water-inhibited ammonia?

It was speculated that cracking might still take place in the part of the tank above the liquid, where a condensed film of liquid ammonia forms when the ambient temperature is the same as or lower than the temperature of the liquid ammonia.

The SCC of steel in ammonia vapor had only been treated in confidential or unpublished work, and the information we had in hand at the time prompted further investigations at the Danish Corrosion Center. This research will be reported elsewhere (*3*) and only the main conclusions will be given here.

In this experiment, use was made of a hollow tensile specimen with a concentric bore. A thick, silver wire was fitted into this bore and used to conduct heat into or away from the gauge length of the specimen. The specimen was subjected to slow straining in saturated vapor above liquid ammonia. This is a very sensitive method for detecting even slight susceptibility to SCC.

In vapor above air-contaminated ammonia, SCC occurred when the specimen was slightly cooled below the temperature of the liquid ammonia, but prevented in case of an equally slight heating (less than 2°C temperature difference).

In vapor above air-contaminated ammonia with 0.2% water as inhibitor, some very interesting results were produced. Again, slight heating prevented cracking. On a slightly cooled specimen (with the end of the silver wire in ice cold water) a few, very small cracks were found; which means that the water had prevented cracking almost completely. On stronger cooling (use of solid CO^2 instead of ice) inhibition was no longer effective and cracking occurred.

These results help to explain the corrosion history of the Danish tanks storing water-inhibited ammonia at ambient temperatures. As mentioned earlier, these tanks are used to full capacity during a short season and left with a small amount of ammonia—but still under pressure—the rest of the year. A large part of the tank interior is therefore exposed to ammonia vapor.

Under conditions of constant temperature, the tank wall above the liquid is covered by an absorbed film of liquid ammonia in equilibrium with the bulk of the liquid, which means that this film can be expected to contain sufficient water to prevent cracking.

During the day outdoor temperatures are above the 24-hr. mean temperature which is the likely temperature of the liquid ammonia, and the drying out of the tank wall brings any SCC to a halt. During a cold night, copious condensation will occur on the tank wall (which is not lagged) and the condensing liquid can no longer be expected to remain in equilibrium with the bulk of the liquid, but will shift somewhat towards the composition of the vapor. Most importantly, the vapor is likely to contain too little water for efficient inhibition.

We therefore recommend the ammonia be kept in pressurized tanks somewhat cooled, which would keep the tank wall dry at all times and at the same time provide an opportunity for continuous removal of oxygen.

Remaining problems to be solved

In light of the knowledge we now believe we have, a number of remaining questions and problems are clearly visible. One of the relates to the complete absence of reported cracking in pressurized storage tanks in USA. Is it because no such tanks are in use or because no one has looked for cracks in existing tanks?

Recent investigation by Southwest Research Institute has revealed that 32 out of 51 samples of production ammonia produced cracking in the laboratory. Furthermore, the sampling procedure was such that the laboratory samples must have contained only one-seventh (theoretically) of the oxygen present in the storage tanks, from which the sample was taken. Of the 35 samples which were chemicaly analyzed, 31 contained less than 0.1% water, and only two of these can be assumed to have contained less than 10 ppm. oxygen in the storage vessel. In European experience 10 ppm. oxygen is more than sufficient to cause SCC.

Another question concerns the effect of temperature. It is comforting to know that no cracking has ever been observed in −33°C storage, but nothing in the available service experience or research data excludes the possibility of cracking—maybe at a much slower rate of propagation—at this temperature.

A third, and in my view very important, group of questions relate to the detailed influence of strain, stress, and metallurgical structure on the cracking. The influence of repeated loading should also be studied. The subject is too vast to be discussed here - even briefly - but it will certainly become an important discussion topic in future research seminars. It is our hope that discussions between active researchers from USA and Europe will help to make more efficient use of the very limited facilities for research in this important field. #

Literature cited

1. Poulson, Bryan, and H. Arup, "SCC of Mild Steel in Liquid Ammonia," Danish Corrosion Center ATV, January, 1975.
2. "The Occurrence of SCC in Large Pressurized Steel Spheres for Liquid Ammonia," Danish Corrosion Center ATV, 1975.
3. Ludwigsen, P.B., and H. Arup, "SCC of Mild Steel in Ammonia Vapor Above Liquid Ammonia," to be published in *Corrosion*.

ARUP, H.

DISCUSSION

Q: What theories or hypotheses are there on the mechanism by which the stress cracking occurs? How does oxygen enable this to happen?

ARUP: Well we do not know enough about this yet. My personal belief is that it is a chemical reaction. It is an electrochemical dissolution of metal in liquid ammonia, and it is not, at least not solely, a hydrogen embrittlement problem, which you could believe. I think this has been brought out very clearly by the U.S. Steel work, although this is being disputed still. I believe this is true.

P.E. KRYSTOW, Exxon Chemicals USA: I'd like to ask

Dr. Arup and Mr. Willie Clark a question. With the emphasis that was made on the unreliability of getting good water and oxygen determinations in the field, I would like to know what your position is as far as its use surveillance coupons as a method for establishing whether the steels in particular ammonia storage tanks will be subject to stress corrosion cracking.

ARUP: Well I'll give one comment of my own perhaps if I may be allowed - that is that I think we should analyze much more than we do, and eventually I hope it will be possible to develop a sort of corrosion monitor which would tell you exactly what the condition is in your tank. It might then be possible to increase the length of intervals between inspections and that is a very great economic advantage.

KRYSTOW: What I meant, and you might not have understood what I said, I was talking about surveillance coupons which would be specially stressed and installed at a convenient location within the ammonia storage facilities. If these stressed coupons show a tendency towards stress corrosion cracking, then you know that you have an oxygen level that could possibly cause a problem.

ARUP: I know many people who have tried to expose prestressed specimens in ammonia for months and months, and found no cracking, even in a condition where we know cracking would be promoted in slow straining. And we believe that if you have welds exposed to the type of varying stresses you have in practice, you will get a cracking situation in a tank because you will get locally a slight degree of plastic deformation.

It's very similar to the stress corrosion cracking phenomenon on pipelines. In gas transmission pipelines you have the problem of extenal stress corrosion cracking and here it has also been shown, that you do not get cracking unless you have a practical chance of local plastic deformation.

W.D. CLARK, Imperial Chemical Industries, Ltd.: We have done a certain amount of work exposing U-bend specimens in ammonia, and we have cracked some of them. But simple tests of this type cannot reproduce the conditions which Mr. Arup has described which require the specimen to be cooled so that it condenses liquid out of the ammonia gas, and the condensed liquid may have a composition different from that of the gas. No one has devised a simple technique for doing such tests in a practical installation.

KEES VAN GRIEKEN, UKF: We purged our Ijmuiden sphere after inspection continuously with about 3 times its volume of about atmospheric pressure nitrogen.

This resulted in an oxygen content in the gas of between 0.1 and 0.2%. The cool roof possibility of a sphere is very informative. However, I think it more applies for colder climates, as you got the stress corrosion cracking in your laboratory experiments only when you had a much colder tensile specimen than the liquid ammonia below it (you cooled with icewater and with solid carbon dioxide in alcohol). Furtheron in a sphere used throughout the year we have a continuous circulation of the ammonia.

In our tank the liquid ammonia re-enters in the top of the sphere splashing open from the roof through the gaseous phase, wetting the wall.

ARUP: Well that's a funny question Mr. Van Grieken, because you made that analysis yourself. We sent a sample of ammonia to Holland, and that's your results that were quoted in our work. Very little work has been done in Denmark on analysis.

VAN GRIEKEN: With the results of the constant strain rate test one can conclude under what circumstances stress corrosion can *not* occur. If it occurs in this test it only proves that propagation of stress corrosion occurs, but does not give an answer whether it can be initiated as the initiation conditions are much more severe than in practice. So the test is very conservative.

ARUP: Well that's the same we are going to do now in our present work. We are trying to work with known compositions of ammonia, and we are measuring the natural corrosion potential of steel, at the same time that we are doing stress corrosion tests. So we shall be able eventually, if we get enough money, to provide some examples of potential measurements in ammonia of various compositions and known stress corrosion behaviour.