Failure of Waste-Heat Boiler after Debottlenecking Process Air Compressor

A few months after raising the efficiency of the process air compressor, one of the tubes in the waste-heat boiler downstream the secondary reformer failed. One possible reason was the malfunction of the water circulation in the tubes of the boiler.

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In November 1991 BASF’s Ammonia Plant No. 3 in Ludwigshafen had an emergency shutdown caused by an untypical failure of the waste-heat boiler downstream of the secondary reformer. The high pressure steam generating system had a sudden loss of water due to a ruptured tube in one of the four boilers.

After cooling down the system and opening the gasline the following investigation on the damaged boiler reported one hole, several small leaks and erosion in one of the tubes and also a small leak in one similar tube in the neighbourhood. Even the part of the tube renewed 6 weeks before had been eroded again.

The whole boiler was replaced by a new one of the same type in a 4-week operation: 27 high pressure tubes and 3 gaslines had to be renewed.

The analysis of the causes for the damage showed that due to the unsuitable construction of the boiler changes in running the equipment were necessary to avoid failures in the future.

THE PLANT

BASF’s Ammonia Plant No. 3 in Ludwigshafen is a single train plant with a daily production of 1300 mtpd NH₃. The plant was engineered and constructed by BASF end of the sixties with a design capacity of 1150 mtpd of NH₃. The process steps are: steam reforming of natural gas, secondary reformer with waste-heat boilers, high temperature and low-temperature shift conversion, adsorption of CO₂ by BASF’s activated MDEA-process, methanation, compression and a synloop operating at 300 bar with a 4-bed-quench-reactor (Fig. 1).
The plant started up with production in January 1971. The capacity was limited by the process-air compressor. To exceed the design capacity the additional use of expensive nitrogen from the central supply net was necessary. This nitrogen was compressed by an electric driven reciprocating compressor and added to the process gas at the methanation.

THE PROCESS-AIR COMPRESSOR

The process-air compressor built by Borsig is a 4 stage centrifugal compressor with two casings: having low and medium pressure stages in one, the high pressure stage in the other casing. The compressor is driven by a 16 bar steam-turbine. Original design capacity was 41,000 m³/h air with a steam consumption of 39 mtph (fig. 2).

After renewing internals, rotors and stators the capacity of the compressor was increased up to 45,000 m³/h with an additional steam-consumption of only 1mtph. The quantity of more process air was sufficient to produce ammonia up to 1300 mtpd without the use of nitrogen from the central supply net.

The increased process air flow also resulted in a higher load of the secondary reformer and the downstream equipment especially of the waste heat system.

THE WASTE-HEAT BOILER

The damaged waste-heat boiler is the most thermally stressed apparatus in the system (gas inlet temperature up to 960 °C, outlet temperature about 440 °C). It is a watertube boiler comprising three main components: the pressure vessel, rectangular boxes built by fin tubes and a vertical tube bundle, which is inserted into the boxes (fig. 4).

The fin tubes form three passes for the process gas: one hotter pass inside and two cooler passes outside. The tube bundle is inserted from the top: 8 harps into the cooler pass, 12 into the hotter pass. Every harp consists of a vertical bayonet type header and 14 riser tubes for the steam water mixture (fig. 5).

The riser tubes are connected by horizontal headers leading the steam water mixture to the steam drum. Fin tubes and tube bundle are fed with boiling water from the steam drum under natural circulation conditions (fig 6).

Due to this construction, it is impossible to empty the waste-heat boiler. Uprising concentrations of salts can only be avoided by draining the steam drum. Also solid components also can only escape via the steam drum. The main technical datas are presented in table 1.

FORMER FAILURES OF THE WASTE-HEAT BOILER

Since start up of production in 1971 there were 8 failures of this waste-heat boiler. The failures are listed in table 2 and the location is shown in figure 7. Three damages may be regarded as single events:

- 1975 hole in a cover plate of a steam header,
- 1980 defect insulation in the gas inlet zone,
- 1988 ruptured U-tube at a header of the fin tubes.
All other damages were situated on the slope or vertical riser tubes. In 1988 the number of problems with damaged riser tubes grew up. So within four weeks the tube bundle was dismantled and the hotter section was completely renewed (fig. 8).

It was worked out that the quality of the boiler feed water and missing addition of hydrazine were reasonable causes for the damages. The bottom covers of the vertical headers contained a handful corrosion products. These might have caused a maldistribution of the boiler water, a local thermal overload and even a dryout of the riser tubes.

Table 1: Waste-heat boiler design data and operating conditions.

<table>
<thead>
<tr>
<th>Design Data</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam generating capacity</td>
<td>130 t/h</td>
</tr>
<tr>
<td>Heat duty</td>
<td>189 GJ/h</td>
</tr>
<tr>
<td>Heating surface</td>
<td>440 m²</td>
</tr>
<tr>
<td>Material of tubes</td>
<td>13 CrMo 44</td>
</tr>
<tr>
<td>and headers</td>
<td>ASTM A387-65B</td>
</tr>
<tr>
<td>Design metal temperature:</td>
<td></td>
</tr>
<tr>
<td>Water side</td>
<td>350/375 °C</td>
</tr>
<tr>
<td>Gas side</td>
<td>350 °C</td>
</tr>
<tr>
<td>Design pressure:</td>
<td></td>
</tr>
<tr>
<td>Water side</td>
<td>122 bar g</td>
</tr>
<tr>
<td>Gas side</td>
<td>34 bar g</td>
</tr>
<tr>
<td>Operating conditions:</td>
<td></td>
</tr>
<tr>
<td>Steam pressure</td>
<td>105 bar g</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>29.5 bar g</td>
</tr>
<tr>
<td>Gas temperature</td>
<td></td>
</tr>
<tr>
<td>Inlet</td>
<td>990 °C</td>
</tr>
<tr>
<td>Outlet</td>
<td>420-500 °C</td>
</tr>
</tbody>
</table>

Since October 1988 the pH-value of the boiler water was set between 9.3 and 9.7 adding sodium hydroxide. Hydrazine was dosed permanently and the blowdown of boiler water from the steam drum was increased. As a measure of precaution a spare waste-heat boiler was ordered immediately. It was used in the repair action in 1991.

Table 2: Failures of the riser tubes.

<table>
<thead>
<tr>
<th>Date</th>
<th>Damages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. May 1985</td>
<td>leak</td>
</tr>
<tr>
<td>2. March 1988</td>
<td>hole (2 mm diameter)</td>
</tr>
<tr>
<td>3. Sept. 1988</td>
<td>oval hole (13 mm by 15 mm)</td>
</tr>
<tr>
<td></td>
<td>small crack</td>
</tr>
<tr>
<td>4. Sept. 1991</td>
<td>leak</td>
</tr>
<tr>
<td>5. Nov. 1991</td>
<td>hole (80 mm by 40 mm)</td>
</tr>
<tr>
<td></td>
<td>2 leaks</td>
</tr>
</tbody>
</table>

FAILURES IN 1991

The damages in 1991 were similar to those in 1988: During a shut down in September a small leak at a sloping riser tube was noticed. The leak was on the offtstream side of the tube and caused only a small loss of water. The damaged part of the tube was cut out and a new piece was welded in.

Six weeks later the plant tripped due to the sudden loss of water in the steam generating system. The steam blew down through the waste-heat boilers, the high temperature shift converter and vented through the flare. We were lucky that the catalyst pellets of the HT shift converter did not entrain with the steam as it happened in 1988. Because of wetting the catalyst heavily and the resulting mechanical stress to the pellets the HT shift catalyst had to be replaced.

After cooling down and venting the system we could inspect the waste-heat boiler: The riser tube repaired six weeks ago was ruptured in the vertical section downstream the renewed part. In neighbourhood to this part just downstream the weld, there was a small leak.
The investigations on the renewed tube reported heavy erosion in the six-week old part. Another riser tube in the neighbourhood in same position had a leak in the slope section. Both leaks and the zone of erosion were situated on the offstream side of the sloping riser tube. The rupture was situated in the vertical section along the ruling line parallel to the gas flow (fig. 9).

INVESTIGATION ON MATERIALS

The metallographic examinations reported similar causes of the damages in 1988 and 1991: In the zones of erosion and leaks the protective magnetite layer was irregularly laminated like a system of independent sandwich-like layers (fig. 10).

We assume: The high gas inlet temperature and the increased gas flow due to the revamped process-air compressor caused a local thermal overload of the waste-heat boiler. Especially the riser tubes in the gas inlet zone tended to be overloaded. Spots of disturbed magnetite layer may have caused a high rate of bubble formation and finally a local dryout of the tube wall resulted. The magnetite layer burst because of the different thermal expansion of steel and magnetite layer. The magnetite layer was formed again by consuming tube material. The thickness of the porous, disturbed magnetite layer grew and heat transport went worse. The result was a further increase of temperature at the tube wall and a burst of the magnetite layer. The permanent repetition of this process caused the erosive pull down of the tube wall until finally a leak or rupture occurred. We noticed damages of only two tubes, in both cases situated on the lowest tube of the harps in the hot gas inlet of the waste-heat boiler.

CAUSES OF THE DAMAGES

The boiler feed water of the Ammonia Plant No. 3 is a mixture of demineralized water from the supply net and reused, untreated condensate of the turbines in the plant.

A part of BASF's demineralized water is produced out of water of the river Rhine. It may contain small residues of chlorinated hydrocarbons which will be cracked under the conditions of the waste-heat system. The aggressivity of the in situ formed hydrochloric acid will be neutralized by higher pH-values. Therefore it is necessary to add sodium hydroxide inspite of the disadvantage of speeding up corrosion and erosion in the case of dryout by settling in the magnetite layer and making it porous. Investigations on the recycled condensates report that they improve the quality of boiler feed water.

When in 1988 the damages had accumulated, the conditioning of the boiler water was thought over and analysis was intensified:

- pH-value set between 9.3-9.7 by addition of sodium hydroxide,
- Addition of hydrazine as an inhibitor,
- Increase of the blowdown of water from the steam drum,
- Weekly analysis of the total steam generating system.

Besides the quality of the boiler-water there are other important facts of influence. The rupture of the vertical riser tube indicates a heavily disturbed flow of the steam water mixture. Formation of bubbles may stop the natural draft circulation which is induced only by a small pressure difference (fig. 3, 5).

It is very dangerous if counterflowing steam bubbles hinder the water supply to the lower, hottest parts of the vertical headers.

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Like steam bubbles, corrosion products and sludge in the bottom covers of the vertical headers prevent the sufficient cooling of the lower riser tubes. Because there is no possibility to drain the vertical headers, corrosion products are accumulated for years on the lowest part (cover) from where the lower evaporator tube is supplied. In 1988 x-ray tests showed a lot of sludge in the covers, which was then removed. In September 1991 video-checks reported only a small amount of corrosion products which mainly escaped in November 1991 because of the rupture.

These special fluid dynamics are a problem at high thermal load of the waste-heat boiler. A check of the process parameters indicates a thermal overload (steam production) of 10% over design. Before the damages in 1988 and 1991 the waste-heat boiler had been running close to the allowed maximum of gas inlet temperature of 990 °C. Finally the revamp of the process-air compressor increased the heat flux furthermore.

**ACTIONS**

Even before installing the new waste-heat boiler it was cleaned because of the problematic fluid dynamic situation. Although stored under conservation conditions (nitrogen) the tubes of the new waste-heat boiler contained a lot of corrosion products in the riser tubes. These were removed by a complicated procedure of steam blowing for several times. The success of this cleaning procedure was controlled by video-checks. To improve the quality of the magnetite layer we started up running the waste-heat boiler according to a special pH-value programm.

Furthermore we used the ASPEN simulation programm to set up economically and technically reasonable process parameters for the waste-heat boiler. The process-air compressor is still running under the conditions we got after the revamp. In order to avoid too high gas inlet temperatures, we run the methane concentration downstream the secondary reformer above a critical level.

By these measures we are sure, that the thermal load of the waste-heat boiler remains at a technically acceptable low value, as we had run the plant before the debottlenecking.

At any shutdown of our plant the riser tubes and their headers will be checked.

All our experiences show that water-tube type waste-heat boilers are very sensitive to thermal load. Especially when they have no drains and when they are run only by the small forces of natural circulation.

**CONCLUSIONS**

There was an untypical failure of the waste-heat boiler after revamping the process-air compressor and increasing the capacity of the Ammoniak Plant No. 3. Due to the construction of the boiler in certain tubes the two-phase-flow of steam and water was disturbed at high energy load conditions. The tubes were eroded. Such a damage was not predictable when we planned the revamp of the process-air compressor.

Since the last repair in November 1991 no signs of tube failures were detected in the waste-heat boiler.
DISCUSSION

T. S. Hariharan, Fertil, Abu Dhabi: I understand that the high heat load is the probable cause for this failure. What do you consider to be an acceptable level for heat load?

Reininghaus: I do not have the numbers at present.

Hariharan: When you ordered a spare boiler did you do any modifications to reduce this heat flux?

Reininghaus: No. It is an identical boiler.

Hariharan: We have a 1,000 tpd ammonia plant, and the fired tube boiler has suffered three failures.

We have come to the same conclusion as you that the high heat flux is the main reason. We are now considering a lower heat rated modification.

P. J. Nightingale, ICI, England: We had a similar experience. Did you monitor the level of chlorides in your boiler and change your operating pattern accordingly?

Reininghaus: It is difficult to be exact. Levels of about 1 ppm could have existed in the drum.
Figure 1. BASF's Ammonia Plant No. 3.

Figure 2. Process-air-compressor.

Figure 3. High pressure steam generating system.

Figure 4. Waste-heat boiler.

Figure 5. Waste-heat boiler.
Figure 6. Scheme of a tube harp.

Figure 7. Location of failures of the riser tubes.

Figure 8. Renewed lower part of inner riser tubes.

Figure 9. Ruptured riser tube.
Figure 10. Irregular magnetite layer.