BRITTLE FRACTURE OF AN AMMONIA SYNTHESIS HEAT EXCHANGER

To avoid hydrogen cracking of the heat exchanger, the preheating temperature of the chamber should be maintained for a few hours after completion of the weld.

H.K. KARINEN
Typpi Oy
Oulu, Finland

On March 19, 1970 an explosion occurred at the Typpi Oy 750 ton/day ammonia plant due to the failure of the forged steel chamber in one of the effluent water coolers in the synthesis loop. The syngas, which escaped from 235 atm. gauge pressure, caught fire. The height of the flame was about 30 m., and the force of the explosion is indicated by the fact that the heat exchanger cover, which weighed about 250 kg., was thrown horizontally about 100 m., and then bounced another 100 m. In addition windows were broken within a radius of hundreds of meters around the center of the explosion.

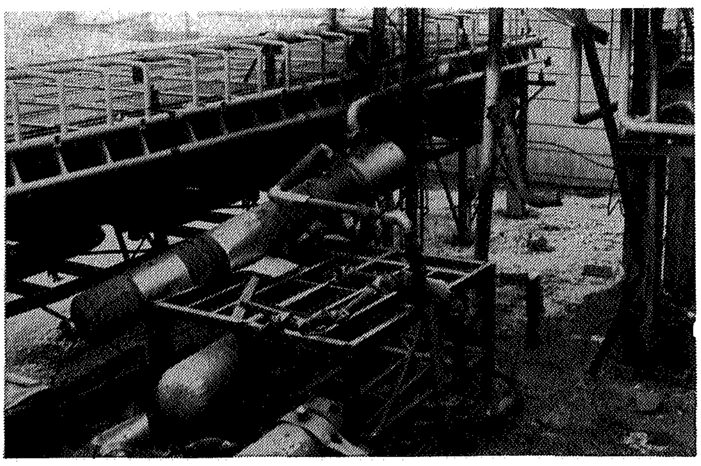


Figure 1. Heat exchangers after the explosion.

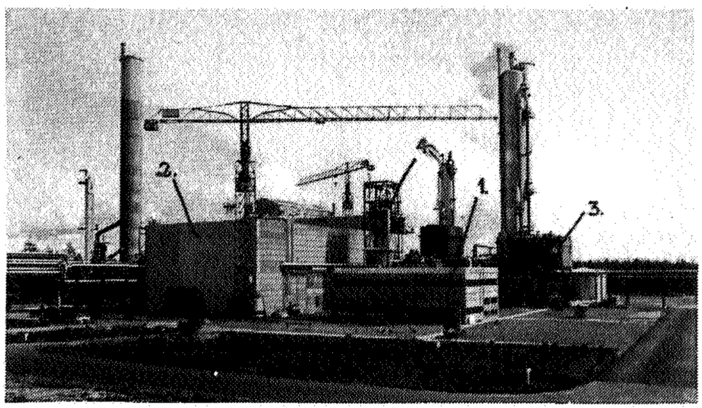


Figure 2. Typpi Oy 750 ton/day ammonia plant: (1) control building, (2) compressor house, (3) Benfield pump house, and (4) ammonia reactor.

The effluent cooler consisted of four exchangers, two of which were completely destroyed. The other two were only slightly damaged, Figure 2. The heat exchangers were surrounded by the compressor house to the north, the control building to the west, and the Benfield plant pump house to the east, as shown in Figure 2. Severe damage was caused to all these buildings by the ensuing pressure wave. The roof and west wall, and a large part of the south wall of the compressor house had to be rebuilt. The west wall of the compressor house was broken by the suction effect of the pressure wave. This means that the wall reacted as designed since it was intended to withstand explosions coming from inside the compressor house up to a differential pressure of 80 mm. W.G.

The wall elements of the control building were loosened from the house frame. During the re-erection the structure was made stronger on the process side. The roof windows, through which the pressure wave damaged the inside walls, were removed and blanked off.

The explosion also damaged the ammonia reactor, which is a multilayer type vessel. The hydrogen flame partly loosened the outermost layer, which was repaired by the vessel manufacturer.

To facilitate the hydrostatic testing of the reactor shell and inspection of the internals, the catalyst had to be discharged and the vessel loaded with new catalyst. No damage was found on the internals despite the sudden loss of pressure.

The air cooler of the synthesis loop was slightly damaged due to the headers shifting from their positions. Because the delivery time for the new water coolers is more than a year, we decided to run the plant without them in the meantime. This is possible with the aid of the said air cooler, having the outlet temperature of about 5- to 10°C above the ambient temperature. Thus, the shortage of the water coolers has a reducing effect on the plant production only during summer when the ambient temperature is around 15- to 30°C. Some damage was also caused to the synthesis loop instrumentation and electrical equipment.

Secondary damage was caused to the boiler system as the boiler LCV closed due to instrument air line junction breakage. This, in fact, left the boiler without water for some time. This damage was small, however, and the problem was resolved by blocking some of the secondary reformer boiler tubes.

The total damages to the equipment amounted up to $750,000, and the repairs and restart took 3½ months altogether. None of the personnel were severely injured and only one laboratory technician suffered physical injury.

Purpose and construction of the heat exchangers

The four heat exchangers were connected to each other on the syngas side as shown in Figure 3. Gas comes into the heat exchangers A and D from the top and goes out from the bottom through heat exchangers B and C, connected in series to A and D. The purpose of the heat exchangers is to condense ammonia from the synthesis gas and to act as a trim cooler for the above mentioned air cooler. These heat exchangers are of the U-tube type, Figure 4, with the high pressure syngas on the tube side and the cooling water on the shell side. The length of the exchanger head section is 1,105 mm. and the outside diameter is 1,090 mm. Wall thickness varies between 85- to 150 mm. and tube sheet thickness is 270 mm. The maximum operating pressure of the heat exchangers is 295 atm. gauge and the design pressure is 310 atm. gauge.

The heat exchangers were manufactured by a Finnish workship, which purchased the H.P. forgings from Sweden. The material specification of the forgings is shown in Tables 1 and 2.

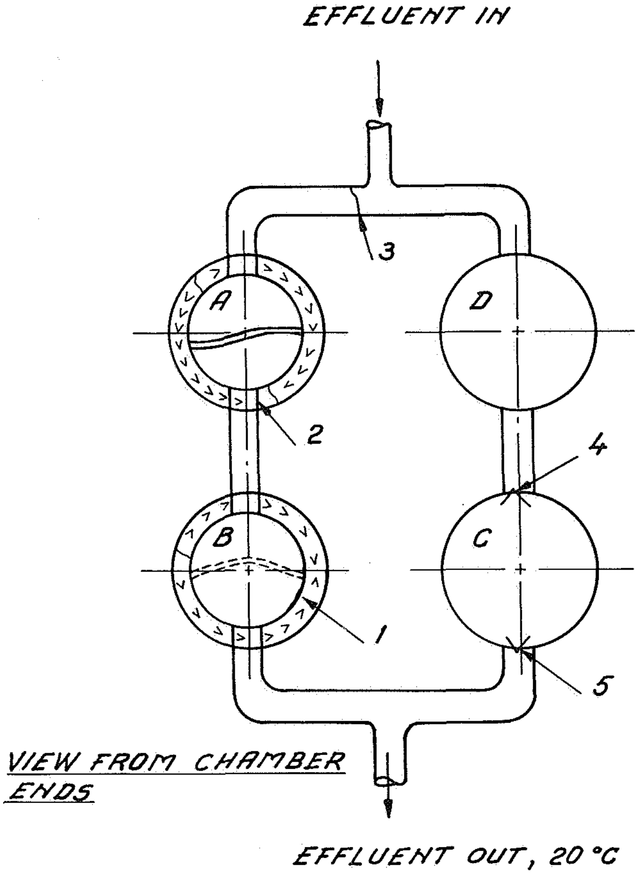


Figure 3. Chamber connections and fracture origins (numbered).

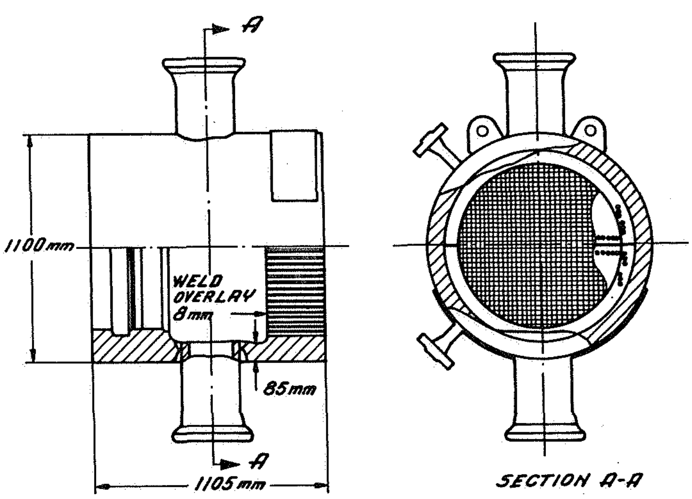


Figure 4. Forged effluent chamber.

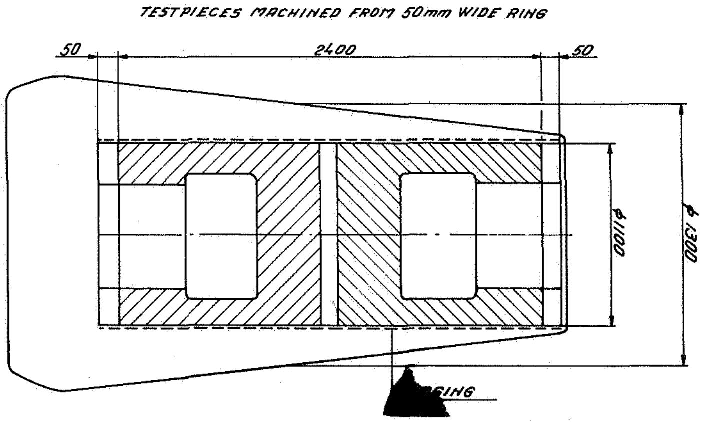


Figure 5. Cast steel ingot.

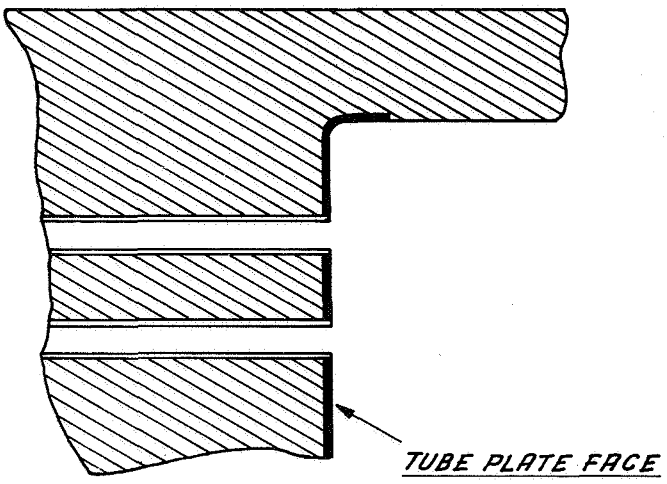


Figure 6. Effluent chamber weld overlay.

Preparation of the forging was started from the cast steel ingot, shown in Figure 5. The outside diamter, originally 1,300 mm., was compressed to 1,100 mm., and then the piece was given an ultrasonic inspection. After this, the forging was normalized at 920°C and pre-machined so as to give chambers with a machining tolerance of 5 mm. The next stage was hardening at 950°C, maintaining this temperature for eight hours according to the workshop, and four hours according to the inspection company. Quenching in oil was then carried out. Finally, the forging was tempered at 675°C. The temperature was increased over a period of 9 hr., kept at 675°C for 10 hr., and then cooled in still air.

For material certificates, a sample ring was machined off from both ends of the forging and fastened to the main piece during the heat treatment.

The forgings were then delivered to Finland, where the final fabrication of the heat exchanger took place. The first stage of the fabrication was the overlay welding of the tube plate, which was preceded by preheating to 150- to 200°C. The weld overlay was carried out using manual metal arc welding, and 6 mm. dia. OK 48.30 mild steel electrodes. Then the nozzles, lifting lugs, and baffle plate were welded in position, after which the chamber was left to cool slowly without taking off the insulation used during preheating.

The post-weld heat treatment was carried out in a furnace. The temperature was first raised to 470- to 620°C over a period of 6½ hr., held at this temperature for 1½ hr., and then stabilized to 530- to 590°C, which was maintained for at least 5 hr. Cooling took place in the furnace over a period of 24 hr. Then the final machining and welding of the tubes onto the tube plate overlay weld was carried out using automatic argon arc welding with a mild steel filler-wire. No preheat was used for this operation.

The complete heat exchangers were subjected to a hydrostatic test pressure of 404 atm. gauge, which was then reduced to 10 atm. gauge and raised once again up to 404 atm. gauge. The pressure was raised 10 times over a period of 3 hr. All heat exchangers passed the test. The vendor gave the forgings, and later the welds, a 100% ultrasonic inspection. The welds were also tested with a dye penetrant.

The heat exchangers were installed in position in the winter of 1968-1969. Before the explosion they had been in operation about 2½ months, the operating pressure varying between 120- to 240 atm. gauge, and the temperature between -5- to +10°C. During the week of the explosion the plant had been started up after a shutdown period of two weeks for repairs. The heating up of the synthesis loop started the previous evening just before midnight with a pressure of 120 atm. gauge. Ammonia production started in the morning when the pressure was slowly increased to 235 atm. gauge and production of 26.8 ton/hr. was obtained. The operating conditions had been steady over a period of 1 hr. before the explosion. The heat exchanger inlet temperature was +10°C, and outlet+2°C.

The failure investigation

Since nothing abnormal could be found in the process before the explosion, and since the nature of the fracture surface gave reason to assume it concerned a brittle fracture failure, the investigations were concentrated on clarifying the properties of the used material. On behalf of Typpi Oy the investigations were carried out by The Welding Institute, Rautaruukki Oy, A Finnish steel manufacturer, and the Oulu University. The expert used by the vendor was UKAEA, and the insurance company used The State Institute for Technical Research. In addition, the forgings manufacturer also made material investigations.

The investigation of the fracture surface showed that the fracture had originated from chamber B, beneath its tube sheet end on the right hand side, Figures 3 and 7. At this point the tube sheet overlay weld extended to the wall of the chamber, Figure 6, and on the fracture surface a crack was detected, which had originated before the postweld heat treatment, Figure 7.

By the force of the reaction power, the rupture proceeded along a pipe nozzle connection to heat exchanger A breaking its exchanger head into pieces. This sequence is also confirmed by the location of the heat exchangers and the fragments thrown from them.

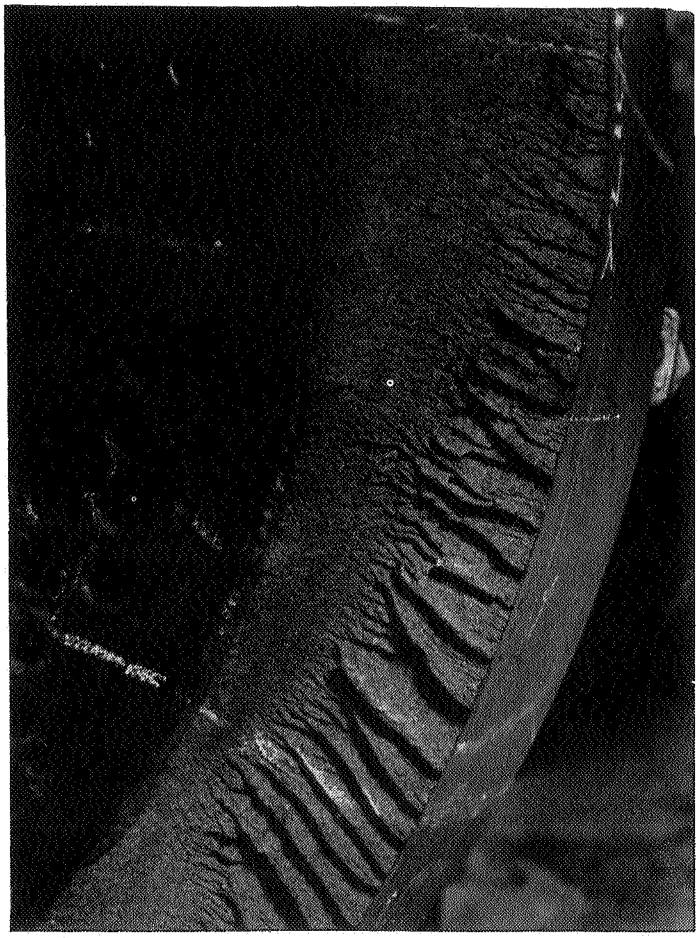


Figure 7. Fracture surface of exchanger B.

Results of the material investigation

1. The analyses of the samples taken from the chamber did not essentially differ from the test certificate results. Similarly, variation between samples taken from various parts of the chambers was small.

2. The tests of the strength properties also agreed closely with the values given in the test certificate. The strength, as shown in Table 2, is very high: 0.2 70 kg./mm.^{2} 40~ √ √^{2}was used for the design calculations of the heat exchanger.

3. The hardness tests showed that the hardness of the parent metal was 250- to 280 HV. On the weld HAZ the hardness peak was 430- to 440 HV.

The hardness of the HAZ could be softened during the tests down to 335 HV by increasing the post weld heat treatment temperature to 660°C.

4. Impact hardness values obtained from this material were very poor. The results of Charpy V notch tests gave +30- to +60°C transition temperature.

According to the material certificate the transition temperature should have been about -60°C. The certificate test was carried out at 0°C, but since the form of the transition curve was know, it was possible to determine the transition temperature fairly accurately. 2.8 kp./cm.^{2} EA (energy absorption) has been used as a criterion of the transition temperature. The FA values (fracture appearance) gave a transition temperature after the explosion of about +100°C (FATT 50%).

5. To determine the critical defect size the specimens were tested with linear elastic fracture mechanics tests, which gave K1c values of 2,030- and 1,870 N/mm.^{2} -mm. With COD tests the values at 2°C temperature were generally less than 0.25 mm.

6. Micro structure investigation showed that the structure was feather bainitic having a high tensile strength, but poor impact hardness. The TTT tests (time, temperature, transformation) showed that perlite formation rate for this material is slow, but bainite formation, again, is very quick. Bainite nose is about 10 sec. at 500°C. When experimenting with various quenching mediums, it was found that quenching in water results in, even with large specimens, a martensitic structure having a good impact hardness, whereas quenching in oil results in feather bainitic structure, which is brittle.

In the structure of the weld HAZ there also appeared some martensitic components and the austenite grain was coarser. In addition, some small slag inclusions were found in the weld seams when examined with radiography. The defects were however fairly small, the biggest inclusion being 2 mm. long.

Reasons for the failure

The basic reasons for the failure are the selection of the material, light forging, and defective heat treatment. The method of heat treatment used resulted in feather bainitic structure, which is brittle.

Sampling technique was the reason that the brittleness of the material was not revealed after the heat treatment, because the cooling speed of a loose sample ring is much higher than of a massive main piece and, consequently, the structure of the ring was apparently martensitic so the test results whoed the material to be tough. Welding of this material gives a HAZ where austenitic grain size is coarse and hardness is high (approximately 400 HV).

The post-weld heat treatment was carried out at too low a temperature 560- to 580°C) and that resulted in precipitation hardening of the steel and added to its hardness. Due to preheating, the tube plate welding had to be carried out under difficult conditions. Because of the structure of the chamber the weld overlay had to be deposited to the very edge where the crack initiated. This is a very critical area in view of the stress caused by operation and residual stresses of the chamber. From this crack the rupture proceeded, apparently with a mechanism of stress corrosion cracking, which was promoted by the moisture left inside during the hydrostatic testing. Crack growth was also assisted by the hydrogen created on the metal surface as well as the high pressure molecular hydrogen of the synthesis circulating gas.

Selecting heat exchanger materials

1. Carbon content should be less than 0.15% to improve the welding properties.

2. Vanadium content should be 0.1% to obtain an acceptable hardness value for kthe weld HAZ.

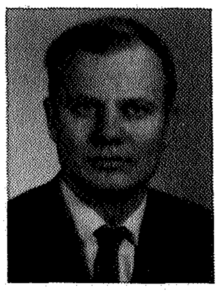
3. The heat treatment should be such as to ensure toughness in the thickest sections. The post-weld heat treatment temperature for CMn steels should be at least 600°C, and for vanadium bearing steels, over 650°C. Stress relieving temperatures should also be above these values.

4. Creation of hydrogen cracking should be avoided during welding. For instance, solid wire CO_2 welding or metal arc welding with electrodes preheated at 400°C should be used. Similarly, the preheating temperature of the chamber should be maintained for a few hours after completion of the weld in order to release any hydrogen.

5. The strength of the material should not be over 55 kp./mm.^{2}

6. The construction of the heat exchangers should be changed so that the overlay welding does not extend to the edge.

Efforts have been made to take these factors into consideration when purchasing the new heat exchangers, but since the delivery time of the equipment is long, the plant operation will suffer from the shortage of water coolers for at least a period of 1 yr.



KARINEN, Heimo