PPChem 101

BOILER AND HRSG TUBE FAILURES

LESSON 4:

Hydrogen Damage

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INTRODUCTION

In Lesson 3 of this course – *Underdeposit Corrosion – A General Introduction* – presented in the December 2009 issue of the PowerPlant Chemistry journal, a general review of features common to all underdeposit corrosion mechanisms relevant to boiler and HRSG tubes was introduced. In this lesson, the focus is on hydrogen damage, which is the most frequently occurring underdeposit corrosion mechanism.

LOCATIONS OF FAILURES FOR FOSSIL PLANTS AND HRSGS

Hydrogen damage – a special type of underdeposit corrosion – may develop solely in locations where excessive deposits, mostly of feedwater corrosion products, are formed. The corrosion products typically originate in the pre-boiler part of the cycle. They are generated in condensate and feedwater touched cycle components and transported with the feedwater into the boiler. Single-phase and two-phase flow-accelerated corrosion of cycle components is the major source of the corrosion products introduced in the boiler or heat recovery steam generator. The transport of iron oxides (magnetite or hematite) depends on the feedwater treatment applied. If copper alloys are employed in the feedwater system then copper oxides will transport into the boiler leaving pure copper within the deposits.

The locations where underdeposit corrosion occurs are those where excessive deposits form. Endangered are all locations where the water flow adjacent to the tube wall is disrupted in some way. There are many possible reasons for the flow to become disrupted. In conventional plants, the most susceptible locations are:

– locations with existing internal deposits caused by
  • locally high heat flux
  • locally high steam quality
  • other deposition mechanisms
– geometrical flow disrupters such as
  • improper welds

  • backing rings
  • poorly executed weld overlays and pad welds which penetrate the tube wall to the inside surface
  • existing internal deposits
  • bends around burners or openings
  • tubes which are not vertical and are heated from above or below such as nose or arch tubes
  • sharp changes of directions
  • tubes bending off lower headers and drums
– localized overheating due to inadequate fireside conditions
  • local overheating of the tube due to fireside flame impingement
  • local overheating of the tube due to burner misalignment
– localized overheating due to operating conditions
  • local overheating as result of fuel changes
  • overfiring or gas channeling
  • local high steam quality
– thermal-hydraulic disrupters as
  • locations with local very high steam quality
  • locations with horizontal or inclined tubes

Figures 1–3 show some geometrical flow disruptors related to incorrect weld repairs.

In HRSGs, deposition and hydrogen damage occur on both horizontal and vertical high pressure (HP) evaporator tubing. On vertical tubing, the deposition concentrates on the inner tube side crown of the tube facing the gas turbine (GT). It nearly always is heaviest on the leading HP evaporator tube in the circuit as these have the areas of maximum heat transfer. The hydrogen damage mechanism occurs in exactly the same areas. Tubes adjacent to a side wall or the gap between side-by-side modules are especially at risk. Exhaust gas bypassing results in greater heat transfer there. On horizontal tubing both deposition and the hydrogen damage mechanism occur on the inner tube side crown facing towards or away from the gas turbine. Damage usually occurs on the side facing away from the GT when poor circulation rates, steaming or steam

blanketing occur. These can lead to stratification of water and steam and subsequent heavy deposition in a band along the top of the tubing.

In these locations, in the presence of excessive deposits, possible acidic boiler water contaminants (for example chlorides or sulfates) may concentrate up to dangerous levels.
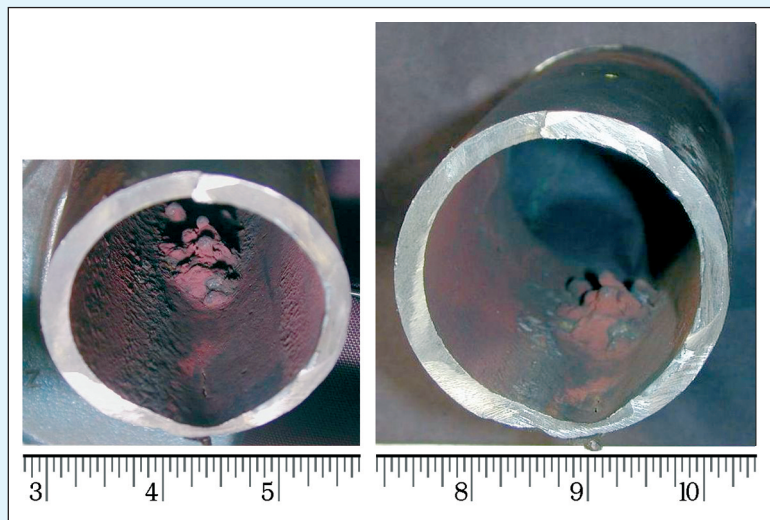

Figure 1:
Tube inner surface showing heavy local deposits from penetration of weld repair to the tube inside.

Figure 2:
Roof tube with pad weld showing penetration through to the tube inside. This penetration acts as a flow disruption.

Figure 3:
Weld repair showing through to the tube inside becomes a flow disruption.

TYPICAL CHARACTERISTICS OF DAMAGE IN BOTH PLANTS

The most important features of hydrogen damage are summarized in Table 1.

Features of failure	• Gouged areas; thick deposits. • Thick-edged, often with "window opening" failure appearance in conventional boilers. • Longitudinal crack is the typical appearance in HP evaporators of HRSGs. • Brittle failure.
Effect on oxide and characteristic deposits	• Oxide growth under stress leads to thick, multilayer scale (alternating layers of porous and dense magnetite), which may be missing as a result of failure incident.
Key microstructural features	• Intergranular microfissures in base tube material linking to form cracks. • Decarburization at inner surface. • Multilaminated, non-protective oxide sometimes containing chloride at the tube/oxide interface.
Root cause	• Deposits formed by a number of root causes plus acidic contamination (several sources).
Cycle chemistry implications	• Source of low pH contamination (acidic) exists. Can be bulk or local concentration only. • Inadequate instrumentation to identify contaminant ingress.
Attack rate	• Very rapid (can be > 10 mm per year). Failures can occur within six months following contamination.

Table 1:
Characteristics of hydrogen damage.

Mechanism of failure

Excessive deposits of feedwater corrosion products such as iron, copper or nickel oxides or oxide hydrates themselves are not sufficient for the development of hydrogen damage. The second condition is the presence of acidic contaminants in the boiler water and their concentration underneath the deposits (e.g., by wick boiling).
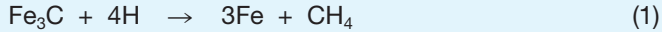
A similar statement can be made with respect to any acidic contamination in the boiler water: it alone does not cause hydrogen damage. Here, again, a second constituent is required – excessive deposits beneath which the concentration of acidic contamination may occur.

The presence of a locally acidic environment at the base of the heavy deposits affects the magnetite growth mechanism. Under favorable conditions (neither excessive deposits on the tube surface, nor acidic contamination), the growth of the protective magnetite layer is a diffusion-controlled process based on the counter-flux diffu-sion of Fe^{2+} ions towards the boiler water and O^{2-} ions to the tube wall. In this way, magnetite is formed at both the tube/oxide and oxide/boiler water interfaces; however, the outer layer is never observed on actual boiler tubes as the magnetite becomes incorporated into the boiler water. The oxide which remains on the tube surface as the indigenous oxide is stress free and thus acts as a protective layer. The growth of this protective oxide occurs parabolically.

At the base of the deposits, the magnetite growth processes changes drastically under concentrating acidic (chloride) conditions. Chloride concentrates under these deposits and iron chloride is formed. Then the magnetite which grows on the tube surface is not stress free and it breaks away from the surface and another layer starts to grow. Repetition of this process produces a thick multi-laminated oxide structure, and the associated growth rate changes from parabolic to a very fast linear rate. The layer

does not growth stress-free and delaminates. Since the hydrogen is generated at the tube surface, it all diffuses into the tube wall and reacts with carbide (cementite, Fe_3C, within the pearlite structure of the carbon steel) according to Eq. (1)

$$Fe_3C + 4H \rightarrow 3Fe + CH_4 \tag{1}$$

Methane concentrates in the tube material and causes intergranular microfissuring at the grain boundaries. The tube material is affected in an irreversible manner and is embrittled. The tube material with distinctively changed microstructure and lower strength is prone to failure. A cross section through a boiler tube affected by hydrogen damage showing the microcracks is shown in Figures 4–6.
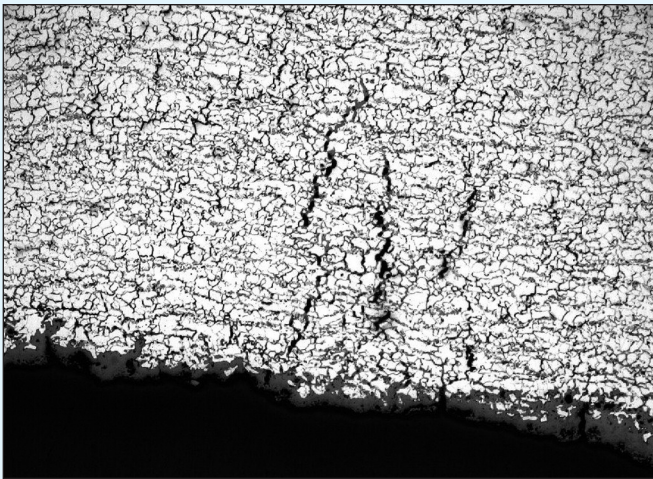

Figure 4:
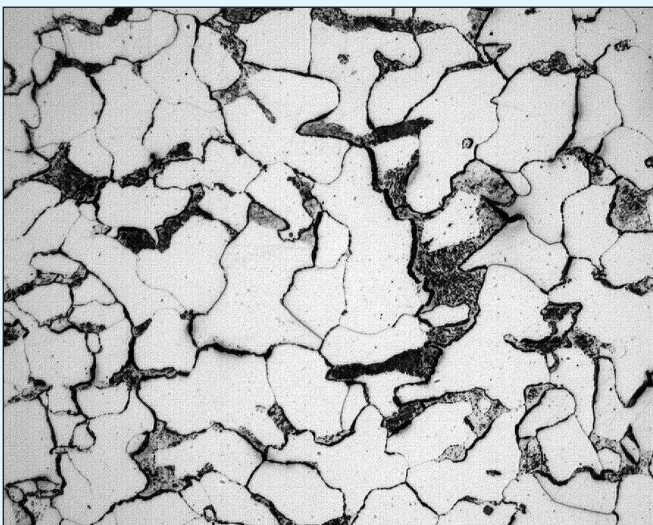Cross section through tube with hydrogen damage showing the microcracks.

Figure 5:
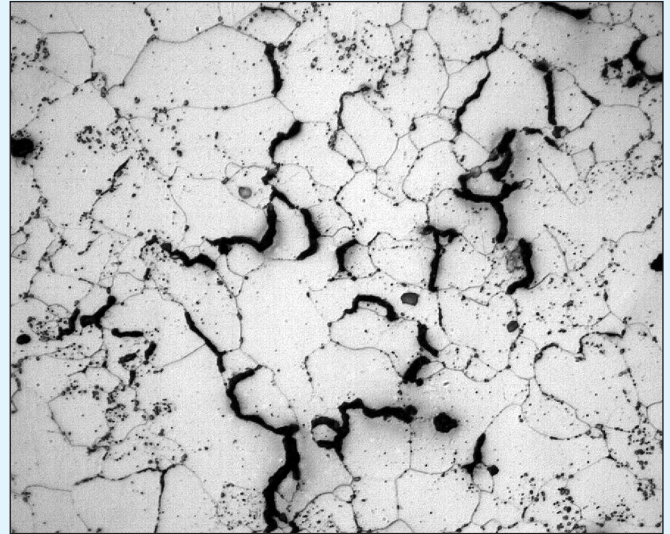Microcracks in detail showing that the cementite (carbide structure) is partially denuded.

Figure 6:
Microcracks in detail showing that the cementite (carbide structure) is completely denuded.

POSSIBLE ROOT CAUSES

The most decisive root causes are all those leading to formation of excessive boiler and HRSG tube deposits and to ingress of acidic contamination in the plant cycle. Some are briefly discussed below:

– Poor feedwater treatment
  typically resulting in high corrosion product levels (iron and copper oxides or hydrated oxides). Corrosion products generated by corrosion or flow-accelerated corrosion in the condensate/feedwater train in conventional units, and in the feedwater and in the low pressure parts of the HSRG, subsequently deposit in waterwalls (conventional boilers) and in the HP evaporator tubing (HRSGs), and form the basis of hydrogen damage mechanisms.

– Flow disruptions to the internal water flow inside the boiler waterwall or HRSG HP evaporator contributing to increased deposition of corrosion products

– Adverse fireside conditions
  as flame impingement and burner misalignment promoting the deposition processes

– Excessive deposits
  being not duly detected (disregarding of tube sampling) and not removed by chemical cleans in a timely manner

– Ineffective chemical cleans
  with deposits remaining on critical places

– Errors in chemical cleaning process
  as incompletely flushing of the cleaning solution or flaked (not dissolved) deposits

– Minor condenser leaks
occurring over an extended period

– Major condenser leaks
with a serious ingress of cooling water in the cycle

– Ingress of regeneration chemicals
from upsets in makeup water treatment units or con-
densate polishers

– Poor or inadequate instrumentation
not meeting the international standard for cycle chem-
istry instrumentation according to the IAPWS Technical
Guidance Document [1], which prevents having ade-
quate cycle chemistry monitoring and control to detect
contaminant ingress

FEATURES OF FAILURES

Figures 7 and 8 show hydrogen damage failures.

POSSIBLE SOLUTIONS

The possible solutions depend on the extent of damage.
For this reason, the condition of the waterwalls or the HP
evaporator tubes of a HRSG have to be evaluated.

In conventional boilers, an ultrasonic examination encom-
passing a complete scan of suspect tubing is a meaning-
ful non-destructive evaluation technique. Since most
hydrogen damage associated with boiler tubing is usually
associated with inner distress in the form of gouging to
some degree, the ultrasonic examinations essentially look
for this tube condition. This method is relatively rapid and
quite quantitative to measure the physical macrodamage
associated with hydrogen damage. However, ultrasonic
examination is not always adequate as sometimes hydro-
gen damage occurs with no wall loss. In addition, this
method does not measure the actual amount of decarburi-
zation of the affected tubing, which can lead to premature
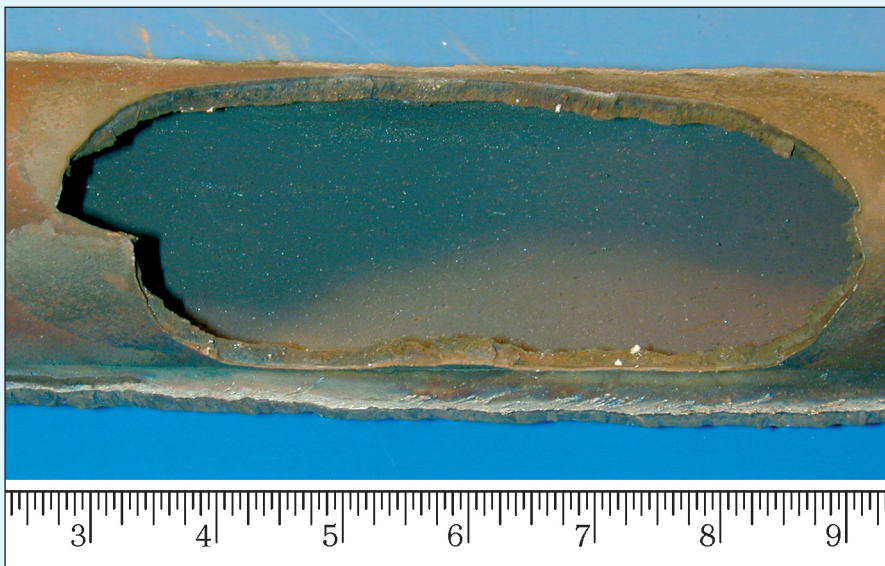rupture of the tubing due to low ductility. The technique

Figure 7:
Hydrogen damage window opening and
thick-edged failure.
Courtesy of David Daniels (M&M
Engineering Associates, Inc.).

Figure 8:
Large hydrogen damage failure.

relies on an attenuation of the ultrasonic backwall signal associated with the inner loss of wall. Tubes are then categorized based on the severity of the damage/wall loss knowing that there could be additional weakened material due to decarburization of the cementite and associated microcracking.

The situation for HRSGs is much more difficult because fiber optics and visual techniques are really the only non-destructive evaluation methods which can be used other than actual tube removal. The emphasis here must be on minimizing the deposits by controlling the corrosion and flow-accelerated corrosion in the lower pressure circuits.

Tube sampling in critical boiler or HRSG regions provides information about the type, extent and thickness of deposits. Evaluation of microsections supplies information whether hydrogen fissures beneath of deposits are present or not.

Immediate Actions

It is very important to react fast to any serious contaminant ingress in the cycle (a major condenser leak, ingress of regeneration chemicals). Immediate shutdown is advised in all cases when the boiler water pH was less than 8.0 and is decreasing (this value refers to the bulk of the boiler water as the pH beneath the deposits in concentrating circumstances will be markedly lower due to the concentration of acidic contaminants). In many cases, chemical cleaning might be required.

If evaluation of tube wastage or thinning indicated hydrogen damage, replacement of all affected tubes to prevent possible ductile failures is necessary. In no case, should pad welding or canoe/window welds be applied as repair or replacement options in hydrogen damage situations.

Long-Term Actions

Any long-term actions for preventing hydrogen damage have to focus on minimizing deposits buildup and avoiding acidic contamination since both are required for initiating hydrogen damage.

Measures to be taken to minimize deposit buildup are among other things:

– Application of an optimum plant cycle chemistry treatment to ensure a minimum corrosion product formation and transport into the boiler.
Focus is on the feedwater in conventional plants and on the feedwater and lower pressure circuits for HRSGs.

– Use of adequate chemistry-related instrumentation and installation of appropriate control room alarms.

– Keeping deposits at an acceptable level and – if necessary – removal of deposits by way of chemical cleaning.

– Removal of all geometrical flow disrupters such as pad welds, backing rings, etc.

– Periodical fireside inspections to avoid flame impingement. A proper burner alignment helps in reducing heat flux at critical locations.

Prevention of acidic contamination is as important as are measures for minimizing deposit buildup. For preventing acidic contamination, the following actions are advised:

– Use of the state-of-the-art instrumentation and minimum key level of instruments as specified in the IAPWS guidance document [1] for detection of minor and major condenser leaks and a consistent approach for their elimination

– Structural upgrade of the condenser to eliminate major condenser leaks (replacement of affected tubes, measures to avoid condenser tube vibrations, etc.). As a rule, alarms in control room and precise authoritative instructions how to proceed in the case of a major condenser leak are advantageous.

– Prevention of upsets in water treatment plants as makeup water systems and condensate polishers. All monitoring and alarm systems in these plants have to be checked for reliability at regular intervals.

REFERENCES

[1] *Instrumentation for Monitoring and Control of Cycle Chemistry for Steam-Water Circuits of Fossil-fired and Combined-cycle Power Plants*, **2009**. International Association for Properties of Water and Steam, Technical Guidance Document. Downloadable at http://www.iapws.org/

AKNOWLEDGMENT