Cause and Effect of Explosion in Ammonia Converter

Thorough inspection of internals following the incident, after 30,000 hours of operation, indicated no mechanical defects or hydrogen attack problems, and some nitriding.

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The first single-train ammonia plants have been in operation about ten years. Operators of those plants are interested in the condition of the ammonia converters with regard to the mechanical design after ten years' operation.

Of special interest is the performance of the materials used for construction of these vessels. In this context it is important to learn how construction materials behaved against hydrogen and ammonia attack under the prevailing operating conditions.

Under normal circumstances, an inside inspection of a large converter with fixed internals is impossible for design reasons, provided one does dismantle the vessel.

The official regulations for examination are different in each country. In Germany, pressure vessels are subject to an inside inspection after four years of operation. After eight years of operation an inside inspection *and* a pressure test are due. Water and, by way of exception, nitrogen serves as the pressure medium.

Erdoelchemie had an explosion in its unit after having operated the plant approximately 30,000 hr. As a result, the converter had to be inspected very thoroughly for safety reasons. It had to be dismantled completely. This is a report on the methods used for the examination and discusses the results.

The extent and the methods for inspection and examination of the reactor were set up in cooperation with the inspection authority and the manufacturer. These included:

1. Visual inspection of the pressure shell and all installations.
2. Examination of the shell and internals by "met-1-check."
3. Examination of all welds by ultrasonic test.
4. Examination of the shell, the basket, and the interchanger by metallographical methods.
5. Examination of the mounting weld by x-ray.

The examination turned out positive on the whole. Both met-1-checking and ultrasonic test showed no indications of damage either by the incident itself or over the long term by operating stresses.

Metallographic methods showed no signs of hydrogen attack at the pressure shell, which was made of ASTM 182, grade F5A, 24 CrMo 10.

The austenitic material ASI 321, V2A (all internals were made of it) was more or less nitrided. Nitriding of the interior and exterior surface of the central tube, for instance, proceeded to a depth of 6 mils. We could show these findings by etelining methods and by a hardness test. Rockwell B hardness (1/16-in. ball) of the nitrided zones was 1,800 - 2,100 ksi, compared with 250 - 280 ksi of the sound material.

The nitrided specimen could be bent about 180°. But cracks, occuring in the nitrided layer, did not propagate into the sound metal.

The tubes of the interchanger, also made of material ASI

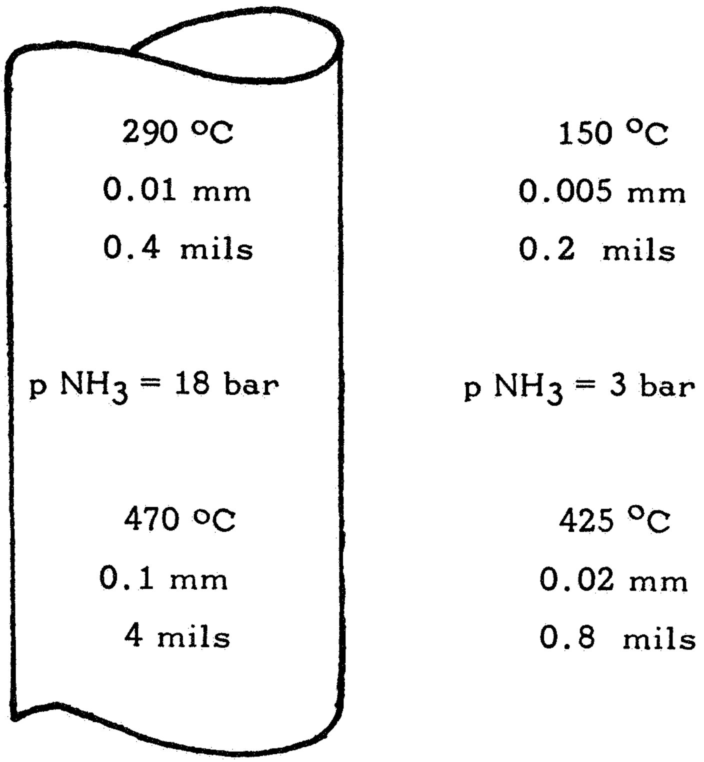

Figure 1. Effects of location on nitriding: higher operating temperature at bottom area of tube bundle and inside tube (where ammonia partial pressure is greater) caused maximum nitriding.

321 V2A, were nitrided differently. Maximum nitriding of 4 mils was found at the bottom area of tube bundle at the inside of the tubes, whereas nitriding at the colder top area was 0.2 mils only. Figure 1 shows that nitriding was more severe where partial pressure of ammonia and operating temperature were highest. This result illustrates very clearly the influence of operating conditions on nitriding reaction.

Conclusions

The examination showed—after 30,000 operating hours—the pressure shell in perfect condition. There were no defects caused by the incident nor was there any minor attack by hydrogen.

This proved that the construction material, ASTM 182 grade F 5a, 24 CrMo 10, was selected appropriately. Therefore we are sure that no problems will arise even after longer operating time.

Nitriding of the austenitic materials, which all internals are made of, was minor only. Nitriding was unobjectionable and therefore continued operation of the vessel was no problem. In our experts' opinion, nitriding of the central tube could have been a problem for welding and mechanical deformation only.

Inasmuch as nitriding is most likely in converters of our design, two questions arise: 1) Does the process of nitriding proceed in the course of working time? or 2) does the said process stop at a certain depth?

We regard the nitriding of the austenitic materials in our ammonia converter as not that problematic, as long as no welding and no mechanical deformation must be carried out, due to repair for instance.

Mechanical deformation strains may cause the bursting of the nitrided layer and as a result, sound metal will nitride further. Also, cracks originating from stresses may propagate into the basic metal.

From the literature, which is not very extensive, we learn that the content of nickel in corrosion resistant steels influences the nitriding rate. Additional nickel makes the material insensitive to nitriding. The literature also shows that the rate of nitriding is a function of operating conditions, e.g. ammonia pressure and temperature. Fortunately, however, nitriding lessens after reaching a certain depth, and it will finally stagnate entirely. According to several publications, nitriding will propagate to a depth of 8—12 mils maximum. The nitriding will continue for one to two years under todays conditions.

The standard austenitic steels have proved correct for use in ammonia converters in general and from an economic viewpoint, according to the literature. *(1, 2, 3, 4, 5)*

The operator must be prepared for more or less nitriding, which could raise difficulties with internals of low-wall thickness, after years. The use of more resistant alloys with higher nickel content needs to be justified economically in particular cases.

Literature cited

1. *Chem.Ing.Techn.*, **39**, 525-530 (1967).
2. *Materials Protection*, **1** (7), 18-19 (162); and **2** (12), 18-19 (1963).
3. *Prumsyl* **15**, 92-94 (1965).
4. *Chem. Rundschreiben* (Solothurn), **19** (17), 529-535 (1966).
5. *Werkstoffe u. Korrosion*, **22** (1), 1-7 (1971).

DISCUSSION

JAN BLANKEN, UKF-Holland: At the site in Ijmuiden we produce ammonia for nearly 50 years. Until 1950 in 150 Bar ammonia synthesis converters with an ammonia outlet concentration of about 12%. In these converters we used low alloy Cr-Mo steels reasonable successfully.

In 1950 we started up two synthesis converters working under 300 Bar with ammonia outlet concentrations of 18% again with internals of low alloy Cr-Mo steel and experienced a hell of a lot problems with nitriding of exchangers and other critical components.

In 1958 we installed two Montecatini steam raising baskets which were much more complicated than the present large converter and we decided to go to one of the best materials to avoid nitriding namely AISI 310.

In 1962 we installed a third steam raising converter this time all internals made of a normal 18-8 type of steel.

These converters behaved very well unitl 1970 when we replaced them all by a single train ammonia plant and we did not have any problems with nitriding.

Based on this experience I am inclined to agree with Dr. Neeb when he says that nitriding of 18-8 steel will not cause problems in a 150 Bar ammonia synthesis converter except perhaps in very thin components.

SALOT, Allied Chemical, Hopewell: I have some data that confirms the data that you have, or adds to it. My data comes from the Slim Jim converter baskets discussed earlier. The Commercial Solvents and Hopewell baskets were in service 8 to 8½ years, which was perhaps double the service time of your basket. The average nitrided depth was 8 to 10 mils, which is about what you predicted.

The only disturbing thing that I could see in nitriding was also pointed out by you. We had some 30 mil thick stainless steel sheet metal in there, and as you predicted, it nitrided completely through. It was warped and shattered, and was therefore removed.