

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

Waterside deposits are the result of one of the following mechanisms:

- 1) iron oxide formed by the reaction of water and steel, usually referred to as scale,
- 2) Water impurities improperly or incompletely removed by treatment,
- 3) Water treatment chemicals intentionally added as part of the water conditioning,
- 4) Contaminated condensate, or
- 5) Corrosion products.

The detrimental effects of waterside deposits come about from two factors. Invariably the thermal conductivity of these deposits is substantially less than that of steel. The thermal conductivity of carbon steel, usually used for waterwall construction is around 300 BTU/hr-sq. ft.-°F/in. Most deposits have a thermal conductivity in the range of less than 1 for a very porous silicate scale, to around 25 BTU/hr-sq. ft.-°F/in. The net effect of this insulating barrier on the waterside of the tube is to raise the tube-metal temperature. Excessive scale and/or deposits can thus lead to creep failures within the furnace tubes of a boiler.

The second effect is that porous deposits can concentrate hydroxide (or acid when there is a pH upset) at the deposit/tube interface. This drastic change in pH leads to under-deposit corrosion and/or hydrogen damage. The mechanism of concentration is: The deposits become saturated with water. At the metal/deposit interface, steam is formed as the tube is hotter than the deposit and water. The dissolved solids that were in the water that is now steam are left behind within the deposit. Thus the local concentration can change the pH to very corrosive levels. Under normal pH conditions (8.5-9.5) the concentrated liquid will have a pH in the 12-13 range, strongly basic. When acid enters the boiler during an upset, or left behind after chemical cleaning, the concentrated liquid will have a pH in the 2-3 range, strongly acidic. The result is under-deposit

corrosion, tube wastage, and/or hydrogen damage.

Both effects, creep damage due to scale formation and under-deposit corrosion, can occur in different locations within the same boiler. Depending on the heat flux, the rate of corrosion, the amount of scale, the tube-metal temperature increase, etc., combinations of creep failures and hydrogen damage have been observed in different locations of the same boiler.

1. The most common waterside scale component is iron oxide. Magnetite scales are endemic, as the boiler is built of ferrous alloys; and even pure water will react with steel to form iron oxide. The oxide can be formed in place or formed elsewhere within the boiler and transported to deposit on the high-heat-flux regions of the furnace.

2. Deposits formed from water impurities are associated with calcium or magnesium carbonate, the so-called "hardness salts", silica, and magnesium chloride. Calcium with anions of carbonate, sulfate, chloride, bicarbonate, or silicates will form the insoluble salts: calcium carbonate, calcium sulfate, and calcium silicate. Magnesium with hydroxide, silicates, or phosphates, will also form insoluble salts of magnesium hydroxide, magnesium silicate, and magnesium phosphate. When there are silicates present, there may also be iron, sodium, or aluminum silicates formed. The formation of complex silicates with mixtures of aluminum and sodium cations is also possible. Under rarer and more unusual conditions essentially pure silica deposits will form.

When magnesium chloride intrudes into high-temperature boiler water as a result of a condenser leak, for example, the precipitation of insoluble magnesium hydroxide leads to the formation of hydrochloric acid. Hydrochloric acid will concentrate within porous deposits, as previously mentioned, and lead to rapid acid attack, wall thinning, and hydrogen damage.

3. Water treatment chemicals, in the

presence of calcium and magnesium, will form insoluble calcium phosphate or magnesium phosphate.

4. Waterside deposits that form as the result of contaminated condensate obviously depend on the form of contamination. Under unusual circumstances, oil will contaminate the boiler feedwater which will carbonize on the hotter tube surfaces. Depending on the level of contamination, this leaves a difficult-to-remove, carbonaceous deposit. Further contamination can come from condenser leaks which would inject raw water and/or sea water, depending on the type of water used for condenser cooling.

5. Products of the corrosion of condensers or feedwater heaters will also show up within the waterside deposits. Condensers and feedwater heaters tubed with copper/zinc (brass) or copper/nickel (monel) alloys will lead to zinc, nickel, and metallic copper within the waterside deposits. In fact, detection of copper, zinc, or nickel will often be the first confirmation of corrosion within the condenser or feedwater heater. Soluble iron, as ferrous bicarbonate, on occasion is present in make-up water. Iron in this form may precipitate when either heated or exposed to oxygen. Iron oxides (Fe_2O_3) will precipitate from the ferrous bicarbonate when it reacts with water to form ferrous hydroxide. The liberation of carbon dioxide gas in this reaction can also alter the pH and lead to corrosion.

Table I lists a typical waterside deposit chemistry. Of the elements reported, iron is by far the overwhelming element present, and is present probably as Fe_3O_4 , (perhaps Fe_2O_3).

TABLE I. DEPOSIT ANALYSIS, %

Fe...67.2	Ca....0.79	Mg....0.15
Si....0.98	Mn....0.40	Al....0.29
Na....0.92	Mo....0.02	Ni....1.25
Cr....0.07	Zn....0.15	Cu....2.10
P.....0.47	Ti...<0.01	Sn...<0.01

The nickel, copper and zinc presumably come from feedwater heaters or condenser corrosion. Manganese is present because the boiler steels contain somewhere between 0.4% and 0.8% manganese. It would be expected to be similar to iron in its oxidation behavior. The other elements detected, calcium, silicon, magnesium, aluminum, are likely to be water impurities. Sodium and phosphorus are from pH control compounds, sodium phosphates.

When waterside deposits have reached some thickness whereby the heat transfer is impeded and tube-metal temperatures may rise to dangerous levels, chemical cleaning is recommended. The Atwood and Hale analysis is the most widely used recommendation for determining the need for chemical cleaning. Basically, this technique removes the waterside deposit from the hot or fireside of the tube and measures the amount. At a deposit loading above 40 gms/sq. ft., immediate chemical cleaning is recommended. For deposit loadings between 15 and 40 gms/sq. ft., chemical cleaning is recommended at the next annual outage. For deposit loadings less than 15 gms/sq. ft., no chemical cleaning is needed.

There can be variations in the actual measurements based on the method of removal of these waterside deposits. There can also be substantial variations in the amount of deposits, from the fireside and cold side as well as along the fireside itself. The most severe deposits will be at the highest metal temperatures which are mid-way between the membranes. From a heat-transfer viewpoint a waterside deposit of 2-3 mils thick, can increase tube metal temperatures by 50°-100°F depending on the heat flux. Thus at a deposit thickness of 3 mils at the thickest measured, it is time for chemical cleaning.

Whatever technique is used to remove these deposits, the intent is to return the heat-transfer surfaces to the clean condition and prevent overheating and under-deposit corrosion of the furnace tubes.

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