

LESSON 5:

Caustic Gouging

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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 given [1]. The following lesson (Lesson 4), which appeared in the February 2010 issue, focused on hydrogen damage, which is the most commonly occurring underdeposit corrosion failure [2]. In this lesson, caustic gouging, the second most important underdeposit corrosion mechanism, will be dealt with.

LOCATIONS OF FAILURES FOR FOSSIL PLANTS AND HRSGS

Caustic gouging – a special type of underdeposit corrosion – may develop only 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 into 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.

In Lesson 4, the locations where excessive deposits form in both the conventional boilers and in HRSGs were discussed [2]. All those locations are the same for caustic gouging.

TYPICAL CHARACTERISTICS OF DAMAGE

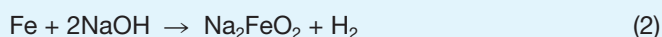
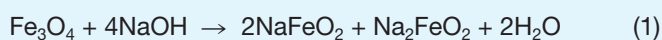
The most important features of caustic gouging are summarized in [Table 1](#).

MECHANISM OF CAUSTIC GOUGING FAILURE

Excessive deposits of feedwater corrosion products in and of themselves are not sufficient for the development of caustic gouging. The second condition is the presence of sodium hydroxide in the boiler water, which concentrates at the base of the deposits next to the tube surface (e.g., by wick boiling).

Underneath deposits, the internal tube temperature and the temperature of the water film on the tube surface increase. The process finally results in high sodium hydroxide concentrations in the boiler water at the tube surface.

The concentrated sodium hydroxide dissolves (fluxes) the protective magnetite layer, Eq. (1), and/or the tube metal, Eq. (2). The products of these reactions are crystals of sodium ferroate and ferroite.



Both of these reactions are fluxing or dissolution mechanisms and as such they do not generate large amounts of hydrogen such as are found with the hydrogen damage mechanism. Thus, there is no gross diffusion of hydrogen through the tube wall and the material degradation mechanism, which is characteristic of hydrogen damage, does not take place with caustic gouging. This important difference in the mechanisms explains why there is no material degradation. This is not to say that if a contami-

Features of failure	<ul style="list-style-type: none"> Gouged areas; thick, adherent deposits. Ductile, thin-edged or pinhole failure. Longitudinal cracks are the typical appearance in HP evaporators of HRSGs since any bulging is restricted by the fins.
Effect on internal oxide and characteristic deposits	<ul style="list-style-type: none"> Sodium hydroxide concentrates at base of deposit and leads to dissolution (fluxing) of protective oxide layer. Deposit usually contains distinctive crystals of Na_2FeO_2 and/or NaFeO_2.
Key microstructural features	<ul style="list-style-type: none"> Material removal only, no microstructural changes in the tube material. No protective magnetite layer.
Root cause	<ul style="list-style-type: none"> Heavy deposits caused by a number of processes and too high a level of NaOH in the boiler water.
Cycle chemistry implications	<ul style="list-style-type: none"> Source of high pH levels (sodium hydroxide) exists. Inadequate instrumentation to identify the actual sodium hydroxide level.
Attack rate	<ul style="list-style-type: none"> Rapid (up to 2 mm per year).

Table 1:
Characteristics of caustic gouging.

nant (chloride) enters the boiler, then hydrogen damage will not occur in the same location. In many cases the mechanisms have been confused in analyses and thus it becomes important to clearly distinguish both the chemistry drivers and the morphology of failure. The final failure is ductile (it is brittle in the case of hydrogen damage) and its appearance is thin-edged or it is a pinhole failure. Intergranular microfissures in the base tube material linking to form cracks and decarburization at the inner surface, both features typical of hydrogen damage, do not develop with caustic gouging. Some spheroidization of pearlite due to localized tube overheating may be observed.

Although the rate of attack is not as high as with hydrogen damage, sodium hydroxide concentration (caustic gouging) can lead to high corrosion rates of up to 2 mm per year.

A typical macroscopic feature of caustic gouging is distinct hemispherical or elliptical depressions on the inside tube surface filled with a thick adherent deposit. Within the layered deposit, needle-shaped crystals of Na_2FeO_2 and/or NaFeO_2 often occur.

POSSIBLE ROOT CAUSES

The most decisive root causes are all those leading to the formation of excessive boiler and HRSG tube deposits and to increased levels of sodium hydroxide in the boiler water. Some of these are briefly listed 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 HRSG, subsequently deposit in waterwalls (conventional boilers) and in the HP evaporator tubing (HRSGs), and form the basis of caustic gouging mechanisms.
- Concentration of sodium hydroxide in boiler water caused by
 - an excessive level of sodium hydroxide under sodium hydroxide treatment
 - an excess addition of sodium hydroxide under all-volatile treatment, e.g., during startup or to overcome acidic contamination
 - too high a level of sodium hydroxide as a pH control chemical under phosphate treatment
- 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 tube sampling) and not removed by chemical cleans in a timely manner
- Ineffective chemical cleans with deposits remaining on critical places
- Ingress of sodium hydroxide from upsets in makeup water treatment units or condensate polishers
- Poor or inadequate instrumentation not meeting the international standard for cycle chemistry instrumentation according to the IAPWS Technical Guidance Document [1], which prevents having adequate cycle chemistry monitoring and control

FEATURES OF FAILURES

Figure 1 is a photograph of a caustic gouging failure showing bulge on the outside of the tube. The internal appearance of the gouge is shown in Figures 2 and 3. This is a typical gouge on the tube inside caused by the flow disruption of the bend.

Figure 3 is a closeup view of the gouge. This is the classic shape of caustic gouging.

Figure 4 shows caustic gouging initiated at a tube to tube weld. The gouging has the typical appearance. Note the dirtiness of the tube internal surface. A view along the inside of a tube with heavy deposits and caustic gouging is presented in Figure 5.



Figure 2:
Internal appearance of gouge.



Figure 3:
Closeup view of gouge from Figure 2.



Figure 1:
Caustic gouging failure.



Figure 4:
Caustic gouging at a weld.



Figure 5:
Heavy deposits and caustic gouging.

As discussed in the section *Mechanism of Caustic Gouging Failure*, sodium ferroate and ferroite crystals are formed by fluxing of the magnetite or the base metal. The appearance of these crystals is one of the most important distinguishing features of caustic gouging. You may see these crystals in [Figure 6](#).

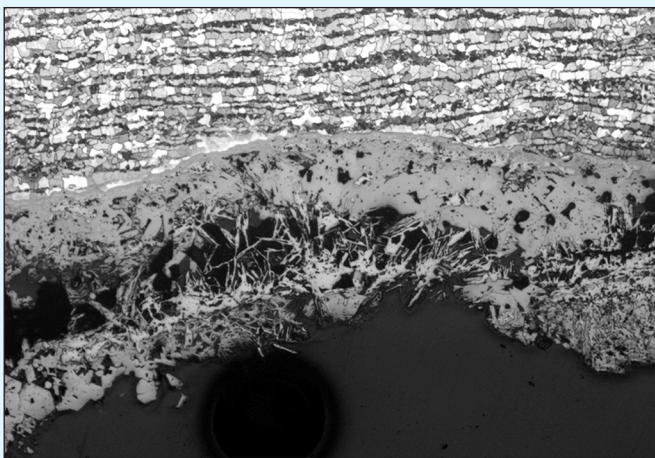


Figure 6:
Typical appearance of caustic gouging. Note the thick deposits and the typical crystals within the corrosion products.

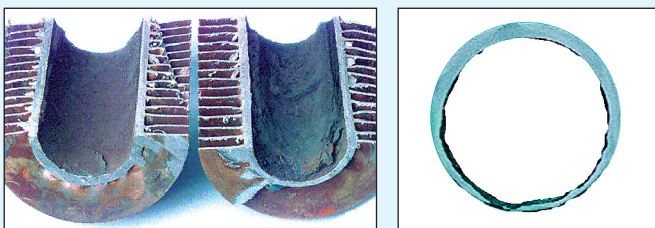


Figure 7:
Caustic gouging resulting from disturbed heat distribution, deposits and a subsequent concentration of caustic [3].

Caustic gouging may also occur in HP evaporators of HRSGs. [Figure 7](#) shows heavy deposits and gouging in a HRSG tube.

POSSIBLE SOLUTIONS

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

As caustic gouging is manifested by tube thinning, ultrasonic testing is a reliable non-destructive evaluation technique to determine the extent of affected tubes in conventional boilers.

Tube sampling in critical boiler or HRSG regions provides information about the type, extent and thickness of deposits.

Immediate Actions

It is very important to identify the source of the sodium hydroxide concentration and to take fast adequate counteractive measures. If the boiler water pH or the sodium hydroxide level is too high, immediate boiler shutdown may be advised. In many cases, a chemical clean might be needed.

In units operated on sodium hydroxide treatment, the level of NaOH addition has to be revised and if needed reduced. High levels of sodium hydroxide in the boiler water can be reduced by increased blowdown. In units operated on all-volatile or phosphate treatment, the excessive additions of sodium hydroxide can be counteracted by increased blowdown. Boiler water treatment specs should be reviewed and optimum treatment control ranges established and applied.

In the case of a serious sodium hydroxide ingress due to an upset in a makeup water plant or condensate polishers, immediate shutdown of the unit, rinsing of the boiler with uncontaminated makeup or condensate, and – in extreme situations – a chemical clean of the boiler might be necessary.

If evaluation of tube thinning has indicated caustic gouging, identification of locations and replacement of all affected tubes to prevent possible ductile failures is necessary. Wall thinning by caustic gouging should never be locally repaired by pad welding or canoe/window welds.

Long-Term Actions

Any long-term actions to prevent caustic gouging have to focus on minimizing deposit buildup and optimizing boiler water chemistry.

Measures to be taken to minimize deposit buildup are the same as those recommended in the case of hydrogen damage:

- Application of an optimum plant cycle chemistry treatment to ensure 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.
- Periodic fireside inspections to avoid flame impingement. A proper burner alignment helps in reducing heat flux at critical locations.

Prevention of excess sodium hydroxide concentrations in the boiler water is as important as the measures for minimizing deposit buildup. To prevent the concentration of sodium hydroxide in the boiler and evaporator water, the following actions are advised:

- Selection and use of optimum boiler water treatment.
- Reliable instruments for boiler water chemistry monitoring

to ensure that any deviations from the normal sodium hydroxide level are detected in sufficient time for immediate taking of counteractive measures.

- Prevention of upsets in 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] Dooley, R. B., Bursik, A., *PowerPlant Chemistry* **2009**, 11(12), 760.
- [2] Dooley, R. B., Bursik, A., *PowerPlant Chemistry* **2010**, 12(2), 122.
- [3] Rziha, M., Wulff, R., *PowerPlant Chemistry* **1999**, 1(1), 3.

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