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Avoiding Stress Corrosion Cracking

Survey of recent experience in incidence of this problem in equipment handling liquid ammonia has led to development of some useful guidelines for meeting the problem.

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The Billingham plant of Imperial Chemical Industries has three of the early Kellogg 1000-ton/day ammonia units designed to run on naphtha, and later (1970-71) converted to natural gas. All three of the 0.5% Mo steel (A204B) vessels have now been replaced, after operating periods of 6-7½ years.

Defects in the vessels probably developed more rapidly than elsewhere because the front ends of the plants cycled much more than is usual with plants on gas feed. Furthermore we were learning to live with naphtha, and difficulties with the make-gas trim boilers led to the inlet temperature to the shift often being high, as much as 410°C as against 370°C in the flowsheet.

The defects in the first vessel to give trouble (No. 2 unit) were found in December, 1971, after 4½ years of operation. The massive repair operation was reported to this symposium in 1972. Basically, it involved the following:

1. The exit nozzle was off-specification and much too hard. Although its cracking led to close examination of the vessel, this should not be relevant to other vessels.
2. All the deep groove welds attaching set-in branches were badly cracked.
3. The top 24-in. of the barrel was badly blistered. The top (and bottom) ends were not blistered.
4. No cracking of the catalyst support beam bracket welds was recorded.

The repair work did nothing for the blistered area, and the vessel was considered unsuitable for long service. A new vessel was therefore ordered—in 1% Cr Mo steel—and inspection of Nos. 1 and 3 vessels brought forward.

The No. 3 vessel was examined in June, 1972, using magnetic crack detection on all welds except the main seams, and ultrasonic examination of nozzle welds, the top circumferential seam, and the area found blistered on No. 2. The vessel was found free from any fault and returned to service.

No. 1 unit vessel was examined in October, 1972. It was found to contain most of the faults of No. 2 including blistering, except that the exit nozzle material was correct. Much repair work was necessary before it could be re-used. As the new vessel for No. 2 unit had just arrived and the repaired No. 2 unit vessel seemed to be satisfactory, the new vessel was put on No. 1 unit and a second new vessel ordered.

The No. 2 vessel was examined again in early 1973 and the repairs were satisfactory. It was replaced by the (second) new vessel in April, 1974.

It was decided to examine the No. 3 unit vessel again in June, 1975, though no troubles were expected. Bad cracking was found, especially at the welds of the brackets supporting the catalyst support beams. While much of the cracking was at the bracket side of the weld, seen in Figure 1, some of the cracks ran into the pressure shell, at one point to a depth of 1¼ in. over a length of 5 in. The top of the barrel appeared laminated but not blistered.

It was considered that some small cracks might have

Figure 1. Crack at Support ring/shell weld.

been missed in 1972 but there was no question that there had been major deterioration in the three-yr. period, during which there had been 16 pressure cycles and an inlet temperature around 400°C. A new vessel was available (delivered in advance for a fourth unit), and it was installed in May, 1975. Incidentally, all three new vessels were installed on the ground, not in the original position above the low temperature (LT) shift.

The bracket welds on the No. 2 vessel had not seemed a problem; on No. 1 they were not examined in detail because the nozzle welds were so bad. After the severe cracking was found on No. 3, bad bracket cracks were found on the scrapped No. 2 vessel.

The assistance of the Welding Institute was obtained, with a view to determining the cause of the cracking, whether it was worthwhile doing a major repair operation on the No. 3 vessel to fit it for some other duty, and what the implications were in relation to other ½% Mo steel vessels in service. No. 3 vessel was lifted out of the plant, and one sample was cut from the blistered region of No. 1 vessel (the remains of which are still *in situ*, as is No. 2 vessel).

After detailed ultrasonic examination, various "boat" samples were cut from the inside of No.3 to permit examination of the cracks, the "laminated" region, and to get toughness data (Charpy V) from the inlet and exit temperature regions on one of the shell plates (NB: each barrel plate extends the full length of the vessel).

The No. 1 converter samples had about 20 ft. lb. Ch V at 20°C, and fracture mechanics (COD) tests indicated that brittle failure might have taken place if the vessel had been hydrotested below about 40°C (before repair). Heat treatment at 650°C gave appreciable improvement.

Examination of the cracks in the parent plate, both in section and after breaking open, suggested strongly that cracking had occurred near ambient temperature; the main crack surfaces were oxidized and indecipherable but there were subsidiary cracks of a cleavage nature. The hardness was 150-200 HV. It is believed that the steel became charged with hydrogen at the operating conditions and on cooling this caused embrittlement and, as the steel was basically not very tough, cracking resulted.

Lamination and blistering inside the top

The original work on No. 2 vessel showed strong evidence that conditions inside the top of the vessel produced lamination and blistering. At the bottom this did not happen to the same plates. It was improbable (1 in 256) that the effects resulted from variations along each plate. The "laminations" arose from the joining up of small inclusion platelets and the steel around the lamination was locally decarburized. In Nos. 1 and 3 there was similar ultrasonic evidence of lamination about 10 mm. beneath the inside surface. No. 1 was slightly blistered. Micro-examination showed inclusion lamellae in No. 1 but no sign of decarburization and little sign that platelets were joining up. The few samples of No. 3 examined showed no features to explain the ultrasonic response.

No faults of any kind have been found in the main longitudinal seams or the welds to the dished ends.

Cracking of the deep groove set-in nozzle welds was a major feature of No. 2 and No. 1 vessels. Many cracks were sub-surface. They were both radial and circumferential and mainly confined to the ½% Mo weld material. Little investigation has been done on these.

The fillet welds attaching the catalyst support ring and the heavy brackets which support the beams have been cracked in all three vessels and also in a number of other vessels, some of 1% Cr Mo. Such cracking, which has been found 30 mm. into the shell plates, is a constant concern. In one brand new 1% Cr Mo vessel it was present and was certainly due to lack of adequate preheat.

Inadequate preheating is a danger with all attachment welds inside vessels, and the smaller the attachment the greater the risk. We cannot be certain that the cracking found in the HT shifts was not the extension of fabrication cracks. We now examine all such welds in new vessels very carefully, toe grinding if the profile makes crack detection uncertain. Where possible we do without support grids and support the catalyst on beds of ceramic balls.

The A240B 0.5 Mo steel was only examined after service. Its toughness was not good. Heat treatment at 650°C increased the toughness to around 40J Ch V, which exceeds normal code requirements. It seems probable that when new the toughness was at least of this order. The hardness was 150-190 HV with 200-220 against the welds. The grain size was somewhat variable, the samples varying from ASTM 4-7. The micro-structure was 80% ferrite, 15% pearlite and some coarser carbides. Under the electron microscope no fine precipitates which could have resulted from ageing at 500-600°C were found.

The analysis was well within specification: C-0.19; Si-0.20; Mn-0.7; Mo-0.5; Ni-0.1; Cr-0.07; Cu-0.11; Al-0.006; Nb, Ti, Pb, Sn, all below 0.01%. Nitrogen was 0.005, oxygen 0.015 on two samples analysed.

General Conclusions

What have we learnt from our rather depressing experience with these three substantial vessels, allied to less severe troubles with a few other ½% Mo steel vessels?

We suspect ½% Mo steel is far more likely to give trouble than, for example, 1% Cr Mo steel. This trouble may arise in various ways:

1. The steel after service at 350°C - 400°C is not very tough and cracks may appear when the vessel is cold.
2. It is perhaps regarded as too easy to fabricate and as a result too little preheat is given when welding.
3. The conventional welding materials used for branches and fillets are prone to severe cracking in service, though main seams give no trouble. There is probably a difference in the amount of straining (due to stress concentrations and thermal gradients) at branch and fillet welds as compared with main seams which causes the different performance.

4. The resistance of ½% Mo steel to hydrogen attack appears to be less than the Nelson curves suggest.

As a result ICI Agricultural and Petrochemical Divisions would not accept any vessel built of ½% Mo steel but would demand a Cr Mo steel. Perhaps this is blind faith, and if we had had as many 1% Cr Mo vessels we might be less certain. We have had trouble with a 1% Cr Mo vessel but this was related to a glaring design/fabrication weakness.

We are increasingly conscious that the shell of a pressure vessel is a rather reliable item. Any decoration with internal brackets, support rings, lugs, etc., makes it less reliable; we try to avoid such items, supporting catalyst on beds of ceramic balls, etc. We look at bracket welds and the like very carefully and if they are too rough for magnetic crack testing, we would grind them locally. We may well find ourselves toe-grinding all such welds. The cost is minute in relation to downtime of a large plant. #

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DISCUSSION

KEES VAN GRIEKEN, UKF: You suggested cracking might have occurred even with 0.2% of water. In this respect I like to add that e.g. in Denmark they used rather high strength carbon-molybdeen weld material. Besides for these tanks they had limited amount of nitrogen to purge the spheres after an inspection so that high oxygen concentration could occur.

In several cases the water content of the ammonia brought from other companies is not checked.

CLARK: I agree that's another thing where analysis needs to be done. You should not just assume that because somebody tells you it contained 0.2% water it does. You ought to go and measure it.

VAN GRIEKEN: I fully agree with the list of suggestions for using and manufacturing spheres.

I only miss the beneficial effect of water.

Stress relieving is a good thing but almost impossible for a storage sphere.

In this case my opinion is that with a non-stress relieved normal carbon manganese steel and matching welding material you normally have a safe situation when you use ammonia with 0.2% of water.

We also have to realize that correct sampling techniques for liquid ammonia are important.

CLARK: The method which must be followed when sampling liquid ammonia for analysis is clear. A small volume of liquid must be trapped between valves in a pipe which is absolutely full of liquid. This volume is then completely vaporized into an evacuated chamber. If any liquid is left unvaporized, then the partition of the oxygen between the vapour and the residual liquid is quite uncertain. Only when the liquid is completely vaporized can it safely be assumed that a sample taken from the vapour will have the same composition as the original liquid.

LARRY ZEIS, Pullman Kellogg: Is it certain that the one failure at minus 20 degrees C. - medium strength steel that cracked - is it certain that that was a stress corrosion crack and not an as built crack?

CLARK: Not wholly certain. That is one of the letouts. It also rams home the point that when you build a tank, inspect it properly, so you know what you started with. The people who have that tank, they believe it is stress corrosion, but I can't say it's proved.

ZEIS: That's a good point because most tanks as built are not magnetic particle inspected, and the first inspection will find cracks and it could be debatable whether they are as built cracks or stress corrosion cracks.

The second question concerns the recommendation of periodic inspection of low temperatures tanks, tanks which have never had reports of cracks. Would you comment on the possibility of introducing oxygen during the inspection. From the look of the tanks we have seen after service, there are surfaces that look like they could absorb or adsorb a lot of oxygen. It might take a long time to get that oxygen out. Have you considered that?

CLARK: I have considered this. The one thing you don't want to do is have a tank like a transport tank which fills and empties, fills and empties, and maybe you get air into it. And what I'm recommending people to do is empty it and get air into it, so you can crawl around the inside in comfort and inspect it critically. Because it's not easy to inspect a tank critically if you're all done up in air lines and so on and so forth. This means that when recommissioning you have to go to a lot of trouble to purge the air out, and this is not easy. you will cause cracking by introducing oxygen. It's better to run that risk than not to know whether you've got cracking at all. We are inspecting our tanks, certainly every six years and possibly more frequently.

JAN BLANKEN, UKF-Holland: A lot of discussion has been going on in our company about the distribution of oxygen between liquid and vapour.

The problem I run into is that if you have 0.2% of water and 1 ppm of oxygen in the liquid ammonia in the sphere we guesstimate that there will be something

like 10 ppm of water and 200 ppm of oxygen in the vapour.

Now with the sphere running below ambient temperature a level pot connected to the top and bottom of the sphere will act as a type of reflux condensor and there will be low water and high oxygen concentration in this pot. Question now is why do we not find stress corrosion cracking in pots like that.

Also when you want to take a sample of the liquid in the sphere, do not take it from a level pot because concentrations could be completely different.

CLARK: I agree. There are very great difficulties in this subject. It cannot be settled on the basis of laboratory tests using ammonia containing various amounts of oxygen, water, etc. You have to look at actual installations and what the conditions are inside them, especially in relation to condensed films on the upper part of a tank.

The next paper by Mr. Arup overlaps mine and I think Mr. Arup may be better able to answer some of the questions which have been raised.