An Ammonia Shift Converter Failure

Brief case history of a metal failure in a high temperature shift converter resulting from hydrogen cracking, and what was done to solve it.

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An extensive investigation into a failure in a high-temperature shift converter in an ammonia plant in Rotterdam-Pernis late in 1975 has led to several useful lessons and ultimately to process improvements for safer operation.

The ammonia plant is a joint venture of the Dutch company, UKF BV, and the German company, BASF AG. It has been producing 1,000 short ton/day of ammonia from natural gas since 1967.

At the beginning of November, 1975, the plant was being restarted after a turnaround and was being heated with process steam. It was then noticed that steam was escaping from the insulation of the high-temperature (HT) shift converter. On removing the insulation, it was seen that the steam was flowing through a crack in the HT converter. Thereupon, the entire plant was shut down.

Magnetic and ultrasonic examinations of the converter's interior revealed one large crack and two adjacent small cracks in the wall, which has a thickness of 80 mm. They were located at the lower end of the cylindrical shell, perpendicular to the weld between the shell and the head. The position and dimensions of the cracks are shown in Figure 1. The large crack was 400 mm. long, with a maximum gap of 0.1 mm. All the cracks run from the inside to the outside. The small cracks are 50 mm. long and have not yet penetrated to the outer wall. None of the cracks starts from a welded part on the inner wall. In addition, a number of smaller cracks were noticed where fittings were welded to the wall in the upper part of the converter.

The most important design data and operating conditions are presented in Table 1.

Table 1. HT Shift converter, ammonia plant at Pernis (design data and operating conditions)

Material	16 Mo 5	ASTMA 204 B
Design pressure	34.2 atm.	486 lb./sq.in.gauge
Design metal temperature	482°C	900°F
Operating pressure	29-30 atm.	413-427 lb./sq.in.gauge
Gas temperature, inlet	350-385°C	662-725°F
Gas temperature, outlet	415-450°C	779-842°F
Operating hours	63,000	
Number of shutdowns, approx.	20	

Figure 2 shows the weld between the shell and the head with two cracks on the inside of the converter. Ultrasonic examinations revealed several of these cracks in the weld metal. It was therefore an obvious assumption that the large crack also originated from an initially small crack within the weld.

A cross-section at right angles to the weld can be seen in Figure 3. The weld was automatically welded from the outside and built up to about 60% of the wall thickness (submerged arc process, Ulme 3 rod, Arcosite Mo powder).

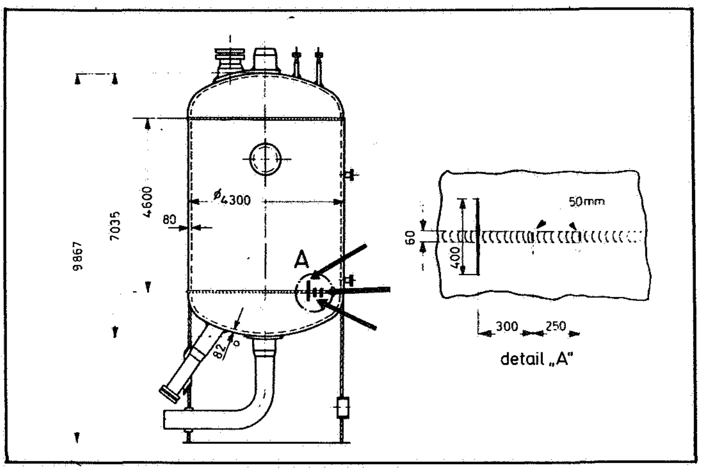

Figure 1. Cracks in the HT shift converter.

Figure 2. Cracks in the weld.

After the root had been machined, the inside of the converter was welded manually with a Philips coated kV2 electrode. The weld was stress relieved at 620 - 630°C, not in a furnace but by local induction heating. According to the manufacturer's report it must be assumed that the local stress relief operation was carried out correctly.

Hardness was measured on four lines drawn over the cross-section of the weld. Fairly high values, i.e., 240 - 270 Hv., were found for the weld metal, as opposed to 170 Hv for the parent metal. The figures for the strength of the weld metal were also close to the upper limit.

Several microscopic studies of the manual weld in the vicinity of the cracks revealed accumulations of pores and minute gas channels in the weld metal of the root passes. Figure 4 shows a horizontal cross-section through the weld. The pores and a crack issuing from one of them can be clearly recognized. A microsection perpendicular to the surface of another crack also revealed pores in the welding material, as seen in Fiture 5. A crack running parallel to the edge of the fracture commences at a large pore. In Figure 6, the details are reproduced of a crack in the weld metal. It can be seen from the polished sections that the cracks are intercrystalline and that their edges are lined with oxides (magnetite). All the cracks in the weld that connect with the inner wall of the converter display this layer of magnetite, whereas the other fine cracks do not.

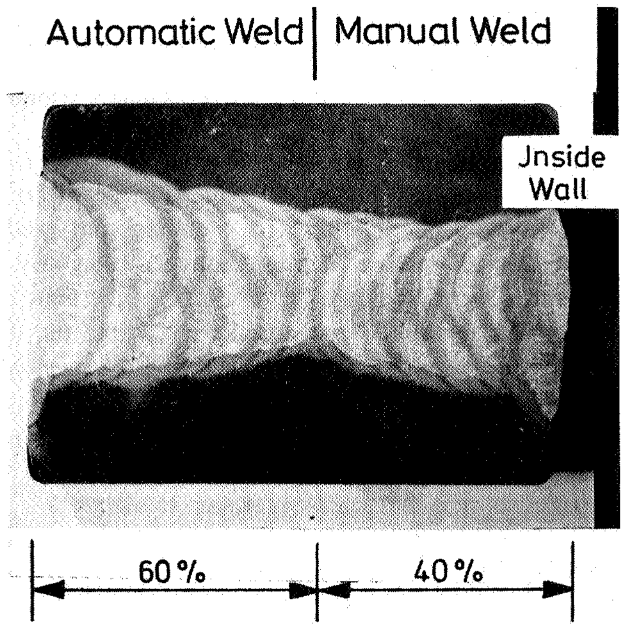

Figure 3. Cross section of the weld.

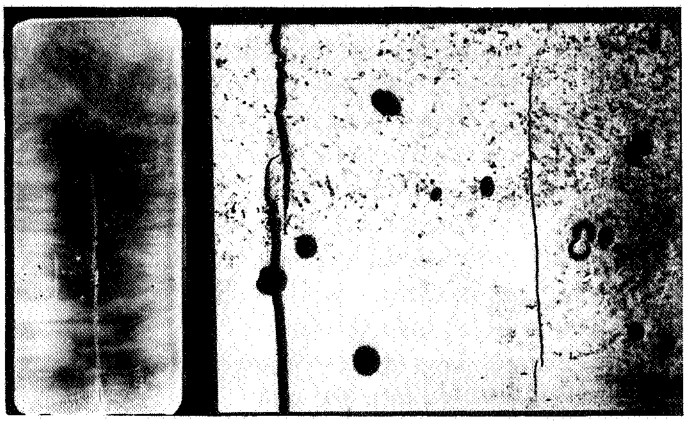

Figure 4. Horizontal section through the weld.

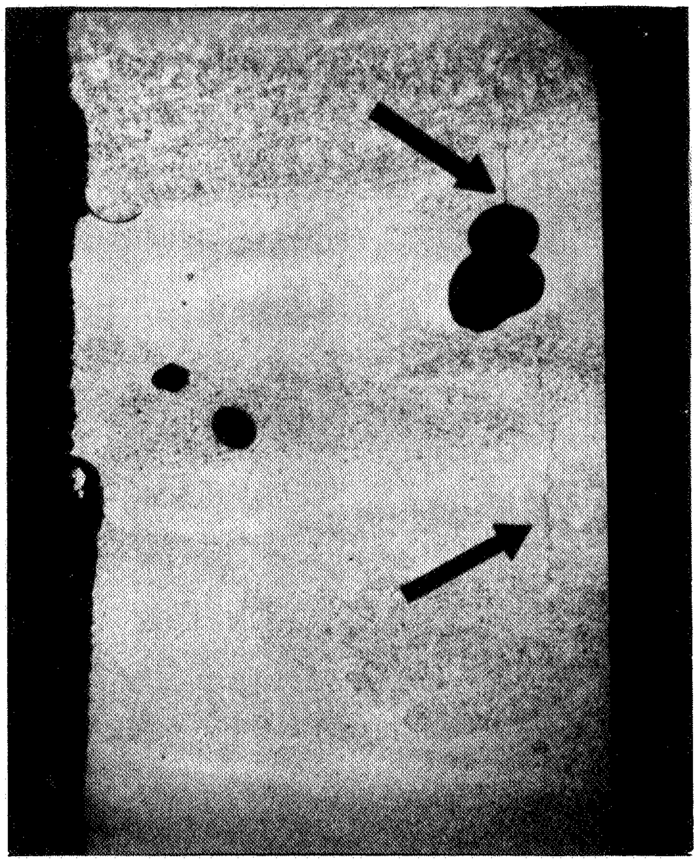

Figure 5. Porous weld.

Origin of the cracks in the weld

The accumulation of pores in the manual weld indicates that the electrodes were moist. In such cases, hydrogen is formed during welding and diffuses into the welding material. The result is "hydrogen cracking." The initial cracks in the weld were probably formed immediately or within a few hours after welding.

According to the Materials Testing Department of the Dutch State Mines (DSM), crack formation was favored by high stresses that were induced during welding in the rigid construction. It is likely that all the stresses were not eliminated in the thick-walled converter by the local stress relieving adopted. The surface of a fracture that was induced in a compact tension specimen during the DSM fracture mechanics investigation shows that there were residual stresses in the weld. Further growth of the cracks could have been caused by strain-aging at the extremities of the cracks, low-cycle fatigue (starting up and shutting down), or local hydrogen embrittlement at the extremities.

The BASF Materials Testing Department considers that the cracks could have arisen in the following manner. If atomic hydrogen that has been dissolved during welding diffuses and moves to the pores and to other inclusions, molecular hydrogen is formed. Since this hydrogen is no

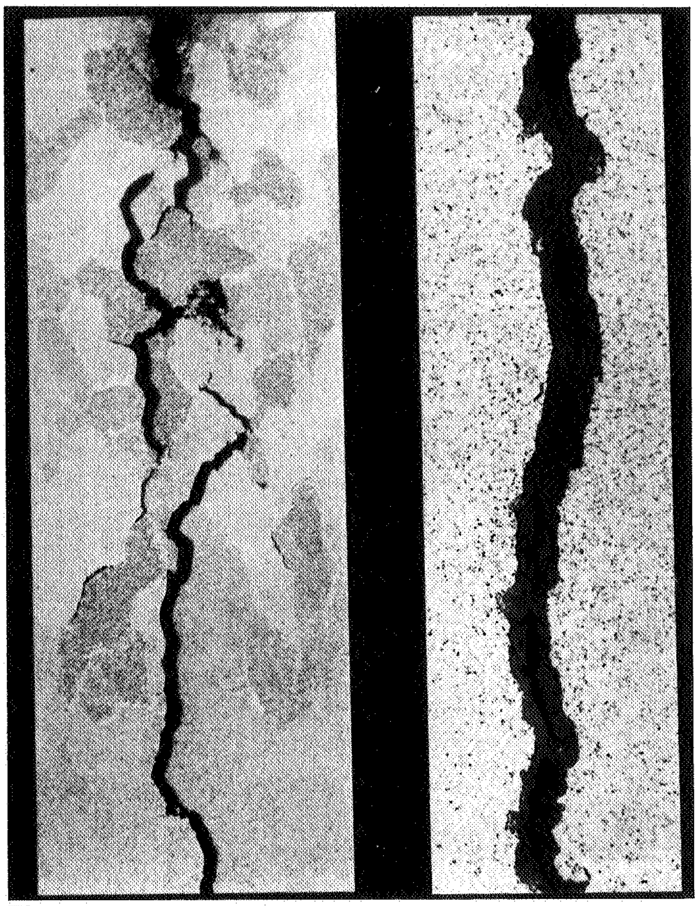

Figure 6. Details of a crack.

longer capable of diffusing, very high pressures are built up in the small cavities. This results in intercrystalline cracks in the material of the weld.

It is also possible that the fine cracks in the vicinity of the pore accumulations did not occur until after a period of operation; for instance, during the first shutdown. In this case, the formation of molecular hydrogen at flaws, together with embrittlement caused by the diffusing hydrogen, would be responsible for the cracks. It is possible that hydrogen from the process gas diffused into the material after the converter had gone on stream. In the course of further shutdowns, a few of the small primary cracks would then be gradually enlarged by the mechanism described until they reached the inner surface of the converter.

The two fracture surfaces of the large crack in the converter are reproduced in Figure 7. Two zones can be clearly distinguished: a) a grey section that lies within the weld metal and on the inside of the converter: and b) a reddish brown and black section that is very probably the extension of the crack.

The shape and size of the grey section are roughly similar to those of the other cracks in the weld. With the aid of X-ray diffraction pictures, it was determined that the very adherent and thick grey layer of oxide consisted mainly of magnetite. The thickness of this layer proves that the grey surface is the initial crack that was in contact with the process gas for a long time and that it is much older than the extension of the crack.

A factor that affects propagation of cracks is the quality of the plate metal for the shell and head. The properties of the plate metal and the weld metal were determined by various means (chemical analysis, metallography, and several mechanical tests including fracture mechanics). Perfectly satisfactory values were obtained for the plate metal by chemical analysis, the tensile test, and the DVM notched-bar impact test, DIN 50115 (20°C). However, the Charpy-V-impact test at various temperatures revealed that the transition temperature (abrupt drop in impact strength) is about +40°C. This is too high for this grade of plate metal and indicates that the quality is not up to standard.

Figure 7. Surfaces of the big crack.

Changes in structure of plate metal

The structure of the plate metal in the original state and after normalizing in the laboratory (930°C/½ hr. cooling in furnace) is shown in Figure 8. The original material has a Widmannstaetten structure and consists of ferrite and bainite. After normalizing in the laboratory, the structure consists of a linear arrangement of ferrite and perlite such as can be expected from a material of this nature that has been subjected to optimum heat treatment. The hardness of the plate metal decreased from 180 Hv. before normalizing to 125 Hv. after normalizing. The conclusion is that the material had not received optimum heat treatment.

The fracture mechanics work carried out in the DSM laboratory revealed the following:

1. The initial flaws in the weld are large enough to allow cracks to be initiated from the weld.
2. The plate metal is of inferior quality, with the result

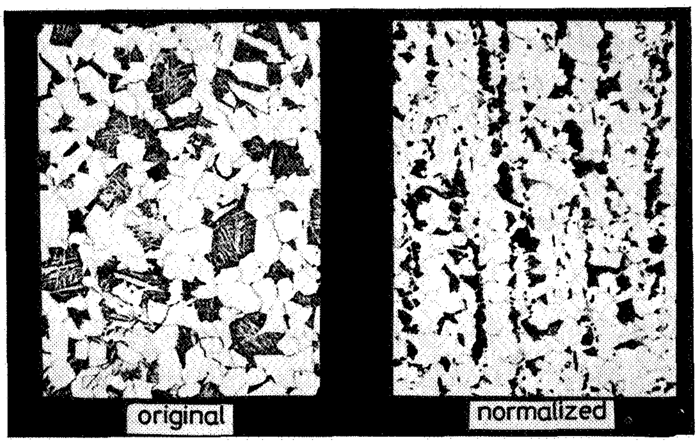

Figure 8. Structure of the plate material.

that instable brittle cracks could be propagated.

In the opinion of the DSM Materials Testing Department, the only reasons that the brittle crack did not finally proceed any further were that a low figure had been taken for the design stress in the material, and that the crack probably occurred during a startup when full operating pressure had not yet been reached.

The BASF Materials Testing Department is of the opinion that oxidation, i.e., the formation of magnetite, played a part in the crack propagation. The process steam penetrating into the crack caused magnetite to be formed at the edges of the crack and atomic hydrogen to be liberated.

Formation of magnetite within the crack is associated with a considerable increase in volume. Thus a wedging effect takes place, forcing the edges of the crack further apart in the material that has been embrittled by hydrogen, e.g., during shutting down. The crack is thus enlarged in stages. After it has attained a critical length, the final phase sets in, consisting of a spontaneous extension of the crack.

The magnetite embedded in the crack exerted an explosive force probably while the shell was cooling during shutting down. The effect was reinforced by the hydrogen embrittlement of the material. This also explains the restricted length of the crack; because if the length of a crack were to become critical while the full internal pressure is being exerted on the vessel, the crack would not come to a halt.

Neither on the inner wall of the converter nor on the sides of the crack were there any signs of decarburization wuch as that which occurs together with methane formation when a metal is attacked at high temperatures by hydrogen under pressure according to the Nelson curves.

Possible provisions to stay onstream

After the crack in the HT shift converter had been detected, and all decisions had to be made immediately and all the necessary measures had to be taken to ensure rapid resumption of production. It was decided to reject the catalyst, which had been in use for two years. Careful oxidation of this catalyst would have taken at least four days, incurred additional costs, and would not have yielded a very active catalyst. It was also decided not to repair the old HT shift converter, because it was not at all certain if it could then be reused, what the costs of repair would be, and how long the repair would last.

Inasmuch as the old HT shift converter was no longer available and since the delivery time for a new one is six to eight months, the problem was how the ammonia plant could be put quickly on stream again at as high a production rate as possible without the HT shift converter. The flowsheet of the Pernis ammonia plant with the CO conversion is shown in Figure 9.

Fortunately, the two LT shift reactors and the HT shift converter have the same design metal temperature, i.e., 482°C. Therefore, it is possible to use one or both of the two LT shift reactors instead of the HT shift converter.

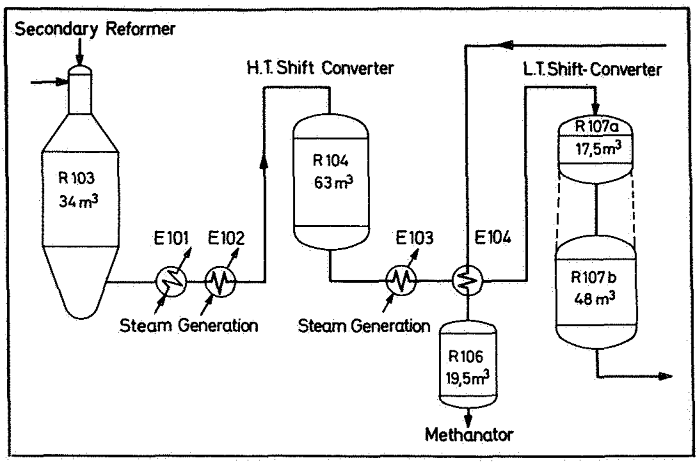

Figure 9. CO shift conversion ammonia plant at Pernis.

Five means were discussed for the rapid resumption of production without the old HT shift converter.

1. Without HT shift conversion. The old HT shift converter should be dismantled and replaced by a length of pipe. Only the LT shift conversion should remain in opera tion.

The advantage would be that due to the comparatively simple assembly work, production could be resumed quite quickly.

Disadvantages would be as follows. The CO content at the LT shift converter outlet would be comparatively high (0.8 - 1.2%). Production would be only about 90% of the design capacity. At the outlet of the LT shift conversion, high temperatures would be reached, viz., 285°C, as a result of which the activity of the catalyst would be impaired more rapidly than usual. If this technique were adopted, the bypass for the waste heat boiler E 103 would have to be opened, and the amount of water for quenching at the outlet of the LT shift conversion would have to be increased.

2. Without LT shift conversion. The two reactors in the LT shift conversion would be filled with HT shift catalyst and would be made to act as the HT shift conversion by installing new pipes.

The advantage — Experience on this had already been obtained, because the plant had been run once before with the HT shift conversion only when the catalyst was being changed in the LT shift converter.

Disadvantages — The CO content at the methanator inlet would be very high (1.8 - 2.4%). The temperature rise in the methanator would amount to about 170°C, and the production would be only about 75% of the design capacity. The assembly work is more difficult and would require more time than in the first case.

3. Filling the LT shift converters with HT shift catalyst and replacing the HT shift converter by a pipe. The assembly for this would be the same as in the first case and could thus be carried out simply and rapidly. However, this particular case is technically infeasible, because the pipes upstream and downstream of the LT shift conversion are unsuitable for the high temperatures and the heat balance would no longer be valid.

4. A total of 48 cu.m. of HT shift catalyst plus 17.5 cu.m. of LT shift catalyst. The advantage would be that the CO content at the outlet of the HT shift conversion would be practically normal.

Disadvantages — The CO content at the outlet of the LT shift conversion would be comparatively high, i.e., about 0.6%. Since the LT shift catalyst is gradually poisoned during operation, the life that could be expected from such a small volume would be quite short.

5. A total of 17.5 cu.m. of HT shift catalyst plus 48 cu.m. of LT shift catalyst. Advantages would be production at more than 100% of the design capacity could be achieved, the CO content at the outlet of the LT conversion would be low, and the LT shift catalyst could be expected to have an adequately long life.

Disadvantage — Assembly would be more difficult and would require seven days more than in the first case. However, this seven days' loss of production would be more than compensated by the higher production capacity. Thus, since the delivery time for a new HT shift converter is longer than six months, the total amount of ammonia produced would be more than in the first case.

In view of the long delivery time for the new HT shift converter, the fifth solution offered the most advantages. It was decided to use the small LT shift reactor as a temporary HT shift converter. Therefore, the upper LT shift vessel was removed and installed in place of the defective HT shift reactor.

Operation with a small HT shift converter

A period of 31 days was required for dismantling the old HT shift converter and connecting the small reactor. After the HT and LT converters had been filled with fresh catalyst, the plant was taken on stream again.

With a high steam/carbon ratio and a temperature of 375°C at the inlet of the HT shift conversion, the CO content at the converter outlet was 3 - 3.5%. Owing to the small volume of catalyst, quite a high temperature was maintained at the inlet of the HT shift conversion, in order to achieve a high rate of reaction. As a result of the debottlenecking effected during the turnaround, the production was 114 - 119% of the design capacity.

A new HT shift converter made of 13 Cr Mo 44 (ASTM A 387-65 B) with a correspondingly thinner wall was ordered. By virtue of the thinner wal it is now cheaper to make a converter from the high-grade material 13 Cr Mo 44 than from 16 Mo 5. The new HT shift converter was to be installed in the autumn of 1976, and 19 days will be required for this purpose. Thus the crack in the old HT shift converter resulted in a total loss of production of 50 days.

Acknowledgment

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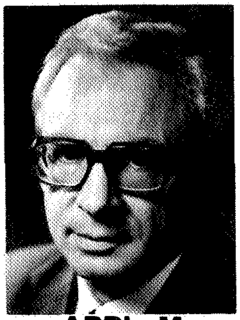

APPL, M.

DISCUSSION

D.J. TRUAX, Standard Oil Co. of California: Your Charpy impact test showed a transition temperature of 40°C. I recognize that the poor microstructure of carbon half-moly plate contributed to that. Did any of your tests look at the possibility of temper and brittleness for showing a higher transition temperature?

LIEBE: The tests were made by the Materials Testing Department of DSM (Dutch State Mines) and perhaps Mr. van Grieken of UKF Ijmuiden, The Netherlands, can answer your question. I don't know if he is informed about this.

VAN GRIEKEN: We discussed temper and brittleness but we didn't go further on in that study.

Q. Your report suggests that hydrogen was in the vicinity of the weld. I'm surprised that hydrogen would stay around at that temperature.

LIEBE: A chemical analysis was made in Ijmuiden and hydrogen was found in the plate material and in the weld metal.

VAN GRIEKEN: Welding with damp electrodes gives hydrogen, which can give you a crack that can initiate further cracking. Further on you have the hydrogen from the process gas that can diffuse into the metal.

This hydrogen only gives decrease of toughness below say 200°C.

To my astonishment after we took a sample out of the middle of the thick wall of the vessel, doing machining at low temperature, we still found several milliliter hydrogen per 100 g.

This blocked in hydrogen could impair toughness and contribute to the stress pattern already existing by bad local stress relieve conditions and results in low critical crack dimension.