DAVID N. FRENCH, INC., METALLURGISTS
ONE LANCASTER ROAD
NORTHBOROUGH, MASSACHUSETTS 01532
(617) 393-3635

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

OXYGEN PITTING

Pitting is a localized attack in which the rate of corrosion is greater in some areas than in others. The pits may be either large and shallow or small and deep. The depth of the pitting is sometimes referred to as the pitting factor, the ratio of the deepest metal penetration to the average metal loss. The most common pitting corrosion is related to excessive oxygen levels in the boiler feed water during operation or air leakage during shutdown periods.

The basic principles of corrosion can be used to explain this type of oxygen attack. Corrosion is an electrochemical process. During corrosion, there is a flow of electrons from one part of the metal surface to another, usually through the metal, but maybe through the water or corroding medium also. Metal loss or wastage occurs at the anode and is called oxidation. In a steel boiler tube, at the anode, iron becomes an iron ion:

$$Fe = Fe^{++} + 2e^{-} \qquad \text{EQ 1}$$

Reduction takes place at the cathode:

$$O_2 + 4e^{-} = 2O^{++} \qquad \text{EQ 2}$$

The electrons supplied at the anode are consumed at the cathode to give the net reaction:

$$2Fe + O_2 = 2FeO \qquad \text{EQ 3}$$

The final result is the formation of a pit or hole at the anode where iron metal becomes iron ions, with the creation of iron oxide as a corrosion product.

The rusting of steel under ambient conditions follows a similar process. However, steel will not rust in the absence of water or moisture. In order for steel to rust, both air (always present in the atmosphere) and water are needed. Remove either one and rusting will stop.

Active rusting or pitting of steel can occur during shutdown periods. Air enters the boiler when stop valves or other closures are opened. Moisture or condensate collects at the bottom of a superheater or reheater pendant, a low point of a sagged horizontal loop in an economiser, or on the inside of waterwall tubes close to the waterwall headers. The most frequent location is in reheaters as most boilers do not have isolation valves for the reheater. The necessary combination of oxygen and moisture is present on the surface of the steel. The thermodynamic driving force for this is a differential aeration cell. The area under the rust scab is low in oxygen and becomes the anode. The edge of the rust blister is high in oxygen concentration and is cathodic. The two anode and cathode reactions proceed as shown in EQ 1 and EQ 2. The final result is the formation of a pit filled with rust, not FeO but a hydrated iron oxide, approximately $FeO.H_2O$. Under each scab is a pit that can and has over several cycles or months led to leaks. Once the boiler is restarted, steam leaks are the result.

Figure 1 shows the ID of a reheater tube that suffers this oxygen attack. The photograph presents the ID surface at the bottom of a pendant style reheater. Two observations: there is a "waterline" which indicates standing water during shutdown, and there are scabs or blisters along the edges of old waterlines. The pit that led to a steam leak is the irregularly shaped hole (white spot) in the center of the tube section. The pitting attack is predominantly at the bottom of the loop, just where there is water present.

Oxygen pitting can also occur on waterwalls. The penetration into the tube wall in such a case is exacerbated by chemical cleaning. Cycling boilers will also see greater pitting damage and in severe cases waterwalls will experience pin hole leaks.

The prevention of oxygen pitting is usually easier said than done. All that is required is to exclude either oxygen (air) or water. One of two general procedures may be used, wet or dry. In the wet procedure, the boiler is completely filled with deaerated condensate at a pH adjusted to 10-10½ with ammonia or cyclohexylamine. An oxygen scavenger similar to hydrazene is also employed. The boiler is pressurized with nitrogen after all vents are closed. In the dry procedure, the condensate is removed and all internal surfaces dried, perhaps by careful firing of the ignitors. The boiler is finally filled with

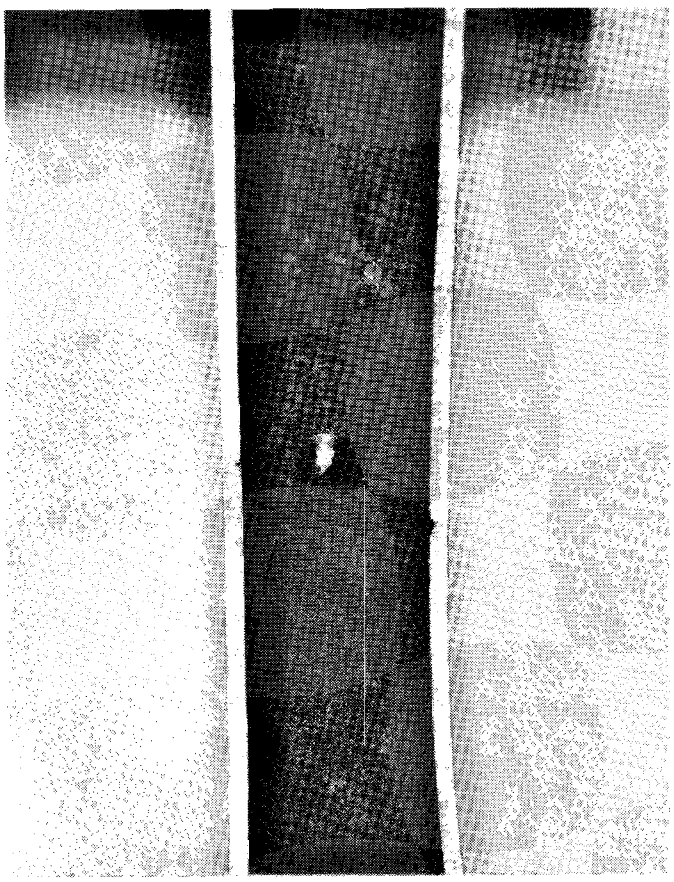

Figure 1

nitrogen under pressure. An alternative to filling the unit with nitrogen is to use desiccants, like silica gel, installed in drums and headers to maintain a moisture-free atmosphere on the water side of the pressure parts.

For units with non-drainable superheaters and reheaters, use of volatile chemicals, ammonia and cyclohexylamine, are recommended. Such chemicals prevent undesirable deposits from forming on the steam side of the pressure parts when the boiler is returned to service.

With this issue of the Newsletter we begin our third year of service to the boiler industry. For those of you who have used our expertise, we thank you. We hope that you have found our advice and counsel beneficial. For those of you who have not yet called, let us remind you of our range of consulting activities. We specialize in solving metallurgical problems in boilers. We provide:

1. Materials failure analysis
2. Materials selection advice
3. Remaining life assessment
4. Stress-rupture testing
5. Chemical analysis
6. Scanning electron microscopy
7. Metallographic analysis
8. Mechanical testing
9. Corrosion analysis and prevention
10. Superheater & reheater problem resolution
11. Materials upgrade recommendations
12. In-house seminars on failure analysis and prevention

We feel that our advantage over other metallurgical laboratories is our intimate knowledge of how boilers operate. Not only do you get expert unbiased metallurgical analysis, but also suggestions on how to prevent further difficulties. Our in-house seminar, "Metallurgical Failures in Boilers" has been used and found useful by nearly a dozen utility groups.

In closing, we hope that you have found our newsletter to be informative. Previous copies are available upon request.

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