Catastrophic Failure of Tubesheet in Fire Tube Reformed Gas Waste Heat Boiler

The reformed gas waste heat boiler failed after nine years in service due to prevalent high heat flux and departure from nucleate boiling. The interim repair, the failure analysis, and replacement of the front section of the boiler are described.

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Introduction

The reformed gas waste heat boiler at the Terra Lambton Works ammonia plant showed signs of a leak in July 1994, after nine years in service. Evidence of a leak was indicated by a drop in gas temperature at the inlet to the boiler. Inspection of the boiler revealed two failures. One was a tube failure just behind the tubesheet-to-tube weld joint. The other was a failure at the tubesheet-to-shell forging weld joint. Repairs were done, and the plant was restarted at reduced rates. The cause of failure was attributed to departure from nucleate boiling (DNB), initiated by an increase in plant rates earlier in the year. It was decided to replace the entire front section of the boiler in October 1995. This article describes the root-cause failure analysis, interim repair, and new front section installation.

Description

Terra Nitrogen operates a 1,120-ton/d ammonia plant at Courtright, near Sarnia, Ontario, Canada. The ammonia plant was based on ICI's AMV process and was commissioned in 1985. Since then, the plant has been consistently producing ammonia above the design rate at 115-120% capacity, with 94-98% onstream time.

C-110 is a firetube waste heat boiler situated at the exit of the secondary reformer. The boiler was supplied by Steinmuller, Germany. It is a twin-compartment, shell-and-tube heat exchanger (Figure 1). Hot process gas at 950°C (1,742°F) flows through the tube side and is cooled to 550°C (1,022°F) at the outlet of the boiler. The shell side is connected to a boiler drum, operated at 125-barg pressure. About 165 ton/h of high-pressure steam is produced from the system. BFW treatment is a zero solids system, using only Custamine (a three-component blend of amines) and Elimin-ox (an oxygen scavenger chemical), supplied by NALCO Canada Inc.

The front compartment has 559 tubes of 38-mm OD with 1,050-mm-long ferrules. The shell OD is about 1,994 mm. All of the shell section, exposed to the gas,
is refractory-lined in two layers. The outer layer is a castable refractory material. The inner layer is a refractory brick lining.

The second compartment has 415 tubes of 38 mm OD with 950-mm-long ferrules. A central gas bypass section is used for exit gas temperature control through operation of a set of three dampers at the outlet end. The central bypass section consists of 12 tubes of 114.3-mm OD. The shell section exposed to the gas is refractory-lined, similar to the first compartment. Both the compartments are connected to the boiler drum by a series of risers and downcomers, facilitating natural circulation.

Failure

Beginning June 27, 1994 and for the next 20 days, a steady drop in the temperature was recorded by the two thermocouples at the inlet of C-110 (i.e., exit of secondary reformer) (see Figure 2). The normal operating value is 940°C (1,724°F). It dropped to 820°C (1,508°F) by July 1 and to 680°C (1,256°F) by July 13. The first indications prompted a check of the calibration of the thermocouples and no deviation was found. The thermocouples could not be replaced as they were fused in the thermowell and could not be pulled out. No other abnormal condition was noticed on the process side. No substantial drop in downstream temperatures was recorded. No noticeable excess condensate flow in the downstream knockout drums was observed. Attempts were made to detect the BFW leak using NALCO's patented TRASAR method by tracking a nonvolatile fluorescent tracer compound injected into the BFW system. These checks showed a small increase in the BFW consumption to the tune of 2 ton/h. This was the only other evidence of a possible leak, but it was not alarmingly high enough to shut the plant down.

A shutdown prompted for other reasons in the plant on August 21, 1994 gave us an opportunity to inspect the C-110 front chamber. Upon inspection, it was found that refractory was spalled in two regions on the tubesheet. One region was in line with the two thermowells. Portions of refractory were cleared for inspection, and failures are confirmed at these locations. Two perforations were present in the tubesheet. One failure was noticed on the forging just above the circumferential weld of the tubesheet, very close to the twelve o'clock position at the extreme top of the tubesheet. The other was an actual tube failure at the backside of the inlet tubesheet. Water leaked from these holes and flashed in the front chamber. It impinged on the two nearby thermowells, cooling them and thus giving a lower temperature on the thermocouple readouts. Significant erosion on the thermowells was also observed.

Failure Analysis

Ultrasonic thickness checks were carried out on the tubesheet around the affected region. The thickness profile near the failure points confirmed a gradual thinning of the metal (see Figure 3). An area of about 20 mm diameter centered around the perforation was found to have significant metal loss. Further UT checks were carried out on selected portions of tubesheet and in some randomly selected tubes to assess the overall situation.

Assistance from NALCO was sought to analyze the failure from a material and corrosion point of view. A 1-in.-dia. (25.4-mm-dia.) plug, centered around the perforation on the forging tubesheet circumferential weld, was cut and removed from the tubesheet. The visible water-side surface of the tubesheet showed severe localized wastage near the perforation. A portion of the failed tubesheet, a tube ferrule, and the leaking generating tube were examined metallurgically at NALCO laboratories.

Description of Samples

Perforated tubesheet

The sections of two pieces of tubesheet near the original perforation were examined. The sections are shown in Figure 4. The smaller semicircular section contains a portion of the sheet near the original perforation. Both sections are severely corroded on the process side; numerous, parallel striations and grooves are present on both sections. Grooves, while parallel, are gently rounded furrows extending into the underlying metal no more than a few thousandths of an inch.
Figure 1. C-110 reformed gas waste heat boiler.

Figure 2. Temperature profile at the inlet and outlet of C-110 during 20-day period when the failure was noticed.

Figure 3. UT thickness profile of tubesheet centered around the failure point.
Surfaces are covered by a thin, dark oxide layer. Exposure of the corroded surface to concentrated hydrochloric acid failed to remove the black oxides after continuous exposure of up to 20 min. Otherwise, surfaces are essentially free of significant corrosion products.

Generating tube section

A 3-1/4-in.-long (82.6-mm-long) section of 1-1/2 in.-OD (38.1-mm-OD) generator tubing was inspected (Figure 5). Water-side surfaces are severely gouged and wasted. Wasted areas consist of smooth, mutually intersecting, shallow depressions separated by partially exfoliated corrosion product layers.

Wastage was somewhat more severe on one side of the tube than the other, but was present in small patches around the entire tube circumference. Additionally, the black, brittle corrosion product layer surrounding the tube section was of approximately equal thickness all the way around the tube circumference.

The internal surface of the received section was similarly covered by a black corrosion product layer. Internal surfaces are covered by a blistered, partially exfoliated corrosion product layer and powdery, black deposits. No significant localized wastage was found on internal surfaces, however.

It should be noted that the wastage on external surfaces appears to coincide almost exactly with the presence of internal tube ferrules. Attack was severe only where ferrules were present inside the tubes.

Tube ferrules

A single-tube ferrule was cut into three equal sections. The tube ferrule on external surfaces was covered by a blistered, partially exfoliated corrosion product layer (Figure 6). The thickness of this layer was approximately 0.025 in. (0.6 mm). A small amount of white deposit adhered to the surfaces near the flared tube end. Internal surfaces of the ferrule generally resemble external surfaces.

Microscopic Examination

The tubesheet microstructure consists of indistinct carbide colonies in a ferritic matrix (Figure 7). The microstructures of both the generating tube and tube ferrule are similar; indistinct, single-phase grains are present everywhere. Some twinning was apparent in places.

External surfaces on the tubesheet have a rolling to smoothly undulating surface contour. A small amount of porous oxide overlies a thin, uniform coating, which in turn overlies the intact metal below.

The generating tube was covered by a thick, dense corrosion product layer on both external and internal surfaces. Grains similar in appearance to those in the metal below are present in the oxide layer above. In corroded areas on the waterside surface, the tube has a rolling, undulating contour with almost no dense oxide present.

Both internal and external surfaces of the tube ferrule are grossly similar. A thick corrosion product layer overlies the surface in most locations. The layer was partially exfoliated in many locations, while in others this layer was firmly attached to the underlying metal. Numerous cracks penetrate the corrosion product layer, obviously producing the fissuring noted in Figure 6. Areas immediately beneath the intact corrosion product layer contain numerous voids and cavities, obviously associated with diffusion phenomena. In places, small needles are present intermixed with what appears to be intergranular corrosion. The overlying corrosion product layer has been converted in places to porous, deteriorated material.

Scanning Electron Microscopy

A scanning electron microscope equipped with an energy-dispersive spectroscopy unit was used to analyze material on external surfaces of the tube ferrules. In areas where the overlying corrosion product was spalled, the surface contains substantial amounts of sodium, sulfur and potassium, as well as nickel, iron and chromium (see Figure 8). Small rods or needles beneath the partially exfoliated corrosion product layer in the intact metal below almost exclusively contain only aluminum and nitrogen. The interface between the partially exfoliated corrosion product and metal surface contains high concentrations of chromium and carbon. The outermost surface of the corrosion prod-
Figure 4. Sections of tubesheet near perforation.

Figure 5. Steam-generating tube section.

Figure 6. Exfoliation of corrosion product layer on tube ferrule.

Figure 7. Typical microstructure of tubesheet consisting of indistinct carbide colonies in what appears to be a ferritic matrix.
Figure 8. Energy dispersive X-ray spectrum of ferrule surface beneath spalled corrosion product.

Figure 9. C-110 before the modifications.
uct layer consists almost entirely of nickel, with lesser amounts of aluminum and small amounts of iron and chromium.

The energy dispersive X-ray analysis data on the tube ferrule is included in Table 1.

Conclusion of Metallurgical Examination

The fundamental issues are: (1) what caused the failure of the tubesheet; (2) what caused the corrosion of the generating tubes on the waterside. Both forms of damage appear to be linked and to have a common cause. Deviations from nucleate boiling occurred against the tubesheet in the vicinity of the thinning, and similar deviations from nucleate boiling occurred along the generating tube, up to the point where the tube ferrules were present. Steam concentrating in these regions of nonnucleate boiling directly interacted with the tubesheet and the generating tube alloys to produce localized wastage. The concentrating effects of the nonnucleate boiling caused very high amounts of aggressive ions to interact with the metal at the steam pockets which greatly accelerated wastage.

Deviations from nucleate boiling create a powerful concentration mechanism for dissolved boiler water solutes. Ions present at very low concentrations in the boiler water are greatly concentrated in areas of stable or metastable steam formation. When surfaces can no longer be rinsed by water during normal boiling processes, the solutes which are concentrated by evaporation can no longer be dissolved from surfaces, because the stable steam pocket prevents liquid water from reaching the metal surface. Additionally, because heat transfer can be locally reduced by the insulating effects of the stable steam, metal temperatures rise, further accelerating the deleterious effects of the concentrated boiler solutes.

Even when small concentrations or virtually no significant boiler solutes are present, deviations from nucleate boiling will cause accelerated thermal oxidation of the metal, ultimately causing significant metal loss and, in the case of the tubesheet, perforation. The thick accumulation of thermally deteriorated metal on waterside surfaces of the generating tube suggests that this tube was operating at temperatures above the so-called “scaling limit.” Scaling limit is the temperature above which thermal oxidation becomes appreciable. Once again, this suggests that nonnucleate boiling

Figure 10. C-110 during the installation of new front section.
Table 1. Energy Dispersive X-Ray Analysis Data on Tube Ferrule (All Numbers are in Wt.% as Compounds)

<table>
<thead>
<tr>
<th>LOCATION</th>
<th>Na</th>
<th>S</th>
<th>K</th>
<th>Mo</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>Al</th>
<th>N</th>
<th>C</th>
</tr>
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<tr>
<td>Alloy</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>16</td>
<td>9</td>
<td>Balance</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Beneath spalled corrosion product</td>
<td>29</td>
<td>15</td>
<td>34</td>
<td>-</td>
<td>10</td>
<td>4</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Needles or rods beneath corrosion products</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>71</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>Interface between partially exfoliated corrosion product and metal</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>51</td>
<td>1</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>44</td>
</tr>
<tr>
<td>Outer surface of corrosion product layer</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>5</td>
<td>Balance</td>
<td>19</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

occurred on the generating tube section. It was reported that similar damage was found only up to a distance equal to the extent to which the tube ferrules were present in the generating tubes. This strongly suggests a link between the tube ferrule positioning and the excessive heat input on the generating tubes. Thus, excessive amounts of steam would likely have been produced and collected near the top of the exchanger, immediately adjacent to the tubesheet. A stable or semistable pocket of steam would have formed near the top of the exchanger immediately adjacent to the tubesheet if the adjacent risers could not carry away the excessive steam generated on the tube ends below.

It should be stated that the above conclusion concerning the accumulation of steam against the tubesheet is speculative. However, the above scenario does explain all observed wastage and the resulting failure.

Incipient metal dusting has occurred on the examined tube ferrule. The so-called catastrophic carburization (metal dusting) has produced substantial amounts of metal wastage on the tube ferrules. It is possible that the growth of the corrosion product layer was sufficient to bridge the gap between the generating tube and the ferrule. Should this occur, heat transfer would likely be greatly increased locally, resulting in high concentrations of steam generation where these ferrules were present. It was also possible that the ferrules may have not been aligned properly, so that they did in fact touch the steam-generating tubes either initially or after a short period of operation. The aforementioned mechanism appears much more likely than the latter mechanism, especially in light of high production rates.

No evidence of attack by cracking, oxygen corrosion, erosion or any other significant form of metal degradation, other than the aforementioned thermal oxidation and nonnucleate boiling phenomena, were observed anywhere on the received sections.

**Repair**

The weld repair was designed by Steinmuller who had also supplied the material and the welders to conduct the repairs. The failure near the forging-tubesheet
circumferential weld was repaired by installing a 2-in. (51-mm) pipe with a cap welded on the end inverted into the damaged area. The tube hole corresponding to the failed tube was plugged and the seal welded. A helium leak test was done and the result was positive.

After the repairs, the plant operated satisfactorily for a full year before the front section was changed. However, the plant rate was restricted to a maximum of 1,270-ton/d ammonia production vs. a previously achieved maximum of 1,330 ton/d to avoid the conditions of critical heat flux inside C-110. The figure of 1,270-ton/d rate was selected, based on previous so-called “no problem experience” and preliminary thermal calculations. No further failures occurred.

**New Front Section**

**Design**

UHDE and Steinmuller carried out thermal calculations on the boiler, based on the actual plant operating data. They indicated that the front section of the boiler was exposed to heat loads crossing the regions of “critical heat flux value” of the metal. The peak heat flux value in the front section was estimated to be around 583 kW/m² (184,933 Btu/h·ft²). Any value above 500 kW/m² (158,605 Btu/h·ft²) was considered not favorable due to the possibility of deviation from nucleate boiling. It was also indicated that the second compartment was exposed to relatively lower values of heat flux. A better heat distribution was desirable. The high heat flux conditions prevailed when the plant was operated at high rates at the beginning of 1994. During these times, the phenomenon of departure from nucleate boiling and associated thermal oxidation of metal occurred and resulted in the failures.

It was decided to install a new front section of the boiler, designed for projected higher plant rates (27% above the original design) and with more equitable distribution of the heat load between the two sections of the boiler. A new riser design was also required in view of the projected increase in steam flow and also to mitigate the formation of regions of stable/semi-stable pockets of steam.

The new design included the installation of larger diameter tubes in the front section to keep the heat flux value below the critical value. This increased the heat flux to the second section, but care was taken to have it within the critical values. The new design necessitated an increase in the diameter of the shell. The new front section has 415 tubes of 42.4 mm OD, and 144 tubes of 38 mm OD, giving a peak heat flux value of 414 kW/m² (131,324 Btu/h·ft²) at full loads. Accordingly, the new front section of C-110 was manufactured by Steinmuller and delivered in nine months. The new section was installed in the October 1995 biannual turnaround of the plant.

**Installation**

A speciality boiler contractor was engaged for the erection of the new front section of C-110 (Figures 9 and 10). The overall job involved:

1. Chemical cleaning and boilout of the new section
2. Partial refractory installation before erection of the equipment
3. Cutting and removing the existing front section
4. Erecting and aligning the new front section, the risers and the downcomers
5. Welding the new front section, the risers and the downcomers
6. Completing refractory job and curing operation.

Chemical cleaning of the new section was done separately before erection. Insertion of ferrules and some partial refractory installation was also carried out before the erection.

High-pressure water mixed with abrasive material was used to cut the shell-side portion of the existing front section. Arc cutting was used to cut the downcomer and riser piping. Temporary supplemental support structures were erected to help install the new front section. A jacking mechanism was used for alignment with the existing section.

The original plan took 15 days for the entire job. However, due to numerous difficulties experienced during the weld surface preparation, alignment, and actual welding operation, it took seven more days to complete the job.

The major welding jobs were:

(a) one large diameter
circumferential shell weld (1,996 mm in OD, 46 mm in wall thickness); (b) two transition piece welds (1,143 mm in OD, 110 mm in wall thickness); (c) 22 piping welds of risers + downcomers [SCH 120.8 in. (3 m) and 10 in. (25 mm) dia.].

According to the original schedule and drawings, only 12 field welds were planned for the riser and downcomer piping. However, the drawings were found to be incorrect, and difficulty was experienced with the alignment of piping. This necessitated an additional ten field welds as a consequence of more cutting.

The welding difficulties were more pronounced in the piping job than in the circumferential welds. The preheat temperature was around 250-300°F (121-146°C) for all the welds. The material is primarily 1 Cr-1/2 Mo alloy steel. Difficulty was experienced in the welding of new piping to old piping.

Ultrasonic, radiographic and magnetic particle tests were used to check the quality and acceptability of the welds. Many welds failed during the radiographic testing. Major problems were slag inclusions and root weld inversions. Preheat temperature adjustment was required for each weld, especially for new pipe/old pipe joints. These procedural modifications were supervised by a welding engineer consultant, engaged by the contractor.

Some additional time was also spent on the weld surface preparation of one of the large-diameter circumferential welds on the existing side of the boiler. The surface was prepared by arc-gouging and hand grinding instead of the originally planned machine preparation.

Six welders in two shifts/day (12-h shifts) were engaged on the job on a round-the-clock basis.

Startup and Operation

The job was completed on October 28, 1995, and the plant was started. The performance of the boiler to date is satisfactory, and the plant has recorded high rates of production (116-120%) consistently.

Acknowledgments

We would like to thank Mr. J.G. Wright, Mr. M. McLeod, Mr. P. McGill, and Mr. D.R. Ross of Terra Canada, who coordinated the project in the procurement, inspection and erection of the new section of the boiler. Thanks also go to Mr. Brian Bloxam, NALCO Canada, for his assistance.

DISCUSSION

Dean Damín, DuPont: When you had the original failure, you had one tube that leaked, which left 558 other tubes. Did you inspect those tubes at the time, and if you did, what type of inspection was that?

Van Praag: We tried to do an inspection. Unfortunately, we didn't have any inspection holes at all in the shell. We did look in through the holes that we had, because we were replacing the tubes and also did some ultrasonic IRIS inspection of some tubes and found some thinning in other tubes, but nothing major. That was about the extent of our inspection.

G. C. Sharma, IFFCO: Did you test the tube's erosion from inside of the tubes? If you are referring to the outside, due to boiler problems, is there some erosion from the inside of that part?

Van Praag: No, there is no evidence of any corrosion on the inside of the tubes. Harvey, do you want to add to that?

Herro: Yes. The thermal oxidation that was seen, that is, the layer of metal that was thermally oxidized, was about the same thickness on the inside of the tube as it was on the external surface of the tube. Other than that, there was no evidence of erosion, cracking, pitting, or any other wastage internally on the generating tubes.

T. L. Huurdeman, DSM: You designed the first part of that boiler in order to increase the water flow especially in the hot areas. Did you redesign the downcomer and riser tubes in that area?

Van Praag: Yes. There were definitely increased diameter risers put in, and the downcomers were
Huurdeman: Another design criterion was that you limited the heat flux to 500 kW/m². How do you control that in practice? Does it limit the plant capacity? How do you avoid overrunning that limit?

van Praag: Well, we kept the plant rate down basically to 1,270 when we thought that we had a problem. With the redesign, we basically calculated what the heat flux would be. We redesigned the boiler for a rate of 1,365 so we put a bit of fat in, obviously. It's basically rate-related. The more you put through, the higher the heat flux. We know when we're running at 1,330, 1,340, and that we're below the new design criteria, which I believe was 418 kW/m².

G. Schlichthärle, BASF: What kind of refractory do you use for protecting the sheet? Did you increase the thickness of the insulation when going to higher capacities?

van Praag: We use a combination of castable refractory and refractory bricks. We did not make any change to the design of the refractory, the type of refractory, or the thickness of the refractory. It's exactly the same as it was before.