Failures in Ammonia Plant Vertical Waste Heat Boilers
Potential Causes & Remedies

The authors were involved in investigations of corrosion problems in Ammonia plant Waste Heat Boilers that had in common, that deposits on the water/steam side were noticed/involved in all cases. The paper will give a brief description of the operating conditions for different designs and shortly resume cases of corrosion in synloop Waste Heat Boilers (WHB) concerning location of the damages. The potential sources of deposits, the analysis of potential causes and the remedies to avoid premature failure will be discussed. Oxidation scale generated during Post Weld Heat Treatment and remedies to further boiler failures will be discussed based on actual inspection results.

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1. Introduction

We investigated the corrosion phenomena observed in vertical WHBs operating in the ammonia synthesis section, including the impact of the Post Weld Heat Treatment method applied in many these type vertical WHB operating in the Synthesis section of Ammonia plants designed by Uhde, Dortmund, Germany. There are basically two different designs for the vertical WHB in use in many ammonia plants designed by Uhde:

Type A1 Shown in Fig. 1: Hot Inlet Field – Cold Outlet Field symmetrically to one axis with cooling bores in the tube-sheet for circulation of boiler water (BW) in order to keep the ferritic tubesheet (2 ¼ Cr) below the nitriding temperature. Square pitch.

It is not applied as a stand-alone evaporator but always in combination with type B2 WHB.

Type B1 and B2 shown in Fig. 2: Hot Inlet in the center of the tubesheet – Cold Outlet Circular Area with pre-heater / economizer, fountain tube arrangement. To protect the tube sheet against nitriding the effluent syngas with temperatures around 320 -340 °C (608-644F) is flushing the hot leg connection tubes and the bottom surface of the tube plate. Type B1 WHB is used in all Uhde design
ammonia plants built after 1980 of up to 1200 MTD capacity. Several damages due to waterside corrosion were experienced in B1 WHBs.

Type B2 is of similar design than B1. This type is used in all plants with larger plant capacities above 1200t/d. The heat duty is used to preheat all BFW for both WHBs A1 and B2.

Configuration C for two converter plants is shown in Fig. 3.

This is a configuration combining Type A1 & Type B2, used in ammonia plants of Uhde design for capacities bigger than 1200 MTD. The B2 type preheats the water for both boilers and the water flows by gravity into boiler A1.

So the boiler A1 receives BFW with already preconcentrated remaining impurities due to steam production in B2 and BW in Type B2 has a very low concentration of impurities due to high “blow-down” rate towards Type A1.

All these type WHBs are of natural circulation and tubes to tube-sheet joint is of in-bore weld type. The material of the tubes and the tube-sheet is 2 ¼ Cr steel due to hydrogen partial pressure require-
ments as per API 941, requiring a post weld heat treatment (PWHT).

In several of these WHBs failures occurred after a relatively short time (one to three years) due to water side corrosion only on the hot leg of the U tubes either close to the tube sheet and/or near the lower baffle of the hot tube shank.

Also corrosion with unspecific locations all along the straight tube length was experienced.

2. Investigation
The discussion about root causes of water side corrosion failures and their relation to design, operation, to water chemistry and material selection is a big issue for plant owners engineering companies, and equipment suppliers.

Many investigations were carried out, large numbers of papers have been presented in Ammonia Safety Symposia and in other technical conferences and rich literature exists on the matter.

During the 2005 Ammonia Safety Symposium in Toronto several papers about boiler damages were presented. “Corrosion Damage in Waste Heat Boilers; Major Root Causes and Remediation”[2] was one of these papers presented by Harrie Duisters and Jo Savelkoul from DSM in the Netherlands.

The paper describes different corrosion mechanisms, which can occur in ammonia plants, for example, first condensate corrosion and flow accelerated corrosion. The main conclusion of the authors was: “Keep your boiler surfaces clean and you will not suffer a damage”.

When a small leak in a type A1 waste heat boiler was suspected, it was decided to investigate the whole BFW, Steam and condensate system of the plant to evaluate potential sources of corrosion, which could transport solids into the boiler.

During start-up of this plant it had been suspected that there was a leak in the boiler, which turned out to be an error due to an analysis failure. During shell side inspection some deposits had been seen in the boiler.

As Mr. Savelkoul had been retired in the meantime Uhde convinced him to join the investigation about possible locations of corrosion as well as potential improvements in BFW, steam and condensate treatments.

Mr. Savelkoul had been the BFW expert in the DSM organization for the last 25 years.

During this investigation some improvements in BFW treatment were developed which are also reflected in the VGB (The Congregation of Big Power Station Operators) guideline R450Le [3] the old Uhde procedures had been following a previous edition of the same standard.

This standard was remarkably amended in it’s December 2004 edition. Also a condensate line was suspected to potentially deliver corrosion products directly to the deaerator without further cleaning.

It was decided to perform a visual inspection program in the upcoming shutdown for a lot of equipments operating in the condensate, BFW and steam system to find evidence for such corrosion products transported into the boiler system via the condensate system.

In a meeting in November 2005 this programme was discussed with the customer to be performed during the upcoming shutdown in April 2006. Short before there had been tube damage in a BFW preheater which was fabricated completely from stainless steel.

It was by pure chance that on the cover of the inspection report for this damage there were photos of the inside of the tubes which showed obvious deposits not originating from this equipment but from the upstream system.
This supported the suspicion of possible ingress of corrosion products into the boilers.

During the plant shutdown a common investigation team was formed by Uhde and customer personnel. Commonly numerous equipment, vessels, heat exchangers and separators were inspected.

There was no evidence found that corrosion products were formed in the suspected condensate system. But there was clear evidence that there was transportation and deposition of foreign matter into the BFW-system as well as into the boilers.

The stainless steel BFW Preheater which had suffered a leak some months before (not due to corrosion), was clean in the inlet channel but as soon as the medium temperature was increased obviously dissolved material was deposited.

Deposits were found in the tubes over the full length of the tube bundle in all tubes.

A lot of deposits were found at the bottom of the outlet channel as well.

The next equipment downstream of this BFW Preheater are the configuration C Synloop WHBs and, on the way to the reformed gas waste heat boiler downstream of the Secondary Reformer; another BFW Preheater.

This has very similar operating conditions than the type B2 Synloop WHB. The shell side of this BFW Preheater showed that also here deposits from the BFW had been formed on the outside of the tubes. The appearance of the deposits was sparkling crystalline and porous. See figure 7.
The same deposits were found in both boilers A1 and B2. All the tube length and also internals showed deposits from the water on all surfaces.

In addition spalled off deposits were found on the tubesheet of B2 WHB, on top of the top baffle of the integral preheating zone and as well on the tubesheet of the A1 WHB also in some cooling bores.
These deposits in the cooling bores probably had been deposited during shutdown of the plant when the flow through the cooling bores stopped and floating spalled off deposits could settle.

The eddy current measurement of the tubes in the A1 boiler, which had developed the leak, showed no specific location of the damage but corrosion all along the tube length of the hot tube shanks.

The deposits from the SS BFW Preheater as well as deposits from the strainer of the BFW pump were analyzed and showed a surprisingly high content of carbon as well as about 1% of sulphur. This cannot be from corrosion products but must have other sources.

Nevertheless the suspected condensate line was rerouted to the BFW makeup unit and the recommendations concerning modified BFW operation according to the new VGB guideline were recommended to the customer.

The joint investigation team agreed in not being able to identify the root cause of the deposits. Following potential contributors and influence factors were identified as fields for improvements:

- Deposits
- Heat Flux
- Circulation rate
- Material of Construction
- Boiler Feed water/Boiler water quality
- Desalination and temporary blow-down

These influence factors should be considered with improvements for a replacement design. The sequence does not reflect a ranking.

Two years after these modifications in February 2008 there was a chance to inspect the shell side of the BWF Preheater shown in Fig. 7. Now the shell side appeared clean as shown in Figure 13 without deposition from the water.

The modifications done for this plant were implemented from the beginning into a new plant under design at the same time which had a very similar setup of the BFW, steam and condensate system. The rerouting of the suspected condensate line was implemented and the modified BFW treatment was operated from the beginning. The temporary blow down of both vessels, which had been manually in all previous plants were implemented as automatically initiated twice per shift into the Distributed Control System of the new plant.

It was decided to inspect the boilers of the new plant after approximately one year during the shut-down before final takeover of the plant.
4. New Suspicion
In a paper presented during the Nitrogen Conference 2007 [4] Pan Orphanides presented the suspicion that oxide layers formed during PWHT of the boilers would not be removed by the boil-out procedure and could cause damages in boilers. He had investigated the PWHT treatments of different manufacturers.

One method was to perform the PWHT in one piece in a furnace. This PWHT has to fulfill the requirements for the thick-walled channel with nozzles, the tubesheet and the tube to tubesheet weld.

Figure 14 shows this configuration

All of the defective WHBs had seen such PWHT during fabrication.

A new licensee of Uhde’s WHB design had performed a different PWHT. The PWHT had been performed only for the channel and tubesheet including a small portion of the tube bundle only for PWHT of the internal bore weld seam. The rest of the tube bundle had been kept out of the furnace.

5. Shell Side Inspection of diverse B1 WHBs
Following the 2007 Nitrogen Conference several inspections of the shell sides of WHBs of B1 design have been performed in order to support or disprove Pan Orphanides theory about detrimental oxide layers formed during PWHT.

The first WHB which was inspected in May 2007 had not been in operation but was still stored under nitrogen atmosphere until scheduled installation in late 2007.

The inspection was done commonly with the customer and the common finding was that there were no major oxide layers visible and the boiler must be considered as clean.

This WHB had been fabricated with the partial PWHT procedure as shown in Fig.14.

Beginning of November 2007 a leakage of a B1 WHB occurred which had been fabricated with the complete PWHT as per Fig. 13. This boiler had been in operation for slightly more than one year. Two tubes were leaking and were plugged. In total only 5 tubes were inspected as the customer wanted to get back in operation as soon as possible. A visual inspection of the shell side could not be done, as no suitable endoscope was available.

A month later a scheduled shutdown in another more or less identical plant with an identical boiler gave the chance for inspection of the boiler with
eddy current method from inside the tubes and a visual inspection of the shell side.

The findings were: an about 100mm (~4 inch) thick layer of spalled off deposits which obviously had been spalled off not from the tubes because the curvature of the oxide layers was different from the tube diameter. Nevertheless the eddy current inspection proved there were no deficiencies and loss of wall thickness on the tubes.

During the time of this shutdown a new leak occurred in the plant, which had suffered a first leak in November. This time a visual inspection could be performed. The finding was that there was also a layer on about 100mm (~4 inch) of spalled off oxide layers with very similar appearance than in the previously inspected plant.

From the optical appearance it seemed, that the density of deposits was higher in the plant without damage than in the plant with damage. This may be due to several filling and emptying cycles after plugging and hydrotest with subsequent draining.

Both boilers had seen a full PWHT, one failed, the other not. Differences may be that beside better BW quality the WHB that did not fail was operated at design capacity or lower, the failed WHB operated at higher than design capacity.

In both plants it was tried to flush out the deposits from the centre of the boiler via the central blowdown pipe and potentially drain out the deposits via two drain bores in the outer circumference of the tubesheet.

In the plant with the damage the deposits could be flushed away from the centre of the boiler but check of the drained water showed that the deposits were probably stuck in the outer tube pass of the preheating zone because of the smaller tube pitch in this area.

In the plant without damage this attempt was less successful. Only part of the deposits could be flushed out.

In both plants the tube portions near the tubesheet surface where the deposits had been flushed away looked like bare metal surfaces without magnetite layer. This was independent from the location of the end of the ferrules.

A regular magnetite layer was found on the tubes above the deposit layers in both cases. In the plant with damage the damage was located approximately 30-40mm from the top of the deposits. The appearance was like a mountain area with pitting like loss of wall thickness.

Fig. 16 shows this area for one leaking tube

Fig. 17 shows a tube of the boiler without damage for comparison.
An inspection of another boiler of identical design but different manufacturer with partial PWHT was done in a plant still under construction. The finding was identical with the first inspection done in May 2007. The boiler was found to be clean no major oxide formation from PWHT could be seen.

Another identical plant with a boiler fabricated by the same manufacturer was inspected during a scheduled shutdown in April 2008. The finding was that the boiler was clean.

The tubes had a regular magnetite layer from approximately 50-60mm (~2inch) above the tube sheet. No indication of wall thickness reduction was found. Single spalled of oxide particles were visible.

6. Conclusion from these inspections

It appears that the theory of Pan Orphanides is correct that a complete PWHT of the tube bundle in the furnace leads to oxide layer formation on the tubes, which are not removed during the normal boil out procedure.

During operation of the boiler these oxide layers spall off and are transported by the natural circulation to the centre of the boiler. They’re under these deposits impurities from the boiler water can concentrate [2] and can lead to under deposit corrosion.

As the example from the plant without damage shows, deposits alone do not necessarily generate damage but in any case they are a risk, which should be avoided.

So the partial PWHT as proposed in [4] could be proven by inspection as superior against the full PWHT.

7. Inspection of a new plant with modified BFW System

The plant with the modification as described in paragraph 3 was inspected in January 2008. Due to
shifting of the shutdown the inspection took place after nearly two years of operation.

The inspection by means of an endoscope revealed that the boilers are clean.

The B2 WHB had no deposits on the tubesheet. The tubesheet was absolutely clean. The tubes showed a regular thin magnetite layer on the tube surface. No deposits were found elsewhere in the boiler on the top and bottom.

When starting the inspection the boiler had been partially filled with water. The water contained minor particles, which appeared like tiny snowflakes.

After draining the remaining water from the boiler a layer of microscopic oxide particles was found settled in the low velocity area around the internal shroud of the boiler. See Fig.23

Also on the tubesheet surface these micro particles were seen. They could have been easily removed by flushing and draining via the cooling bores.

The endoscopic inspection of the B1 WHB came to the conclusion that in general the boiler tubes are clean.

![Fig. 20 Tubesheet of B2 WHB](image)

![Fig. 21 Tube bundle of B2WHB](image)

![Fig. 22 Tubesheet of A1 WHB](image)

![Fig. 23 A1 WHB very fine sludge on tubesheet](image)
By miscommunication the customer was of the opinion that Uhde had not intended any inspection of the boilers. So the customer had prepared the pulling of the shell of both WHBs.

Based on the findings of the visual inspection the pulling of the B2 WHB shell was skipped.

However the customer decided to pull the shell of the A1 WHB. Surprisingly after pulling of the shell spalled off oxide layers were seen on the tubesheet surface via the bottom shroud openings on the hot half of the tubesheet. This had not been seen with the endoscope.

After these findings it was decided to remove the internal shroud as well.

The tubes mainly on the cold half of the tubesheet as well as the tie rods still had some oxide layers on the surface, which had not yet been spalled off.

These oxide layers were noticed up to a height of approx 2m from the tubesheet. Above that all tubes had a regular magnetite layer. This was a surprising finding because it had not been expected as the A1 WHB had seen a partial PWHT only.

The whole tube bundle was cleaned with high pressure water jetting and the spalled off and remaining oxide layers were removed as well as the sludge on the tubesheet.

After cleaning of the boiler it was clear that there was no damage on the tubes. Neither near the tubesheet nor above or below the support baffles where damages had been found at previously experienced damages. Also no under deposit corrosion was found.

All upstream and parallel BFW preheaters were found with a regular magnetite/hematite layer free from any deposition from the BFW other than described in paragraph 2.

7. Conclusions from this inspection

Obviously the modification of the steam condensate and BFW system with improved BFW operation and automatically operated intermittent blow down system had prevented damage on the tubes even under the deposits.

The findings prove that even partial PWHT is not sufficient to prevent formation of oxide layers, which in this case probably occurred due to temperature conduction under insulation.

8. Consequences

All boilers, which had experienced failures in the past, had seen a full PWHT in the furnace without protection of the tube bundle from oxide formation.

It was decided that all new boilers would see a PWHT under nitrogen atmosphere to avoid any oxide formation. As recommended also in [4] Figure 25 shows the configuration with an auxiliary shell with nitrogen filling during PWHT in the furnace.
Fig. 25 PWHT of tube bundle under nitrogen atmosphere in the furnace

Fig. 26 A1 WHB after PWHT with auxiliary shell.

Fig. 26 shows the first WHB after PWHT with auxiliary shell. This will replace the A1 WHB described in paragraph 2 which has been successfully modified by gas flow reversal (GFR) [5] to prolong lifetime and operates without further damage since then.

Fig. 27 shows the tube bundle after removal of the auxiliary shell. As you can see the tube bundle is free of any oxides from PWHT.

Fig. 27 A WHB after removal of auxiliary shell

Figures 28 and 29 show T22 tubes of the tube bundle of a B1 WHB after PWHT under nitrogen. The surface is still shining with visible numbering from tube insertion sequence.

Fig. 28 B1 WHB tubes after PWHT

Furthermore all plants will be equipped with an automatically operated intermittent blowdown system. This eliminates any doubt whether the intermittent blow down is operated as per operating instructions or not.

The BFW treatment will be operated strictly according to the revised VGB Guideline R450Le, which has been implemented into all new operation handbooks.
The use of oxygen scavengers will be limited. According to the VGB guideline other than in the past some content of remaining oxygen is useful to maintain the magnetite layer. In the new plant dealt within in paragraph 7 an oxygen scavenger dosing system is installed but was never operated as the remaining oxygen content of the water leaving the deaerator was below the VGB value.

The shining surface of the bottom part of the tubes near the tubesheet which had been found in several plants was discussed with the VGB Materials Laboratory and judged normal as the conditions for magnetite formation in that location are not given. [6]

The shining surface is obviously no sign of corrosion attack or loss of wall thickness if you compare Fig. 18 before boil out and 19 for another identical boiler after one year of operation.

When you compare Fig.19 from a plant with oxygen scavenger dosing and Fig. 20 from a plant without oxygen scavenger dosing it is obvious that the formation of a regular magnetite layer without dosing of oxygen scavenger starts earlier.

With dosing of oxygen scavenger the oxygen for formation of an oxide layer can come only from dissipation of steam.

This may explain the shining areas where the produced steam does not provide enough dissipated oxygen for magnetite formation.

9. Acknowledgements

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Bibliography


[6] VGB Material Laboratory Essen, Dr. Gereon Lüdenbach, personal communication.