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DAVID N. FRENCH METALLURGISTS

Corporate Headquarters

2681 Coral Ridge Road

Brooks, KY 40109

Phone: 502.955.9847 Fax: 502.957.5441

www.davidnfrench.com

DAVID N. FRENCH METALLURGISTS

2681 Coral Ridge Road

Brooks, KY 40109

View From the Penthouse

January 2006

First Quarter Topic

Reducing Condition Corrosion

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View From The Penthouse

The DNFM Quarterly Newsletter

DAVID N. FRENCH METALLURGISTS

Ph 502.955.9847 Fax 502.957.5441 www.davidnfrench.com

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 compositions but all contain carbon and other hydrocarbons. All give off heat energy when burned and 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:

$2H_2 + O_2 = 2H_20$ EQ 1

this 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:

$2C + O_2 = 2CO$ EQ 2

$C + O_2 = CO_2$ EQ 3

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

$CH_4 + 2O_2 = CO_2 + 2H_2O$ EQ 4

$2CH_4 + 3O_2 = 2CO + 4H_2O$ EQ 5

What is important in EQ's 4 and 5 is the ratio of oxygen to methane, 2/1 in EQ 4 and 3/2 in EQ 5. When lack oxygen occurs, the carbon won't burn at all and comes out of the flame as soot or carbon black:

$CH_4 + O_2 = C + H_2O$ EQ 6

The oxygen-methane ration here is 1/1. EQ 6 is the basis for manufacturing 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 combustion of the hydrogen in the wax. Prove it to yourself by holding a clean piece or glass or steel well above the 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:

$4Fe + 3O_2 = 2Fe_2O_3$ EQ 7

Once this oxide forms, the steel underneath 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 manufacturing of steel from iron ore, mainly Fe_2O_3 plus impurities, starts with the reduction of iron oxide by carbon or carbon monoxide:

$3C + Fe_2O_3 = 2Fe + 3CO$ EQ 8

$3C + 2Fe_2O_3 = 4Fe + 3CO_2$ EQ 9 or:

$3CO + Fe_2O3 = 2Fe + 3CO_2$ EQ 10

When methane is burned with inadequate oxygen in EQ 4 for complete combustion to carbon dioxide and water vapor, conditions are said to be "off stoichiometric" or "reducing". The ration of CO/CO_2 can be large enough to destroy the protective oxide scale on the external surface of furnace tubes. "Reducing condition corrosion" is the name given to this attack on the boiler.

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

$S + O_2 = SO_2$ EQ 11

$2S + 3O_2 = 2SO_3$ EQ 12

These gases alone do enough damage, 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.

$CO+2H_2S = Fe_2O_3 = 2FeS + 2H_20 + CO_2$ EQ 13

Sulfide scales are not as dense, hard, or protective as oxide scales. They are porous, fragile, and easily abraded, and come off with ash and slag removal. Corrosion deposits that contain sulfides are clear evidence of "reducing condition corrosion" has occurred. Sulfides are also the easiest compound to detect, since they leave 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 fireside is 0.191" and on the cold side is 0.286" two years after low NOx burners were installed. 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.

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 to the cold side of the water wall tube. The wall thickness, excluding the grooves, is 0.149" while on the cold side it is 0.269". 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 necessary. Thus, this is a form of corrosion fatigue.

"Reducing Condition Corrosion" has three condition requirements: reducing conditions, variable axial stress, and liquid phase in the ash deposit. Reducing conditions attack the iron oxide, and 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, promoting slag falls, and also causes temperature spikes. Chordal thermocouple measurement records show 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 found going 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. Adequate air to produce complete combustion of the CO_2 with little (a trace) or no CO and carbon free ash deposits, is required, excess oxygen in the flue is not enough. On average, everything may look like an oxidizing atmosphere, but local conditions can be quite different. Burners may be out of alignment, fuel and air may not be properly mixed, staged combustion to reduce NOx 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, resultant tube wastage, and finally tube failures.

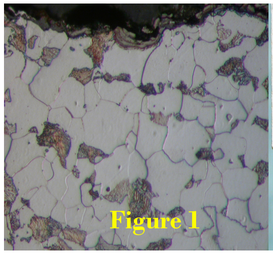

Figure 1

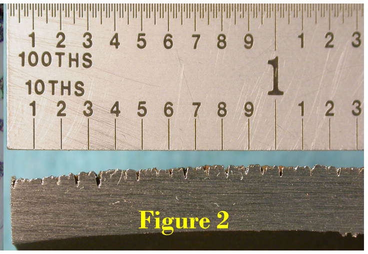

Figure 2

Topic Ideas ? Please email inquiries@davidnfrench.com