

LESSON 6:

Acid Phosphate Corrosion

R. Barry Dooley and Albert Bursik

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 mechanism [2], and Lesson 5 (March 2010) dealt with caustic gouging, the second most important underdeposit corrosion mechanism [3]. In this lesson, acid phosphate corrosion will be addressed.

LOCATIONS OF FAILURES FOR FOSSIL PLANTS AND HRSGs

Acid phosphate corrosion can only develop in locations where excessive deposits, mostly of feedwater corrosion products, are formed. In Lesson 4, the locations where excessive deposits form in both conventional boilers and HRSGs were discussed [2]. All these locations are the same for acid phosphate corrosion.

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.

Acid phosphate corrosion occurs in units experiencing phosphate hideout problems and thus the mechanism is most often active in the high pressure boilers and HP HRSG evaporators operating above about 10.3 MPa

(1 500 psi). The most susceptible locations are those where both deposition and concentration of boiler water treatment chemicals (phosphates) occur.

TYPICAL CHARACTERISTICS OF DAMAGE

The most important features of acid phosphate corrosion are summarized in [Table 1](#).

MECHANISM OF ACID PHOSPHATE CORROSION

Damage by acid phosphate corrosion begins with the accumulation of feedwater corrosion products. The combination of the deposits, the local environment with low sodium-to-phosphate molar ratios (lower than 3:1), and thermal-hydraulic concentration processes leads finally to dissolution (fluxing) of the protective magnetite layer on the boiler or HRSG tube. Sodium phosphates exhibit retrograde solubility, i.e., solubility decreases with increasing temperature. This also assists the local concentration processes.

Phosphate hideout itself does not necessarily lead to acid phosphate corrosion. However, it is important to note that both the precipitation (phosphate hideout) and the hydrolysis (phosphate hideout return) are incongruent reactions in which the composition of reaction products differs from that of reactants. In both cases solid reaction products are more acidic (lower sodium-to-phosphate molar ratios) and the dissolved ones more alkaline (higher sodium-to-phosphate molar ratios) [4]. When hideout occurs with phosphate treatments with sodium-to-phosphate molar ratios less than 3 (such as with congruent phosphate treatment) then this is where the acidic hideout compounds interact with the magnetite and in some cases with the actual metal surface: These interactions may occur very rapidly.

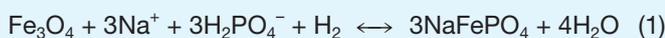
Sodium phosphate hideout in high pressure boilers is caused by reversible reactions between aqueous phosphate and magnetite that result in the formation of the sodium iron phosphate compounds maricite (NaFePO_4) and an iron(III) phase, sodium iron hydroxy phosphate

Features of failure	<ul style="list-style-type: none"> • Gouged areas; thick, adherent deposits. • Ductile, thin-edged or pinhole failure.
Effect on internal oxide and characteristic deposits	<ul style="list-style-type: none"> • Low pH at base of deposits leads to dissolution (fluxing) of protective oxide layer. • Two or three distinct layers, of which the inner layer is NaFePO₄ (maricite).
Key microstructural features	<ul style="list-style-type: none"> • Similar to caustic gouging (no intergranular hydrogen fissures). The innermost deposit layer is composed of maricite. • No protective magnetite layer.
Root cause	<ul style="list-style-type: none"> • Heavy deposits caused by a number of processes and too low pH over hideout return periods. This is typical for the use of phosphate treatments with sodium-to-phosphate molar ratios less than 3, such as congruent phosphate treatment.
Cycle chemistry implications	<ul style="list-style-type: none"> • The local (underneath deposits) sodium-to-phosphate molar ratio is markedly lower than 3, in particular during dissolution of hidden phosphates (hideout return). • During hideout, the bulk sodium-to-phosphate molar ratio increases; in contrast, this ratio decreases underneath deposits. Both an increased blowdown (loss of sodium!) and dosing of acid phosphates to reduce the bulk sodium-to-phosphate molar ratio exacerbate the local problem by forming an acidic environment.
Attack rate	<ul style="list-style-type: none"> • Rapid.

Table 1:
Characteristics of acid phosphate corrosion.

(Na₄Fe(OH)(PO₄)₂ · 1/3NaOH) abbreviated as SIHP. Maricite is always found within the deposits when acid phosphate corrosion has occurred and is the key indicator of the acid phosphate corrosion mechanism. The iron(III) phase SIHP is unstable under ambient conditions in the presence of water, and redissolves in boiler water on cooling [5].

Hideout from boiler water at low sodium-to-phosphate molar ratios (≤ 2.0) causes extensive attack on magnetite to form maricite (NaFePO₄) and hematite (Fe₂O₃), along with the formation of neutral, oxidizing conditions in the local aqueous phase:



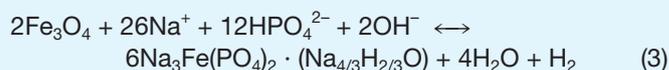
It is the consumption of hydrogen by Reaction (1) that drives the conversion of magnetite to hematite:



This is probably the mechanism for the severe corrosion of carbon steel boiler and HRSG tubes in some stations operated under congruent phosphate chemistry treatment [5–8].

At higher sodium-to-phosphate molar ratios (> 2.8), the formation of sodium iron hydroxy phosphate (SIHP) and hydrogen from the oxidation of magnetite by sodium

phosphate may be the major reaction controlling water chemistry under hideout conditions.



The reaction yields local conditions which are reducing and alkaline and thus does not result in serious corrosion of the boiler or HRSG tube as acid phosphate corrosion does. The reaction may yield beneficial effects which inhibit corrosion and thus compensate for modest reductions in pressure tube thickness if the hideout reaction takes place on the passivating film rather than on loose magnetite deposits [8].

POSSIBLE ROOT CAUSES

Acid phosphate corrosion requires both the formation of deposits and the concentration of acidic phosphates.

Excessive deposits are typically the result of or are encouraged by:

- 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 pres-

sure parts of the HSRG, subsequently deposit in waterwalls (conventional boilers) and in the HP evaporator tubing (HRSGs). These heavy deposits are the locators of the under-deposit corrosion mechanisms and thus of acid phosphate corrosion.

Monitoring of total iron around the cycle may supply information on whether the feedwater treatment applied is optimum or not. In conventional units, the total iron concentration of $< 2 \mu\text{g} \cdot \text{L}^{-1}$ (all-volatile treatment reducing) or around $1 \mu\text{g} \cdot \text{L}^{-1}$ (all-volatile treatment oxidizing) or around $0.5 \mu\text{g} \cdot \text{L}^{-1}$ (oxygenated treatment) is achievable. In combined cycles with HRSGs, operating within the "Rule of 2 and 5" ($< 2 \mu\text{g} \cdot \text{L}^{-1}$ iron in the feedwater and $< 5 \mu\text{g} \cdot \text{L}^{-1}$ in each of the drums) provides some indication of minimum risk for both FAC and under-deposit corrosion [9].

- Flow disruptions to the internal water flow inside the boiler waterwall or HRSG HP evaporator tubing contributing to increased deposition of corrosion products
- Adverse fireside conditions such as high heat flux locations, flame impingement and burner misalignment promoting the deposition processes
- Deposits which are 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

The cause of the concentration of phosphates underneath deposits is very often phosphate hideout. Under congruent phosphate treatment chemistry and/or when disodium and/or monosodium phosphates are added to the boiler or HRSG HP evaporator, the phosphates which hideout have a lower sodium-to-phosphate molar ratio than the bulk boiler water, dissolution of hidden out phosphates (during shutdown or reduction in load) results in pH decrease both in the local environment underneath deposits and in the boiler water. The pH reduction in the endangered locations may intensify acid phosphate corrosion.

Poor or inadequate instrumentation not meeting the international standard for cycle chemistry instrumentation according to the IAPWS Technical Guidance Document [10], which prevents having inadequate cycle chemistry monitoring and control, typically contributes to acid phosphate corrosion-related problems.

FEATURES OF FAILURES

Figures 1–4 show examples of acid phosphate corrosion on conventional boiler tubes.



Figure 1:
Hot side of a boiler tube with a gouge caused by acid phosphate corrosion.

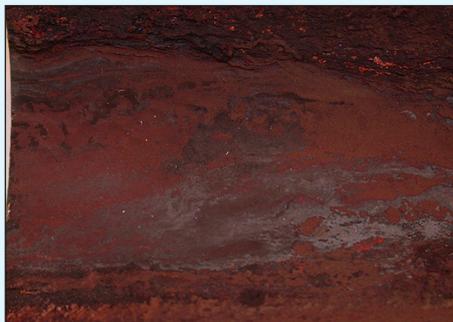


Figure 2:
Hot side of a tube where acid phosphate corrosion is active but has not yet caused a leak as shown in Figure 1.

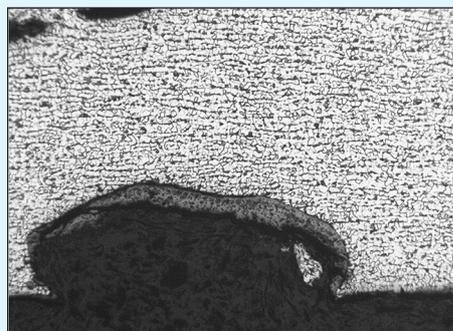


Figure 3:
Tube with acid phosphate corrosion gouge.



Figure 4:
Acid phosphate corrosion gouges in cross section.

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. Acid phosphate corrosion is manifested by tube thinning; ultrasonic testing is a reliable nondestructive evaluation technique to determine the extent of damage in affected tubes in conventional boilers.

Tube sampling in critical boiler or HRSG regions provides information about the type, extent and thickness of deposits [9].

Immediate Actions

- **Immediately stop using monosodium and/or disodium phosphates or mixtures of these for boiler water treatment.** Use either trisodium phosphate plus up to $1 \text{ mg} \cdot \text{L}^{-1}$ sodium hydroxide (NaOH) or trisodium phosphate alone always ensuring that the sodium-to-phosphate molar ratios are greater than 3.
- Establish and apply respective treatment control ranges.
- Take care that a minimum boiler water pH (corrected for ammonia) of 9.0 is maintained to provide a reasonable level of boiler corrosion protection in the event that acid forming contaminant ingress is experienced. This is particularly important when low phosphate levels are used. Note that a minimum phosphate concentration of $0.2 \text{ mg} \cdot \text{L}^{-1}$ or $0.3 \text{ mg} \cdot \text{L}^{-1}$ in seawater cooled units should be detectable. To counteract possible ingress of acidic contamination, some free sodium hydroxide must be present to ensure that the boiler water pH is ≥ 9.0 [7].

If evaluation of tube thinning has indicated dangerous tube conditions, identification of locations and replacement of all affected tubes to prevent possible ductile failures is necessary. Wall thinning should never be locally repaired by pad welding or canoe/window welds because this may increase deposition on the internal surfaces in the region of the repairs.

Long-Term Actions

Any long-term actions to prevent acid phosphate corrosion have to focus on optimizing feedwater treatment, minimizing deposit buildup and optimizing boiler water chemistry. In the event of excessive deposits confirmed by nondestructive evaluation or tube sampling, removal of deposits by way of chemical clean might be necessary.

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

- Application of an optimum feedwater 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.
- Upgrade cycle chemistry instrumentation to the IAPWS fundamental level 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 flame impingement and excessive heat flux at critical locations.

Optimization of phosphate treatment is as important as the measures for minimizing deposit buildup. To prevent the concentration of acidic phosphates underneath deposits, the following actions are advised:

- Use trisodium phosphate plus up to $1 \text{ mg} \cdot \text{L}^{-1}$ sodium hydroxide (NaOH). The only chemicals under the phosphate regime which should be dosed in the boiler water are trisodium phosphate and sodium hydroxide. This will ensure that acid phosphate corrosion will not occur even in cases of severe hideout. [7].
- Alternatively, use sodium phosphate with a sodium-to-phosphate molar ratio of 3:1. This means that the only chemical dosed in the boiler water should be trisodium phosphate. If the boiler suffers from phosphate hideout resulting in an increased sodium-to-phosphate molar ratio in the boiler water, **on no account should chemicals with a lower sodium-to-phosphate molar ratio (disodium and/or monosodium phosphate or mixtures thereof) be applied.** In doing this, the bulk chemistry will appear to be optimized; however, the sodium-to-phosphate molar ratio underneath deposits will be even lower than before. In this way, the optimum conditions for acid phosphate corrosion will be created.
- Ensure that a minimum boiler water pH (corrected for ammonia) of 9.0 is maintained to provide a reasonable level of boiler corrosion protection in the event that acid forming contaminant ingress occurs; with low trisodium phosphate dosing rates some free sodium hydroxide must be present to maintain the pH at or above 9.0 [11]. Minimum phosphate concentration of $0.2 \text{ mg} \cdot \text{L}^{-1}$ or $0.3 \text{ mg} \cdot \text{L}^{-1}$ in seawater cooled units should be always ensured.
- Use reliable instruments for boiler water chemistry monitoring to ensure that any deviations from the normal sodium

and phosphate levels and the pH are detected in sufficient time to immediately take counteractive measures.

- Prevent 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.

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Phone: +41-44-9402300
E-mail: info@waesseri.com

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