

may confirm the acid phosphate corrosion. The presence of sodium ferroate and sodium ferroite via X-ray diffraction may confirm the caustic gouging.

#### Prevention Methods

1. Periodically clean the boiler tubes to reduce the risk of UDC. Avoid the combination of oxygen and moisture when the unit is idle. Carefully dry the unit with the igniters before opening it to the atmosphere.
2. Investigate and prevent the source of contamination in case of thick deposit. Shutdown the unit immediately in case of contamination ingress.
3. Reduce flow disruptions in the tubes. For example, avoid using backing rings during butt welding.
4. Maintain equilibrium phosphate control. Use of mono or di-sodium phosphate should be avoided.
5. Monitor the high heat flux zones.
6. Feedwater chemistry should be under control in terms of caustic levels.
7. Keep the amount of particulate iron oxide as low as possible by blow-down to prevent build-up of thick scales.

#### Bulletin Board

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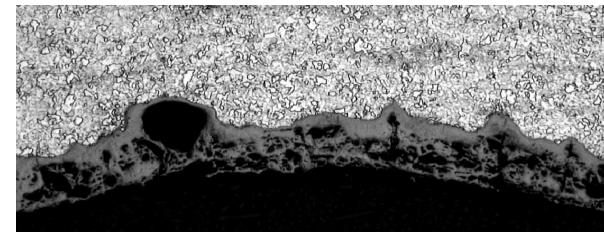
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#### Under-Deposit Corrosion Issues in Boiler Tubes

Water reacts with steel to form iron-oxide on the ID surface of the waterwall, and economizer tubes. Additionally, the particulate iron-oxide that formed elsewhere in the boiler, intentionally added feedwater chemicals, and feedwater corrosion products, will deposit on the tube ID surface. These deposits settle where gravity and flow disruptions (root pass of tube butt welds) are present. Also, the high heat flux zones (the burner elevation) are susceptible to form thick deposits. In water touched tubes, usually the inner thinner layer is dense due to reaction of steel and water as shown in **Fig. 1**, and the outer thicker layer is porous due to deposition of solid particles. Under-deposit corrosion (UDC) is often seen in roof tubes, the bottom of horizontal economizer tubes, and the top of the nose arch where significant deposits collect. Waterwall tubes in the high heat flux zones are also susceptible to UDC. As deposits develop, the tube temperature increases, as the thermal conductivity of the deposit is much less than the steel tube. The net result is higher metal temperatures, thicker deposits, and more rapid corrosion underneath.



**Figure 1.** Thin, dense iron-oxide inner layer and thick porous deposits. 100X

#### Mechanism and Appearance

##### Under-Deposit Corrosion

Deposits form at the ID surface by settling suspended particulate solids, usually iron oxide, and feedwater chemicals collect by boiling within the porous deposit. A localized acidic or basic corrosion environment can form underneath the thick deposits, leading to significant wall wastage. Dissolved oxygen also promotes the wastage rate. Additionally, during shutdowns, water can stay in the horizontal tubes exposed to oxygen from the air, and oxygen corrosion can occur.



# View From The Penthouse

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## Under-Deposit Corrosion Issues in Boiler Tubes

Significant tube wastage occurs underneath the thick deposits as shown in **Fig. 2**, due to UDC.

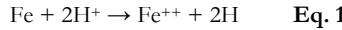


**Figure 2.**  
Tube bulge  
underneath  
the thick  
deposits

The thick deposits cause overheating of the tube resulting in bulges and creep deformation. Thick deposits along with the right corrosion environment may also promote hydrogen damage, acid phosphate corrosion, and caustic attack at the ID surface.

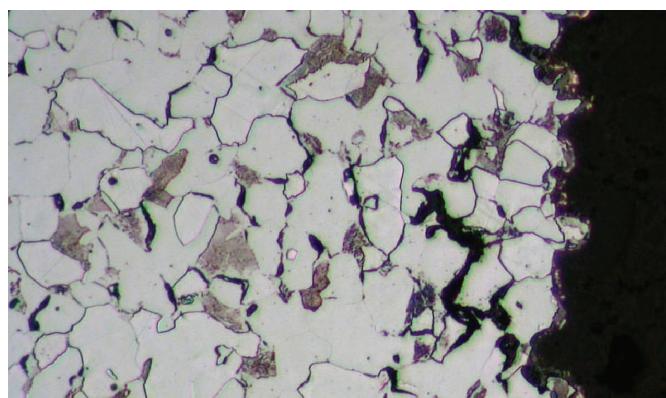
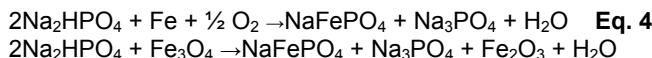
### Hydrogen Damage

Hydrogen damage is the principle mode of waterside UDC. Hydrogen damage rarely occurs with little or no wall thinning, but in most cases, develops with significant wall wastage. Under acidic conditions, the hydrogen ion reacts with steel to form positively charged iron ion, and atomic hydrogen as shown in **Eq. 1**. Hydrogen damage is more prevalent in acidic environments, but it can also occur in strongly basic environments. Under basic conditions, the hydroxide ion reacts with iron to form iron ferroate ion, and atomic hydrogen, as shown in **Eq. 2**. The atomic hydrogen is trapped underneath the deposits and diffuses into the steel along the ferrite grain boundaries. Iron carbide in the steel reacts with diffused hydrogen to form a large molecule of methane as shown in **Eq. 3**. This large methane molecule cannot diffuse through the grain boundaries, so collects there and develops significant pressure leading to grain boundary cracks, **Fig. 3**, and eventually creates a thick-edge, low-ductility failure. Depending on the extent of damage, a complete decarburization may also occur in the microstructure. The end result is a microstructure that contains inter-granular cracks and is decarburized.



### Acid Phosphate Corrosion

Acid phosphate corrosion is the second mode of waterside UDC. Phosphate corrosion occurs where thick deposits are present with the right combination of feedwater chemicals, localized flow disruption, or localized concentrating mechanism. The excessive addition of mono or di-sodium phosphates in the water treatment chemicals leads to phosphate corrosion, as shown in **Eq. 4-6**. The corrosion product will be white or grey marcite ( $\text{NaFePO}_4$ ). The addition of tri-sodium phosphates does not cause acid phosphate corrosion. This corrosion is localized where the phosphate hide-out occurs. The local environment is very acidic underneath the deposits, although the bulk water is within the acceptable limits. The affected area may be gouged with distinctive layers of deposit; the inner layer will be white or grey marcite, and on the outer layer reddish hematite may present. The gouged surface appears very smooth after removal of the deposits. The failure may be a pin-hole leak, **Fig. 4**, thick-edge crack, or ductile overload fracture with no micro structural changes.



**Figure 3.** Hydrogen induced cracks and decarburization in the carbon steel. 400x

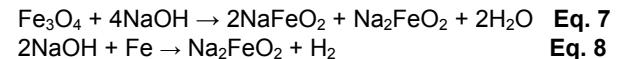
### Caustic Attack

The third form of UDC is caustic attack. Caustic concentrates within the deposit by evaporation of water leaving behind the hydroxide. The wastage occurs between the thick deposit and the steel. A second form is caustic gouging. Under the "right" flow and pH conditions, caustic may concentrate at the edges of steam bubbles formed. An upset of the boiler chemistry with too much sodium hydroxide ( $\text{NaOH}$ ), or localized concentration of hydroxide, increases the tube wastage dramatically. In this case, no deposit exists and the resultant morphology is one of a smooth, rippled, clean ID surface. Caustic removes the



**Figure 4.** Pin-hole failure. 5x

protective iron oxide, and bare steel reacts with  $\text{NaOH}$  to form sodium ferroate ( $\text{NaFeO}_2$ ), or sodium ferroite ( $\text{Na}_2\text{FeO}_2$ ) as shown in **Eq. 7** and **Eq. 8**. The affected surface appears to be smooth and undulating.



### Deposit Analysis

The areas of the boiler where caustic gouging occurs are limited to the high heat flux regions of the furnace. The areas of the boiler where caustic attack occurs are similar to that of hydrogen damage and acid phosphate corrosion. Careful attention towards the appearance of the fracture surface, microstructure evaluation, and chemical analysis via energy dispersive spectroscopy are required to characterize the failure. The microstructure of grain boundary cracks, voids, and decarburization confirms the hydrogen damage. Deposit peaks of sodium and phosphorus, along with a white or grey layer of marcite,