

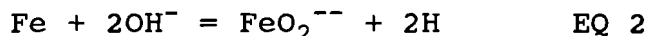
A VIEW FROM THE PENTHOUSE: USEFUL INFORMATION FOR THE WORLD OF BOILERS

HYDROGEN DAMAGE - AGAIN

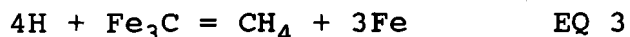
Hydrogen damage and the associated failures are a continuing problem within utility boilers. The conventional wisdom on the damage mechanism may be summarized as: Hydrogen damage occurs in high-pressure boilers, that is, boilers with pressures greater than about 1,000 psi, under thick, usually quite localized deposits, on the water side of the boiler tube. The heavy deposits act as a site for a concentrating mechanism that accentuates the pH condition of the water. Under acidic conditions as the water within the sponge-like deposit is evaporated, the pH drops to very acid levels. The hydrogen ion reacts with steel to form iron ion and hydrogen, as shown in Equation 1.



Under basic conditions, the same concentrating mechanism raises the pH to very high levels, and the hydroxide ion reacts with iron to form the ferroate ion and hydrogen, as shown in Equation 2.



In both cases, one of the corrosion products is atomic hydrogen. The hydrogen is generated at the deposit/steel interface and is trapped between the steel and the scale. Some of the hydrogen then diffuses into the steel where it reacts with iron carbide to form methane and iron, as shown in Equation 3.



Methane is a large molecule and cannot diffuse from the steel and therefore collects at the ferrite grain boundaries. When sufficient methane collects and the pressure becomes great enough, grain-boundary cracks develop that weaken the steel. The microstructure contains both the methane-induced cracks and decarburization that are characteristic of hydrogen-damaged steel. The ultimate proof of hydrogen damage is a metallographic examination that finds these microstructural features.

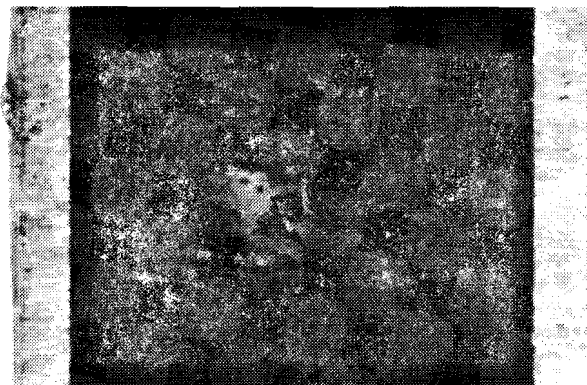


Figure 1.

Hydrogen damage usually occurs under localized and thick water-side deposits. Figure 1 is such an example.

Hydrogen-damaged microstructures always contain intergranular cracking and often substantial decarburization to the point where there may be no pearlite remaining within the structure, see Figure 2. Depending on the age of the damage, the intergranular cracking that is almost always connected to the ID surface will contain (and be filled with) iron oxide as a result of the

reaction of the crack surface with boiler water. This is the same reaction that forms the protective iron-oxide scale throughout the entire boiler.

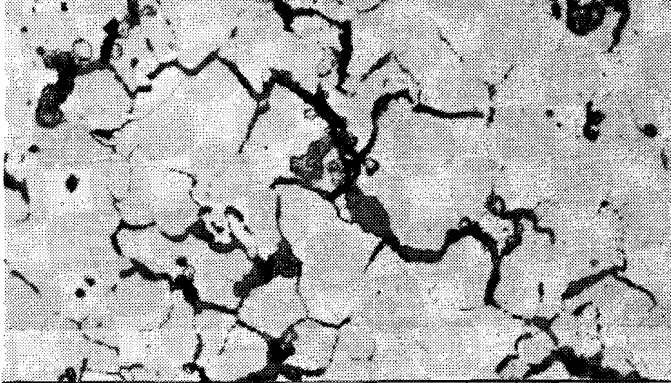


Figure 2.

There are two questions that need to be addressed concerning how the localized but exceedingly thick deposits form when the vast majority of the tube surface is quite clean, and the fact that hydrogen damage failures may occur long after corrective action has been taken to prevent hydrogen damage.

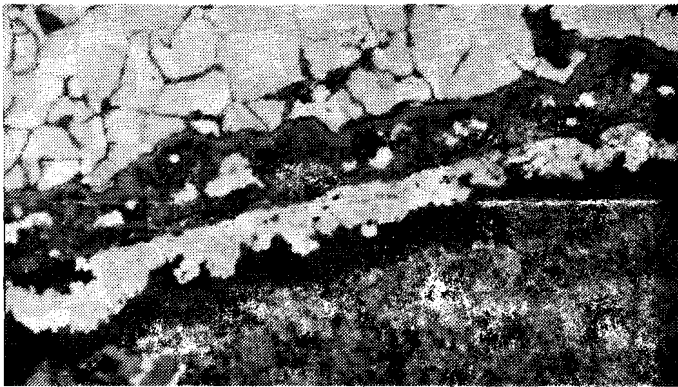


Figure 3.

One possible explanation for the initiation of scab-like, localized deposits is the incomplete removal of both copper and oxide deposits during chemical cleaning. Figure 3 shows an ID deposit with several alternating layers of copper and oxide. In order to remove both oxides and copper, a two-stage chemical cleaning is required, one stage to remove the iron oxide and a second stage to remove the copper. However, if there are multiple layers of copper, then this two-stage cleaning cycle needs to be repeated. Once a deposit has formed, and the chemical cleaning has not totally removed the entire deposit, the scab-like final deposit has a start. Subsequent chemical cleanings do not have time to remove a still thicker deposit.

There are examples of deposit analyses associated with hydrogen-damage failures that include both copper and zinc long (more than 10 years) after brass alloys have been removed from both the condenser and low-pressure feedwater heaters. Thus the copper-zinc corrosion debris had been incompletely removed during subsequent chemical cleanings and remained in the deposit. In one case, the unit had been chemically cleaned twice since the removal of all copper alloys.

In light of these delayed failures, a more thorough chemical cleaning may be necessary to completely remove all of the localized water-side deposits. To assure complete cleaning, a borescopic examination or sample removal for visual inspection may be necessary. In the final analysis, hydrogen-damaged tubes may have to be completely replaced; as there is no known method for repair of hydrogen-damaged tubes except to replace them.

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