Cracking and Blistering in a Shift Converter

Although an investigation could not definitely determine the cause of cracking in the exit nozzle weld, the material of construction is suspected to be the source of trouble.

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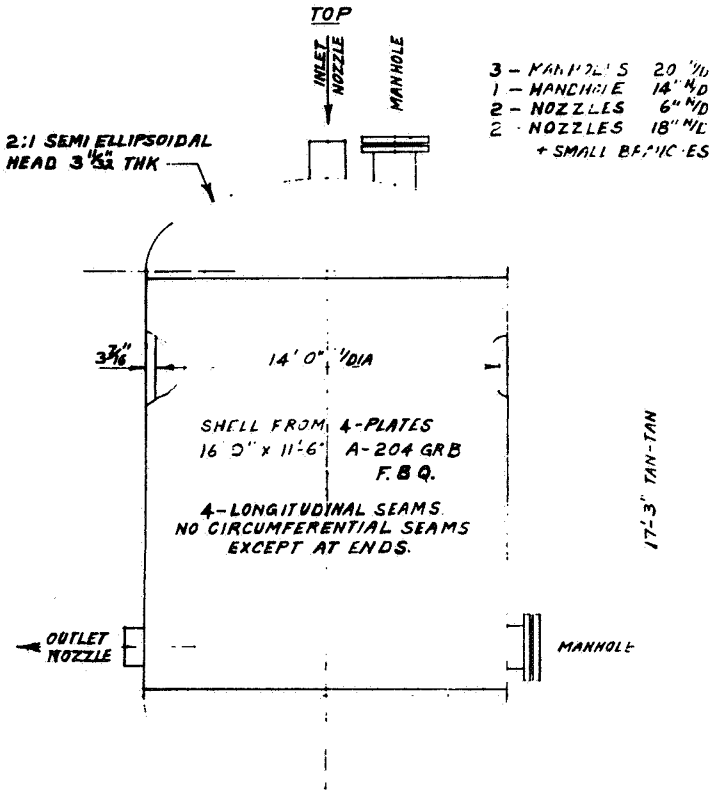

Figure 1. General arrangement of the high temperature shift converter.

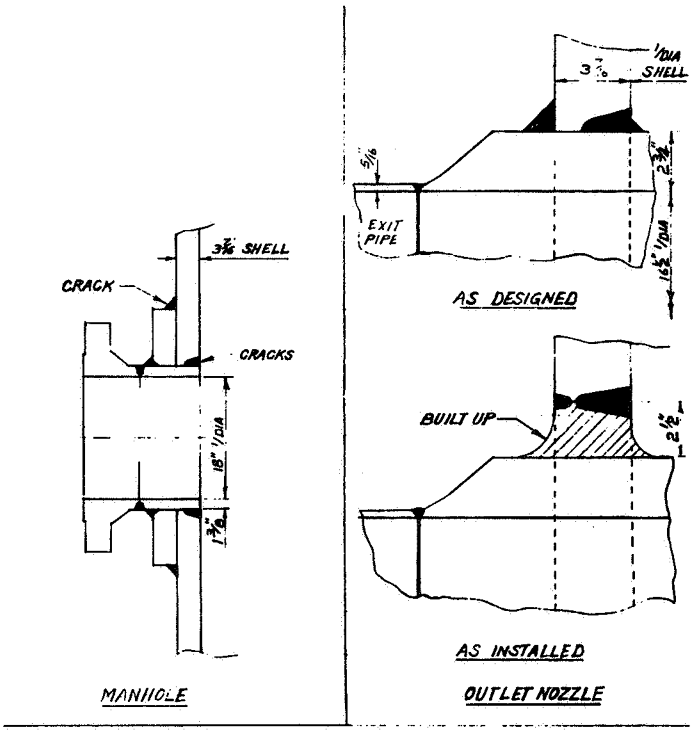

Figure 2. Details of the high temperature shift converter.

The ICI facility at Billingham has three nominally identical 1,000 ton/day ammonia units, originally on naphtha, and now on natural gas. In December 1971, a small leak at the exist nozzle pipe weld on No. 2 unit high temperature shift converter fired and caused a shutdown. Salient details of this vessel are shown in Figure 1. The plant had been on and off line 88 times since 1967. Investigation showed that the 18 in. nozzle was a forging and had an axial crack running back from the weld. Orthodox attempts to cut out the crack and repair the forging soon ran aground when it was found that there were dozens of axial cracks and that the forging was abnormally hard, about 300 Vickers.

Consultation with the makers of the vessel showed that they had cracking troubles in making the deep groove weld to attach the set-through forging, Figure 2, and had finally scrapped the forging and hurriedly obtained another. This had been built up with weld metal so that it could be butt welded into the shell, and after building up was normalized, but not given any mechanical tests. The stress relief after testing was expected to produce the normal level of mechanical properties. As, however, this forging had an analysis at or a little above the top end of the specification (A192 F1), and contained in addition about 0.5% Ni and 0.2% Cr, it was resistant to the tempering/stress relieving operation and went into service with an abnormally high hardness. It is assumed that the combination of this hardness with the service conditions: 420°C (790°F) 400 lb./in.^{2}, 162 lb./in.^{2} partial pressure of hydrogen, was the cause of the cracking. During the examination it was found that some of the cracks were so 'tight' that magnetic and ultrasonic methods failed to find them. Only metallurgical etching could show up some cracks an in. long and of considerable depth. Most of the cracks were internal and did not reach any surface.

Nozzle Replacement

After various schemes had been considered, it became clear that there was no option but to replace the nozzle, and this was done by building up a new forging so that it could be welded in at a larger diameter than the cracked nozzle. This was done by Billingham staff and took some 30 days, including stress-relief of a 60 in. band round the vessel.

Rather little attention had been paid to other parts of the vessel (except the inlet nozzle which is similar to the exit nozzle but was found to be of normal hardness and with no detectable cracks) and there was considerable despondency when on pressure test at 1,000 lb./in.^{2} a leak came from a bleed hole in a manhole compensating plate. Examination now showed several radial and one 8 in. circumferential crack in the internal deep groove weld attaching the set-through manhole, and excavation showed more cracks both on this and other manholes and branches. They were picked up by magnaflux, the usual ultrasonic methods being ineffective. At least 50 quite large cracks were found, mostly reaching the root, and a few extending from the weld into the parent metal up to an inch.

It was clear that the leak had not been present before the plant was shut down, and as some of the welds now found to contain cracks were outside the zone possibly affected by thermal stresses from the stress relief operation, it was concluded that the cracks had been there while the plant was running and the pressure test stresses had caused one of them to extend to form a leak path.

A crack was also found in the fillet weld attaching a compensating plate to the shell. It showed near the compensating plate surface a few inches long, and excavation showed that at the root of the weld it extended almost 360°. Various bracket welds were also found cracked. However, no faults were found in the main seam welds.

The details of the welding procedure used by the fabricator were obtained and showed no obvious grounds for criticism. The only conclusion was that insufficient care had been taken on preheat, dryness of electrodes etc. and many subsurface cracks had been produced. Service conditions had affected at least one crack so that it spread under the pressure test stresses. Excavation of the weld which leaked showed a rather excessive root gap had been present which would add to the risk of cracking.

All the nozzle, manhole, and branch welds were excavated to remove the cracks. In several cases, little weld metal was left. The welds were then remade, except in the case of two redundant branches, which were closed by a plate fillet welded over the hole on the inside of the vessel. The whole vessel was then stress relieved in situ and pressure tested successfully.

The only tests done on the material near the cracks was on a silver of weld metal detached by grinding. This was quite ductile. Various tests were done on redundant catalyst support beams from the bottom of the vessel. These were of 1 in. ½% Mo steel plate, and impact tests on plate and on weld metal showed no signs of embrittlement, values of 40- to 100 ft. lb. Charpy 'V' at room temperature being obtained.

Blistering

A separate matter was that a group of seven blisters were found about 6 in. below the weld to the top dished end. The biggest was 4 in. dia. and 3/16 in. high. Ultrasonic examination showed that there was a lamination about 3/8 in. from the inner surface extending 12- to 24 in. down from the weld, right around the vessel, i.e., on each of the four plates from which the barrel had been constructed (there were four longitudinal welds, but no circumferential welds except ot the dished ends). No other parts of the plates were laminated. If the original plates had been laminated near one surface at one end, the chance that they would all be assembled with the effected area 'top inside' is only 1 in 256. It therefore appears highly probable that the 'lamination' had been caused by service conditions.

Three of the blisters had cracked across the crown. From a fourth a sample of gas was collected by drilling a small hole, and analyzed as 71% CH_4, 28% H_2. It was estimated that the pressure in the blister was perhaps 60 lb./sq. in. at the time it was tapped, whereas it would have taken at least 3,500 lb./in.^{2} to cause the bulging. A small piece was cut out of the crown of the blister. The cavity was clean and empty, the 'lamination' had been a colony of small platelike inclusions rather than a single sheet, and the steel adjacent to the lamination was heavily decarburized, whereas adjacent to the i.d. of the vessel it was quite normal, Figure 3. Its hardness was normal.

A methane found in the cavity ties up with the

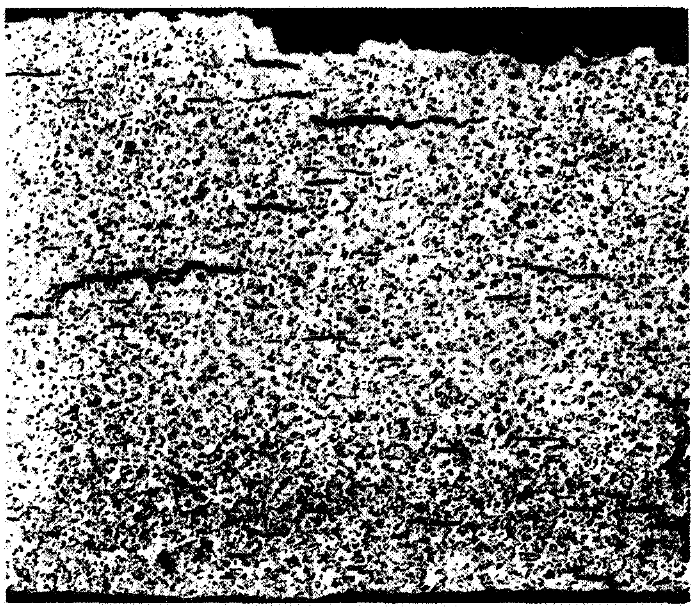

Figure 3. Section of the cap of a blister taken from the inner wall of the vessel.

decarburisation found, but according to the Nelson curves, hydrogen attack would not be expected below about 1,000^{o}F with 160 lb./in.^{2} partial pressure of hydrogen, and the service temperature had not exceeded 800^{o}F.

A well-known mechanism of blistering is the injection of hydrogen by a corrosion mechanism, which can induce very high internal pressures. Some attention has been paid to the fact that potash from the reformer catalyst (on naphtha) tends to collect on top of the high temperature shift catalyst, i.e., in the blistered region. Could this be causing a corrsion reaction which injected hydrogen into the steel? The blistered area showed no sign of corrosion, and injected hydrogen would be expected to cause decarburization as a surface layer, working inwards, and not wait until it has reached a colony of inclusions. Some laboratory work has been done to assess whether a combination of potash, carbon oxides, hydrogen, and steam can cause more hydrogen to diffuse into the steel than the partial pressure of hydrogen alone. The results show an increase in diffusion rates by a factor of up to 10 but this does not fully explain the production of the laminations.

The blisters, open to the contents of the vessel, reduce the effective wall thickness. It was not considered practicable to repair the blisters and the lamination. As the vessel had been designed to ASME VIII Division I it was decided that on a short term basis it was perfectly safe to run it. A new vessel has, however, been ordered.

Obviously, the condition of the high temperature shift vessels on Nos. 1 and 3 units required thought. The same fabricator made all three, Nos. 1 and 2 together, No. 3 a little later. No. 3 vessel was examined and no fault found. No. 1 is at present being examined and appears to be in the same state as No. 2, though its exit nozzle is not hard and cracked, and laminations are not so extensive. The internal nozzle welds, however, contain radial cracks.

It is significant that ultrasonic operators reported very high attenuation on Nos. 1 and 3 vessels, presumably due to dirty steel, but that No. 2 vessel did not show this. While inclusions in the steel can obviously be important in relation to the blisters, it is less likely that they could cause the cracking, which was mainly in the weld metal.

Up to the present time, it has not been possible to cut any significant specimens from the vessels for metallurgical examination. It is hoped that when the replacement vessel is installed a full examination can be done on the scrapped vessel.

Other Vessels and Piping

The 18 in., 5/16 in. wall piping inlet and exit of the high temperature shift vessels is of 0.5% Mo steel and there have been some eight leaks at butt welds for which no adequate explanation has been found. The welds are not very good, but the leaks are not at the worst points; stress calculations show nothing exceptional. Repaired welds are being stress relieved and when possible 1% Cr-Mo piping substituted progressively.

Two 0.5% Mo steel exchanger shells in the shift system of a Texaco unit built in 1958 have been found to have extensive cracks in the back fillet attaching the 6 in. thick main flanges to the head and 4 ft. dia. shell. The cracks were some 3 ft. long and had spread from the root. The No. 1 ammonia unit hydrodesulfurizer vessel (0.5% Mo steel) had a leak through the bleed hole of one manhole in 1968 and the groove weld required repair. It was a very similar case to that of the high temperature shift vessel reported above, but a local repair was effective.

The above troubles with 0.5% Mo steel vessels make us suspicious about this steel. On paper it appears a very adequate and cheap steel for many duties, but because it is nominally not very sensitive to fabrication details, we suspect that it is a source of trouble. We prefer 1% Cr-Mo steel, a little more expensive, needing considerable care in fabrication but, in general, being treated appropriately, and having a wider range as regards hydrogen attack. The replacement for the No. 2 unit shift converter has been ordered in this steel.

It is perhaps relevant that recent Japanese work has shown that in certain conditions of heat treatment which may arise from welding, the resistance to hydrogen is some 200^{o}F below that promised by the Nelson curves. On the other hand, practically all the troubles reported are in the 0.5% Mo weld metal rather than the parent plate. Consideration was in fact given to using 1% Cr-Mo weld metal for the repairs to the high temperature shift vessels and piping, but as there was no obvious reason why it would be better, and the use of a non-matching weld metal would tend to confuse the situation, it was decided not to do this. #

DISCUSSION

ED JOHNSON: Allied Chemical: What is your procedure for stress relieving after you pass on this material?

GEORGE: If you'll give me a moment while I try and delve through the mass of papers. We were very concerned about stress relief, concerned that someone should make a mistake in its execution and, as I mentioned, we arranged 46 thermo couples inside and outside, particularly on manholes. The set up was that various big manholes had electric heaters put on, whereas the main vessel had the hot-air system. You'd like to know the temperatures?

JOHNSON: The temperatures?

GEORGE: Yes, six-fifty for three hours. There was about 50 degrees an hour temperature rise to that level, and the same coming down – so it's about 50 degrees centigrade an hour up to six-fifty, hold for three hours, and down again to about 200^{o}C, after which lagging was removed and the vessel allowed to cool naturally.

JOHNSON: And subsequent to this you had no cracking embedded in the repairs?

GEORGE: Not after this very massive final repair. It was again thoroughly inspected, and nothing untoward was found.

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