Stress Corrosion Cracking in Storage Spheres

Specific prevention procedures were developed to solve a series of problems involving stress corrosion at weld joints in ammonia spheres

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Experience and records of investigations over periods of up to five years with stress corrosion cracking in ammonia storage spheres and railroad tank cars has been helpful in the development of useful operating and maintenance procedures to prevent more of such cracking problems.

The experience was in U.K.F. ammonia facilities in several locations: a storage sphere at New Ross, Ireland; other spheres in Rotterdam and Ijmuiden, Netherlands; and railcars at Ince, England. Figure 1 shows one of the spheres.

Observations and conclusions from the investigations follow:

Stress corrosion cracking in a C-Mn steel sphere (Mn up to 1.6%, average C 0.20%) welded with C-Mn electrodes (typical Mn 0.75%) and used for ammonia with considerable volumes of air, can be prevented by addition of 0.2% of water.

Purging of oxygen to low oxygen levels after inspection of a sphere is difficult, but it is important even with water addition as a secondary safety measure. Venting the gaseous ammonia, preferably by using it in the plant, can be an effective way to control the oxygen content.

Regular checks on the oxygen in the ammonia are important.

A fracture mechanics test is a valuable tool to check stress corrosion conditions.

Stress relieving could be ineffective if not controlled in detail. It is a very difficult and expensive procedure for large vessels and spheres; and it seems to be unnecessary when a good combination of plate material, welding material, purging techniques, oxygen checks, and water addition is used.

Further attention to this type of stress corrosion is important because it is possible that stress corrosion may depend upon a combination of plate material and welding material for certain oxygen and water levels.

Oxygen infection may occur when using a ship for transporting different loads, or after a ship tank inspection without applying proper purge techniques. It may be caused by improper purge technique on the sphere after inspection, and may even occur during the production of ammonia, e.g. at the suction side of the first compression step of the ammonia compressor.

For certain purposes, coatings for prevention of this stress corrosion cracking problem are now under further investigation.

The 48 ft. 6 in. diameter sphere at New Ross, made of plate material containing about 0.2% C and 1.3-1.6%

Figure 1. One of the ammonia storage spheres.

Mn, welded with low-hydrogen electrodes with about 0.1% C and 0.75% Mn, has been in use since Dec., 1967. It has been almost entirely supplied with ammonia from the U.K.F. plant in Pernis, Netherlands, by pressurized tankers and using a vapor return line.

The first statutory inspection took place in 1972. Magnetic particle testing was done on all T-joints in both directions for about 50 cm., and later on 100% of the horizontal seams.

Such a great number of cracks was found, all of them on the fusion line, that they could not possibly have been due to construction defects. It was concluded that stress corrosion cracking was the cause; and it was decided to grind out the cracks and not repair them by welding unless necessary. The maximum crack depth was 5 mm., maximum individual crack length was 135 mm. A fusion line crack is seen in Figure 2.

Figure 2. Crack in lower fusion line of horizontal **weld in sphere.**

Results of grinding were also checked by magnetic particle inspection. The certificates of the plates were checked for the analyses. The carbon content varied from 0.175 to 2.05% , with one case of 0.26% . The carbon equivalent varied from 0.39 to 0.53. No correlation was found between these data and the location of the cracks. By decreasing the pressure relief-valve setting from 181 to 140 lb./sq. in. (normal working pressure is 110 lb./sq. in.) we could use the sphere, relying on normal stress calculation methods, without repair-welding. We did so and decided to re-inspect after one year.

The following actions were also taken:

1. A calculation of the critical crack dimension was asked for. This resulted in a maximum allowable crack penetration of 13.5 mm. (which is 7.5 mm. below the calculated wall thickness for 140 lb./sq. in.) with a maximum allowable crack length of 58 mm. before local yielding could occur. There would always be a leak before break situation.

2. We studied repair welding methods.

3. We discussed a test specimen for stress corrosion cracking, and addition of water to ammonia.

The second inspection was in 1973. Although all cracks had been ground out during the -1972 shutdown, a great number of cracks, again on the fusion line of the horizontal welds, were found.

Maximum crack depth found by grinding and magnetic particle inspection was 10 mm., which was within fracture mechanics criteria, as the cracks had limited length. After all cracks had been removed, it was decided to decrease the pressure relief valve setting to 118 lb./sq. in.

A fracture mechanics WOL-test specimen of welded C-Mn plate made by B.W.I, was installed in the ammonia inlet line of the sphere with a crack initiated at the fusion line of the weld and loaded to 80% of yield strength of the plate material.

Before start-up, the 60,000-cu. ft. sphere was purged with 200,000 cu. ft. of N_2 , which resulted in an oxygen content of $3\frac{1}{2}\%$ in top and bottom of the sphere. Moreover, oxygen was removed by purging gaseous ammonia into the water until no more oxygen bubbles rose to the surface. The oxygen content in the sphere was not

checked after this operation.

Steel test samples lined with various types of rubber lining were installed in the bottom of the sphere to investigate their suitability as protection of the welding zones against stress corrosion cracking.

Four months after this 1973 start-up, the first shipment of ammonia with 0.2-0.3% of water arrived, after which another fracture test specimen of the same construction was installed.

The third inspection, in 1974, included examination of fracture toughness specimens. The first test specimen, exposed for 4 months in ammonia without water addition and 6 months in ammonia with water, showed an extension of the crack length from 2.5 to 7 mm. The second test specimen, exposed for only 6 months in ammonia with 0.2-0.3% of water, showed no increase in crack length.

This proved that 0.2-0.3% of water prevented stress corrosion cracking under the prevailing conditions of materials, stresses, and oxygen content.

The rubber lining test specimens were all unsuccessful as a result of loss of adhesion, so they could not be used as a second safeguard.

As expected, again a certain number of cracks were found in the sphere, as water addition was used only for a part of the year. With the success from water addition, it was decided to repair-weld all ground-out areas deeper than 5 mm. and to increase the pressure relief valve setting to 150 lb./sq. in. Twenty locations, ground out over a length varying from 50 to 800 mm. (average of 125 mm.) and a depth of 5-10 mm. were repair-welded. No stress relieving was done.

Radiographie and magnetic particle inspection proved that all repair welding was perfect. The start-up procedure at the end of July was the same as the previous one.

About 25 shipments of ammonia were supplied in the period up till the 1975 shut-down. Several inert gas analyses were made in liquid ammonia samples from the sphere. The second shipment in August, 1974, contained 63 ppm. v/v of O_2 and 297 ppm. of N_2 ; the 7th shipment in October contained 82 ppm. v/v of $O₂$ and 303 ppm. of N_2 ; the 12th shipment in November only had 3 ppm. of O_2 and 7 ppm. of N_2 . In all cases, oxygen concentration vs. nitrogen suggests infection by air.

Investigation into the sudden decrease of oxygen content between 7th and 12th shipment showed that the 9th shipment had been delivered without a vapor return line. This could mean that oxygen was vented away instead of to the ship and returned to the sphere by the next shipment. Consequently, we now try to use both liquid and gaseous ammonia in the plant.

The fourth inspection was in 1975.

The sphere, with a total length of 2,500 mm. of nonstress relieved repair-welding, and with ammonia containing high concentrations of air and 0.2 to 0.3% of water, showed virtually almost no cracking at all. Only four minor cracks with a depth of 1-4 mm. were found on non-repair welded areas, and had probably been overlooked in the 1974 inspection.

As for the ammonia sphere at Ijmuiden, the plate analysis is about the same as for the New Ross sphere. Analysis of the welding material shows a higher Mn content.

At the first magnetic particle inspection, applied to all T-joints after about 11 production years, no cracks were found. Each T-joint was inspected after grinding the welds in all directions over a length of about 1 meter.

About three years later, during same type of inspection on all the welding seams, cracks with a length up to 20 mm. and a depth of 1 to 3 mm. were found in the welds—even in the areas that had been ground and inspected during the first inspection.

During the past few years, the sphere has been increasingly used for ammonia from other sites. The sphere will probably be inspected in spring of 1976, and arrangements have been made for water injection.

In a group of 12 stress-relieved ammonia railcars at Ince, in use for five years, all constructed of highstrength steel "Ducol W 30" (1.2% Mn, 0.8% Ni, 0.12% C with an ultimate tensile strength of 41 ton/sq. in.) and high-strength welding electrodes with 1.4-1.7% Mn, 1% Ni and 0.5% Mo and an UTS of 50 ton/sq. in., eleven were inspected. Seven showed stress-corrosion cracks in the circumferential welding seams up to a depth of 7 mm. (local wall thickness: 18 mm.).

These tanks had not shown this cracking during the two earlier inspections. Initial discussions showed that purging techniques have recently been improved for other reasons than stress-corrosion cracking. Possibility of adding water is under investigation.

je. **K.A. van Greiken**

DISCUSSION

BILL SALOT, Allied Chemical Co.: I would like to ask if you found in any of these inspections, oil on the surface of the tanks, and also whether you checked for oil contamination in the ammonia.

VAN GRIEKEN: I'm not fully aware of how far we checked oil content in the ammonia. Perhaps Jan Blanken knows more about it. I know we definitely found oil on the surface of the sphere in New Ross, and I thought in the earlier times also in the sphere in Umuiden but that was perhaps from the old production unit. That's what I can tell you at this moment. Perhaps Jan can give you an idea of the analysis of the oil in the ammonia.

JAN BLANKEN UKF: I am sorry, I can't I'm afraid. True is that the Umuiden sphere had no cracks after eleven years of operation with the old reciprocating compressors plant and we found oil when we inspected it. We found cracks after we changed to the centrifugal type plant, where we have a minimal amount of oil.

But whether there is a relation is very difficult to say. Because after we installed the centrifugal type plant also the amount of ammonia transferred through the sphere increased, and it is difficult to say how far contamination of the ammonia during transport has influenced the cracking. VAN **GRIEKEN:** In the last year we had more transport between the plants—that's perhaps also a point for the different behavior of the Umuiden sphere in the past and nowadays.

DON BAGNOLI, Exxon Chemical: In reference to your estimates on leak before burst, I wonder if you could give us an idea of what type of wall thickness would be required to have, using your calculations, a burst before leak condition.

You explained that you went to a lower pressure. I'm just wondering how close you were to your particular calculation to a burst before leak. In other words, what sort of wall thickness would take you into that condition?

VAN **GRIEKEN:** I'm not in the possibility to give you the mechanical calculations right now. Penetration of cracks was smaller than allowable from fractures mechanic calculations done by B.W.I. That's what I can tell you now. Is that a part of the answer?

BAGNOLI: Well it seems there are many ways of making this estimate. Exxon has an approach that was used for other types of vessels as reported by Lambertin and Vaughan at the October, 1974 ASME Petroleum— Mechanical Engineering meeting in Dallas. I was curious as to your approach. The one that was used here because eventually you reach a—condition where your wall thickness is too high to accommodate the critical defect for a given material This is what distinguishes a safe from an unsafe operating condition.

MAX **APPL,** BASF, Germany: What is your feeling according to reliability of test specimens in liquid ammonia? We tried it several times, and we never succeeded to get cracks in test specimens, with one exception—when using a steel with a very high yield strength which is used for making springs. The reason probably could be a very low oxygen content in the ammonia because we vent the inert gases from the spheres. There was no difference between water containing and water free ammonia.

VAN **GRIEKEN:** I must say our experience is not so wide but one—perhaps of the specific things is that we

used fracture toughness specimens, that always have a fatigue crack as crack-initiation. I think these specimens are more sensitive than a normal tensile test, or a spring. On the other hand, I know that some research has been done with these fracture, toughness specimen also in liquid ammonia, and even there it seems to be rather difficult to come to stress corrosion cracking in liquid ammonia with oxygen.

The other specific point might be that we made a fracture toughness specimen out of a plate with a weld and we initiated the fatique crack in the fusion line of this weld. Without the water we had an increase of the crack length, and with the water we did not have that increase.

Q. You mentioned the possibility of developing coatings for preventing this type of cracking. Could you say what type of coatings you have in mind, and what applications would be suitable for coating?

VAN **GRIEKEN:** We have done tests on steel plates containing a weld in it. We applied different rubber lining over the weld and two or three inches on each side of the weld. As we found the cracking in the sphere especially in the fusion line or at least close to the welding, we had the idea that application of a lining or coating on the welds could give us more safety. We used several kinds of rubber linings and several types of adhesives for the rubber lining. Later on we did some tests in a small vessel in the circulation loop of our Umuiden sphere.

Here we investigated some more putty type coating. In all cases we had loss of adhesion probably occurring during depressurizing the sphere during the shutdown.

We have not yet tested some metallic coatings in the liquid ammonia.

BERNARD BRODWIN, M.W. Kellogg Co.: Have you had any opportunity to take a hardness traverse through the weld heat effective zone and base metal after stress cracking, or after welding at any time.

VAN **GRIEKEN:** We haven't done it and I agree in general hardness testing is a good thing. There are always hardness peaks in the heat affected zone of a non-stress relieved steel weld. But on the other hand our C-Mn steel New Ross sphere was welded with welding electrodes containing only 0.7% of manganese which is a definitely lower manganese content than in the parent material. It is my opinion that, with the normal welding technique this combination won't give high local hardness peaks in the heat affected zone.

Q. Is there any relationship between the temperature and pressure for the sphere with the stress corrosion?

VAN **GRIEKEN:** Our spheres in the Netherlands and in Ireland work without refrigeration on the normal temperatures. The normal working pressure was so low that it gave us the possibility to go down with our setting pressure to about 115 psi. Does that give you an answer?

BLANKEN: May I add that we inspected two atmospheric storage tanks and never found any stress corrosion cracking.

And as far as I know no stress corrosion cracking was ever found in an atmospheric storage tank.

VAN **GRIEKEN:** You are right, Jan. The explanation could be that first of all, all chemical reactions slow down when you are on a lower temperature, and secondly that the refrigeration system on an atmospheric pressure tank, removes the oxygen to the condenser. On the other hand, what I wanted to state with this paper was that with the 0.2% of water in this sphere, constructed with normal medium strength C-Mn steel, we have a good and safe system. We found the water addition in our circumstances worked pretty well.