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

HYDROGEN DAMAGE

Hydrogen damage has been a plague on the boiler house for several decades. There is now considerable information and understanding of how to prevent it. However the problem still occurs and the ailment usually appears abruptly with the first tube failure. It is more common in older boilers that have been chemically cleaned several times but new boilers are not immune. Indeed, in at least one case hydrogen damage was observed in a boiler within six months of first commercial start-up.

Hydrogen damage is confined to the steam generating tubes, often in the highest heat release zones of the furnace. It is also usually associated with heavy, thick scale deposits on the inside of the tube. Corrosion of the boiler tubes proceeds under these deposits liberating atomic hydrogen. Two scenarios explain the formation of hydrogen:

1. Under thick, porous scales the water is turned to steam which in turn concentrates the hydroxide present in the boiler water. As the pH increases, the corrosion rate of steel also increases. The reaction of hydroxide with steel forms the ferroate ion and hydrogen, thus:

$$2OH^- + Fe = FeO_2^= + 2H$$

2. Under acidic conditions hydrogen ion reacts with steel to form ferrous iron ions and hydrogen

$$2H^+ + Fe = Fe^{++} + 2H$$

Low pH conditions can arise from a poor chemical cleaning. Acid is left behind, saturating the porous internal deposits that are not removed by the cleaning operation. Incomplete neutralization of the acids used leave the deposits in an acidic state. Rapid corrosion and release of hydrogen follows when the unit is restarted. This will explain the often spotty, random nature of the areas within the boiler that often characterize the hydrogen damage.

In either case the atomic hydrogen is trapped between the tube surface and the scale. Some of the nascent or atomic hydrogen enters the steel, reacts with the iron carbide in the steel, and forms methane:

$$4H + Fe_3C = Fe + CH_4$$

Atomic hydrogen is a small atom and can easily diffuse through the steel; methane is a large molecule and cannot diffuse through the steel. Methane collects at grain boundaries and forms cracks as the pressure increases. Under a microscope the structure of hydrogen-damaged steel shows numerous fine cracks or fissures and a loss of carbon, see Fig. 1.

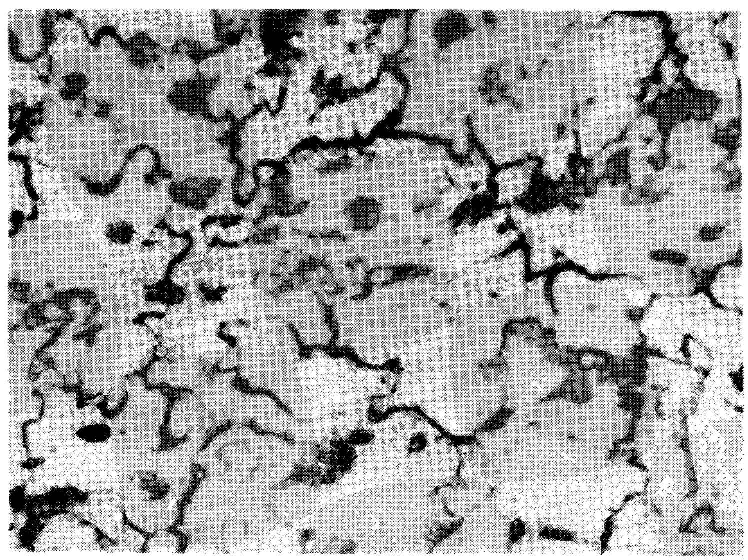

Figure 1

In extreme cases the carbide phase is completely consumed and only ferrite and grain boundary cracks remain. On a macroscale, the steel tube loses both strength and ductility. Failures are characterized by thick edged, blunt appearing fractures. Often a window is blown out of the tube. The ID surface is rough, wasted, and reflects the corrosion that has occurred. At the moment of rupture, any remaining scale is blown out leaving the fracture area relatively clean and deposit-free. Usually the first sign that a boiler suffers from hydrogen damage is, indeed, a failure. There is, however, no such thing as a little hydrogen damage.

There are several ways to survey a boiler for hydrogen damage. First, however, it is desirable to study a failed tube carefully over a length of 20 feet or so, 10-12 feet either side of the failure. The sample is cut open along the membrane so the fire side of the ID of the tube may be viewed over its entire length. All too frequently the thick internal deposits that indicate potential hydrogen damage are spots no loarger than a silver dollar, spaced several inches to a few feet apart. With the 20 foot section as a guide, wall thickness measurements are taken and the existence of hydrogen damage confirmed by microstructural examination. With the expected morphology of hydrogen damage for the particular boiler established, and the expected wall thickness measured at the regions of hydrogen damage, the boiler can be surveyed for the extent of damage.

UT thickness guages may be used and are usually the most convenient tool. The crown wall thickness of each 10th or 20th tube must be measured over as long a distance as indicated by the 20 foot test tube. Not a simple or easy task to do! Once the unit has been surveyed and the extent of damage determined, replacement is the only way to fix the boiler. Boroscopic examinations from the ID of the tube may also be performed. Some of the fiber optic devices available today give excellent resolution and aid in finding the most likely locations of hydrogen damage. With the advent of miniature television cameras it is now possible to inspect the internal surfaces of boiler tubes over their whole length from the upper waterwall headers. Suspected locations can then be examined by UT and removed for metallographic confirmation. In general it would be desirable to perform such a TV monitoring after each chemical cleaning to assure complete removal of all internal deposits. Keeping the boiler free from these deposits is the surest way to prevent a return of this plague.

There are two relatively simple tests for hydrogen damage:

1. Cut a ring section 1/2" - 3/4" long from the suspected location. Squeeze the ring section in a vise with the fire side of the tube aligned with the jaws of the vise. This orientation will put the hydrogen-damaged region in tension when squeezed. Since the internal cracks reduce ductility, if hydrogen damage exists the ring will break in a brittle fashion. The casing side of the tube will be unaffected and will merely flatten. No cracks or brittle fracture will occur in the absence of hydrogen damage.

2. Use a similar ring section as described above and place in boiling hydrochloric acid for several minutes. The hydrogen-damaged area will be attacked more rapidly than sound metal. The result will be a fuzzy gray, thinner region where the damaged zone exists.

Upon discovery of hydrogen damage the boiler feed water upsets that cause the corrosion in the first place <u>must</u> be corrected. Leaks in the preboiler circuits, condenser, feedwater heater, etc., need to be fixed. Upgrade the boiler feedwater treatment to assure water of the proper chemistry at all times. Unfortunately, unless these water treatment steps are taken, the hydrogen damage that has been so expensively repaired is likely to return.

The addition of chromium to ferritic steels reduces the tendency to hydrogen damage. Plain carbon steels, similar to SA-210, or SA-178 can be replaced with SA-213 T-11, or T-22. Chromium stabilizes the iron carbide so the reduction to methane by hydrogen does not occur as readily. There is, however, no known method for the repair of already damaged tubing, replacement is the only way. Removal of the deposits and correction of water chemistry will prevent further damage and arrest the process, but not repair these existing defects.

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