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

REDUCING CONDITION CORROSION

All fossil fuels contain both hydrogen and carbon in various amounts and compounds. Natural gas is nearly pure methane, CH_4, 75% carbon and 25% hydrogen by weight. Fuel oils usually have less carbon and more hydrogen. Coals are widely different in their composition but all contain carbon and other hydrocarbons. All give off heat energy when burned and all behave in a similar fashion when burned with air in a boiler.

The hydrogen, H_2, component burns first and completely in air or oxygen, O_2, to water vapor, H_2O:

$$2H_2 + O_2 = 2H_2O \qquad \text{EQ 1}$$

and gives off considerable heat energy. The carbon, C, behaves in a different fashion. There are two common oxides of carbon, carbon monoxide, CO, and carbon dioxide, CO_2. Depending on the relative amount of air, (oxygen) one or both of these oxides of carbon will form, thus:

$$2C + O_2 = 2CO \qquad \text{EQ 2}$$

$$C + O_2 = CO_2 \qquad \text{EQ 3}$$

Combinations of hydrogen and carbon in fuel, eg. CH_4, will burn to water vapor and carbon monoxide or carbon dioxide:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \qquad \text{EQ 4}$$

$$2CH_4 + 3O_2 = 2CO + 4H_2O \qquad \text{EQ 5}$$

What is important in EQs 4 and 5 is the ratio of oxygen to methane, 2/1 in EQ 4 and 3/2 in EQ 5. As an aside, with very little oxygen, the carbon won't burn at all and comes out of the flame as soot or carbon black:

$$CH_4 + O_2 = C + 2H_2O \qquad \text{EQ 6}$$

The oxygen-methane ratio here is 1/1. EQ 6 is the basis for the manufacture of carbon black used as a pigment in paints and automobile tires. Unburned carbon gives a candle its light. Carbon particles are heated to a glow by the combustion of the hydrogen in the wax. Prove this for yourself by holding a clean piece of steel or glass well above a burning candle for a few minutes.

Boiler steels develop oxidation and corrosion resistance by the formation of an iron oxide scale in air or oxygen, to wit:

$$4Fe + 3O_2 = 2Fe_2O_3 \qquad \text{EQ 7}$$

Once this oxide forms, the steel below is protected from further oxidation.

There are three oxides of iron, FeO, Fe_2O_3, and Fe_3O_4. The temperature and oxygen concentration will determine which oxide will form when steel is oxidized in a boiler. Conversely, the manufacture of steel from iron ore, mainly Fe_2O_3 plus impurities, starts with the reduction of iron oxide by carbon or carbon monoxide:

$$3C + Fe_2O_3 = 2Fe + 3CO \qquad \text{EQ 8}$$

$$3C + 2Fe_2O_3 = 4Fe + 3CO_2 \qquad \text{EQ 9}$$

or:

$$3CO + Fe_2O_3 = 2Fe + 3CO_2 \qquad \text{EQ 10}$$

When methane is burned with less oxygen than shown in EQ 4 for complete combustion to carbon dioxide and water vapor, conditions are said to be "off stoichiometric" or "reducing". The ratio of CO/CO_2 can be large enough to destroy the protective oxide scale on the external surface of the furnace tubes. "Reducing condition corrosion" is the name given to this attack on the boiler. Figure 1 shows a cross section of a waterwall tube wasted by this mechanism.

What we have discussed is a simple, single fuel system with pure methane as a fuel. Most real situations involve impure fuels that contain measureable amounts of sulfur. Sulfur burns in air to sulfur dioxide and sulfur trioxide:

$$S + O_2 = SO_2 \qquad \text{EQ 11}$$

$$2S + 3O_2 = 2SO_3 \qquad \text{EQ 12}$$

These gases do enough damage alone, but under reducing conditions the sulfur is in the form of hydrogen sulfide, H_2S. When reducing conditions exist along a furnace wall, some of the protective iron oxide scale will be replaced by sulfides.

$$CO + 2H_2S + Fe_2O_3 = 2FeS + 2H_2O + CO_2 \qquad \text{EQ 13}$$

Sulfide scales are not as dense, hard, and protective as oxide scales. They are porous, quite fragile, are easily abraded, and come off with ash and slag removal. Corrosion deposits that contain sulfides are clear evidence that "reducing condition corrosion" has occurred. Sulfides are also the easiest compound to detect, by means of a sulfur print.

The appearance of this form of corrosion will show a rather smooth surface and may have severe wastage, see Figure 1. The wall thickness on the fire side is 0.119" and on the cold side is 0.268". If the corrosion deposits are still intact they will contain sulfides. Stress is not a factor in this morphology. There may or may not be a liquid phase present, see Vol. I, No. 3 of this newsletter.

Another form of "reducing condition corrosion" results in deep, finger-like circumferential penetrations into the tube wall, see Figure 2. There is also the metal loss as the wall thickness has been reduced compared with the cold side of the waterwall tube. The wall thickness, excluding the grooves, is 0.222" while on the cold side it is 0.260". Thus most of the corrosion wastage is confined to the deep grooves. Corrosion deposits also contain sulfides. There is also a liquid phase present, and an axial stress is necessary. Thus, this is a form of corrosion fatigue.

The mechanism requires three conditions: reducing conditions, a variable axial stress, and a liquid phase in the ash deposit. Reducing conditions attack the iron oxide, form sulfides, as has been discussed. The axial stress comes from sharp temperature spikes that follow soot blower action. The liquid within the ash weakens the ash, promotes slag falls, and also causes the temperature spikes. Chordal thermocouple measurements have recorded temperature increases up to 200°F. As the ash reforms the temperature returns to normal until the next soot blower cycle or slag fall occurs.

The temperature increase may crack or craze the oxide film, especially when it is already weakened by the reducing conditions. These cracks from an axial stress are then going to be across or circumferential to the tube surface. With repeated cycles the cracks grow into the tube wall as shown in Figure 2. Invariably the ash deposits contain free carbon from unburned coal and are reducing.

Correction or prevention of "reducing condition corrosion" is easier said than done. Simply assure plenty of air to produce complete combustion to CO_2 with little (a trace) or no CO and carbon free ash deposits. A measurement of excess oxygen in the chimney is not enough. On average everything may be OK but local conditions may be quite different. Burners may be out of alignment, fuel and air may not be properly mixed, staged combustion to reduce NO_x production to meet environmental requirements may lead to a fuel rich condition along some zones of the furnace, etc. All of these factors and more lead to localized reducing conditions, the resultant tube wastage, and finally tube failures.

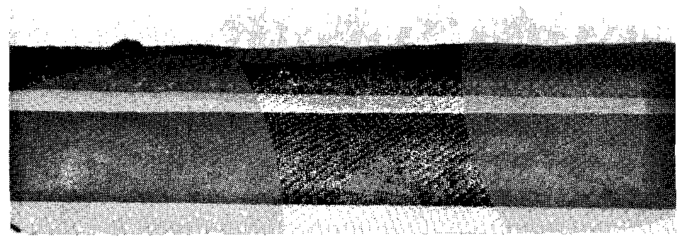

Figure 1. Waterwall wastage, corrosion

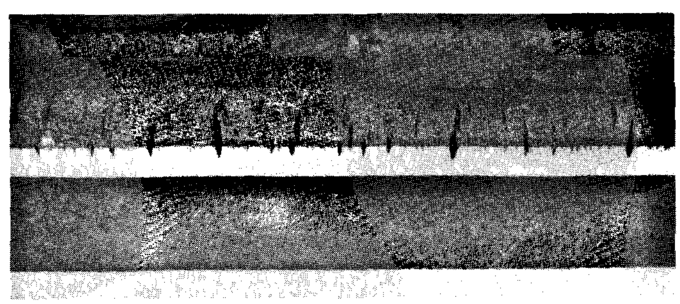

Figure 2. Waterwall wastage, corrosion fatigue
Photo courtesy of Mr. John Alice, GPU, Reading, PA.

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