Corrosion, Slag and Fouling Challenges for Boilers Burning Biomass Fuels

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Abstract

Burning biomass fuel presents a more challenging environment than burning fossil fuels. The relatively low BTU content, high moisture/volatiles content and higher alkali earth metals content create additional challenges not normally seen when burning fossil fuels such as coal. Even though the ash content in biomass is less than the coal, the lower BTU and higher moisture content means that more fuel needs to be consumed to create the same amount of energy. The volatiles content also creates a more difficult combustion process. Biomass fuel inherently contains higher alkali earth metals, in particular potassium. All of these issues contribute to a much higher slag and fouling environment.

The challenge of burning biomass is further complicated when high chloride content creates a situation where the slag and fouling ultimately results in a much higher rate of chloride induced corrosion. This presentation includes a discussion of specifics associated with burning biomass fuels and mitigating chemical technologies that will help improve efficiency, thus reducing high corrosion rates.

Background

Fuel Tech has gained significant experience in slag/fouling and corrosion control by treating several different types of biomass burning facilities. For example, it has been known for many years now that Waste to Energy (WTE) facilities have dealt with the vexing problem of chloride induced corrosion. Experience with treating facilities burning municipal solid waste (MSW) lends itself to the appreciation for how aggressive chloride induced corrosion can be at the specific temperature and/or conditions. It has also led itself not only to the understanding of the corrosion mechanism, but also intellectual property on how to interrupt the chloride induced corrosion cycle. (Refer to US patent # 7,845,292 B2 entitled *Process for Slag and Corrosion Control in Boilers.*)

Industrial Power Plants burning poultry litter mixed with agricultural products has also help reveal some of the nuances regarding high slag/fouling rates if left untreated. Other Industrial Power Plants burning biomass fuel that are cogenerating steam and power also helped in understanding the mechanism behind severe slag/fouling/corrosion due to biomass fuel. Once this mechanism was understood the treatment program for controlling slag/fouling and ultimately interrupting the corrosion cycle became ever clearer.

Finally, the Industrial Power Plants that use olive pit residue, wood waste, hog fuel and processed nut residue, often times in some combination co-firing with fuel oil helped define the complexity and variation of the fuel that is being fired. The one thing for certain, regarding biomass fuel, is that it will change, often times on a day-to-day basis.

In year 2013, 777 MW of biomass capacity came online in the US.[1] This additional capacity includes new operators to the biomass industry that may or may not have an appreciation for some of the unique difficulties that lie ahead. Many of these biomass units have been converted from burning coal to burning 100% biomass, which exacerbates the slag/fouling and corrosion issues.

Measuring and Analyzing Corrosion Rate

One of the biggest challenges in this industry was the development of a reliable method of determining the effect of corrosion rate changes in a relatively short period of time. There are currently no "real time" methods of measuring corrosion rate. Corrosion measurement (wall thickness) of heat transfer surfaces in biomass units have been limited to periodic Ultrasonic Testing (UT) measurements during outages which may be as much as a year apart or highly sophisticated (expensive) instruments to measure the corrosivity of the flue gas. Fuel Tech developed

a proprietary method of on-line measurement system that includes exposure of a constant temperature metal sample, called a coupon, which could be removed on-line and subjected to UT measurements as frequently as weekly. The coupon is attached to a probe that is made of highly corrosion resistant material (usually hastelloy) and air-cooled. A drawing of the first generation prototype used for this test is shown in Figure 1. The items identified are essentially the same for the current redesigned corrosion measuring system.

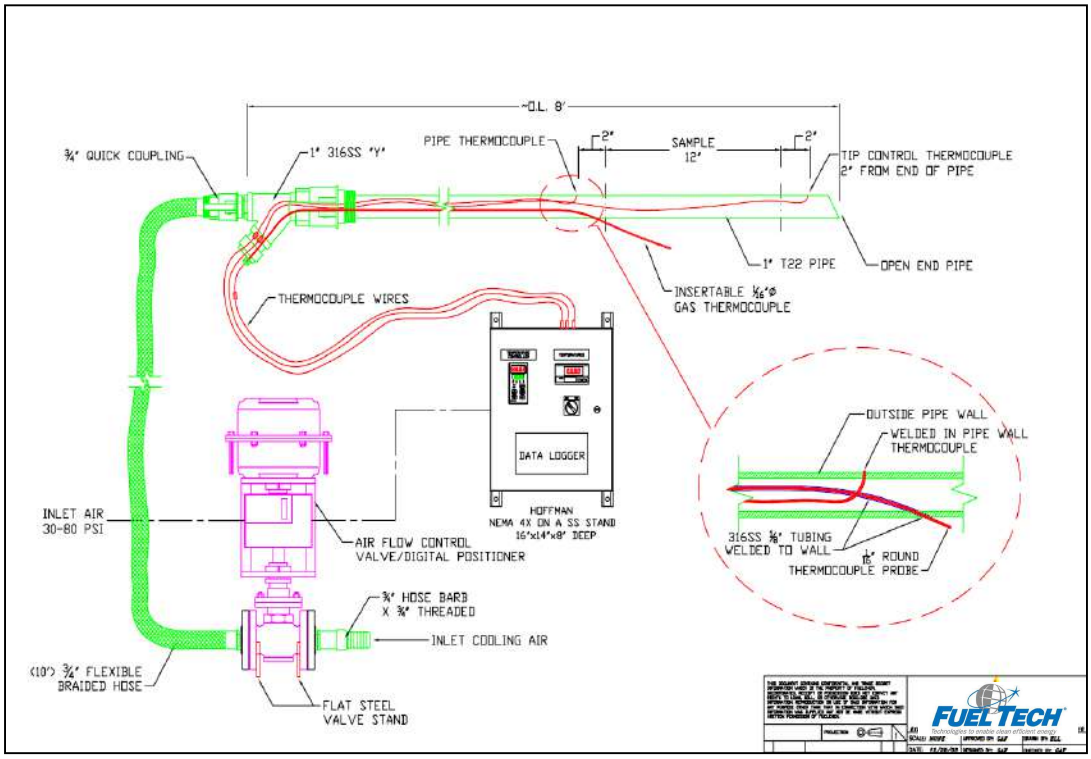

Figure 1. Corrosion Rate Measurement System, Original Design with First Generation Probe

The major elements of the Corrosion Rate Measurement System shown in Figure 1 consists of:

1. Air Flow Control Valve
2. Control Panel and Data Collector
3. Probe with Coupon

In pursuit of continual improvement the Corrosion Rate Measurement System has gone through several minimal design reviews and incorporated improvements. The coupon is only six inches in length. (Figure 2)

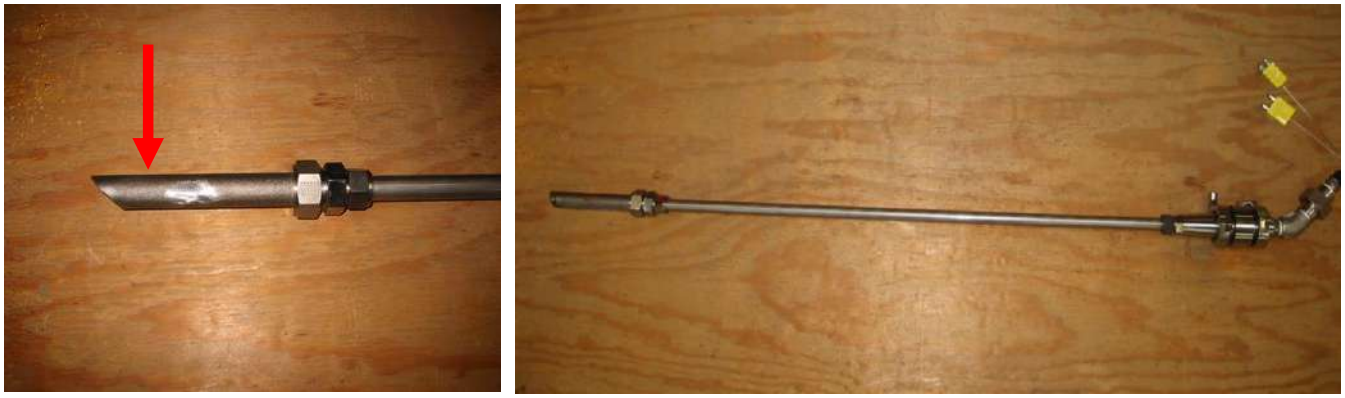

Figure 2. Probe with six-inch coupon attached, the red arrow indicates direction of the gas flow.

The purpose of the Corrosion Rate Measurement System is to duplicate the same environment, as much as possible, as the heat transfer surfaces in question. Therefore, the coupon material is the same as the heat transfer surfaces in question and the temperature is held at close to the same level as the skin temperature of the tube surface. Previous experience confirmed the criticality of temperature as it relates to corrosion rate.

"*The results showed no correlation between Cl content and rate of corrosion, but showed a correlation between the rate of corrosion and the metal temperature used."*[2]

In short, concerning chloride induced corrosion, it should be noted that temperature "trumps" concentration. Therefore the corrosion control probe is air cooled to ensure that a constant coupon temperature is maintained. This is particularly important when comparing the difference between the baseline run and the treatment phase to determine the relative corrosion rates.

The corrosion control panel and air valve (Figure 3) not only modulates the temperature, it contains a data logger that records the temperature. The second generation data logger is wireless and can be accessed remotely at any time.

Figure 3. Corrosion Control Panel and Air Valve

Analyzing the Corrosion Coupon Slag Deposit

There are several key aspects that are necessary to properly analyze the corrosion coupons. First off the deposit that forms on the coupon, in theory, should be very representative of what the deposition is that is forming on the heat transfer surfaces in question. Same material, same skin temperature and co-located as near as possible to the heat transfer surface in question is the thought process for duplicating the environment. Normal techniques are sufficient for "characterizing" the slag deposit.

Figure 4. Corrosion Probe with Coupon and Slag Deposition.

Elemental analysis involves X-ray fluorescence (XRF) and Energy Dispersive X-ray Spectroscopy (EDS). In lieu of XRF and EDS, Laser Induced Breakdown Spectroscopy (LIBS) has been used as well. Qualitative Analysis for compounds involves X-ray Diffraction (XRD). In Figure 4 the deposition was too friable to do a layered approach analysis, however, if possible a layered approach does provide the most information.

In Figure 5 the treatment phase involved a TIFI® Targeted In-Furnace Injection™ program. The baseline percent concentrations for Cl, K, KCl and NaCl went down significantly during the treatment phase. These are key elements and compounds involved in chloride-induced corrosion, indicating that the corrosion rate has decreased. Corroborating data is also indicated by the increase in Fe_3O_4 which is the reduced state of Fe_2O_3. The mechanism for chloride-induced corrosion is well understood and it is a corrosion cycle. During the corrosion cycle the Fe_3O_4 oxides to become Fe_2O_3. In the most severe cases of corrosion the metal surface has a spalling or peeling effect. (Refer to figure 6)

TABLE 1
ESTIMATED WEIGHT CONCENTRATIONS (%)
WITHIN 1-2µm EDS ANALYZED LAYER

SAMPLE	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn
treated	0.39	26.34	6.50	1.00	1.82	1.37	0.30	2.62	19.98	4.62	16.26	0.26	1.74	0.43	12.14	2.90	0.23	1.10
untreated	0.35	21.68	12.00	0.72	1.23	0.80	0.26	2.40	31.14	7.76	10.23	0.18	0.76	0.02	7.76	1.03	0.05	1.63

TABLE 2
XRD MATCHES
Approximate % MATCH

SAMPLE	Anhydrite ($CaSO_4$)	Sylvite (KCl)	Halite (NaCl)	Quartz (SiO_2)	Magnetite (Fe_3O_4)	Calcium Aluminum Chloride Silicate ($Ca_3Al_2(SiO_4)_3$)
treated	38.22	19.31	19.31	1.93	15.44	5.79
untreated	26.25	29.92	34.67	0.74	4.95	3.47

Figure 5. Corrosion EDS and XRD Results

Note how the surface of the metal appears to be peeling. This phenomenon is due to the cyclical nature of chloride-induced corrosion.

Figure 6. Severe chloride induced corrosion

Measuring the Corrosion Coupon Wall Thickness

The bottom line for determining a relative corrosion rate between baseline and treatment phases is determined by measuring the coupon wall thickness. Since corrosion and erosion work synergistically to create wear pattern, it is usually aspect dependent. For example the airflow may be biased to one side of the heat transfer tube or the other, which then creates a bias in the wear pattern. Or the leading edge may wear faster, however ironically the trailing edge may even be the area with the faster wear rate. This is due to the airflow creating a reducing condition that forms behind the heat transfer tube. When this happens slag deposition increases due to the fact that the ash fusion temperature in reducing conditions can be significantly lower than in oxidizing conditions.

In Figure 7 the treated and baseline coupons were exposed for 21 days and then eight wall thickness measurements taken starting at the leading edge and every 45° clockwise thereafter. Figure 8 shows the original unused coupon measurements, the baseline measurements and the treated coupon measurements. The red arrow indicates gas flow. Note that the unused coupon (Green) measured fairly consistently at .202". The baseline coupon (red) was aspect dependent on its left side. The treated coupon (Blue) may have worn a little more on the leading edge, however it was generally none aspect dependent, indicating that the treatment program was effective.

Figure 7. Treated – Baseline – Unused Coupons

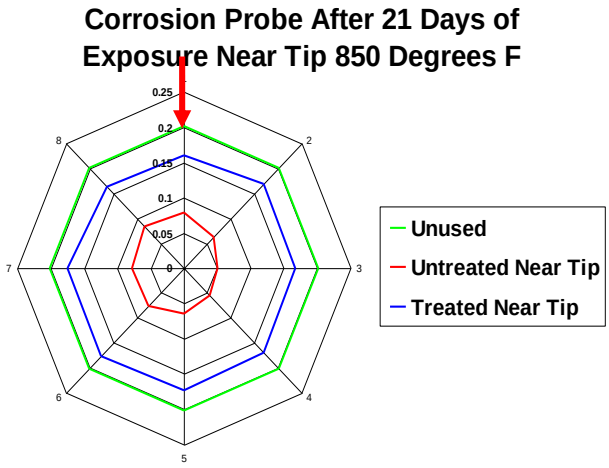

Figure 8. Wall Thickness Measurements

Using a Layered Approach for Analyzing Slag Deposition

One of the most revealing techniques for analyzing slag deposition is employing a layered approach.

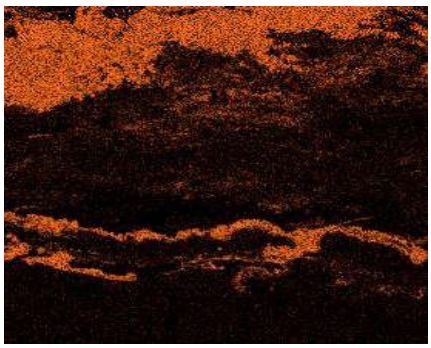

Figure 9. Potassium Color Coded Orange

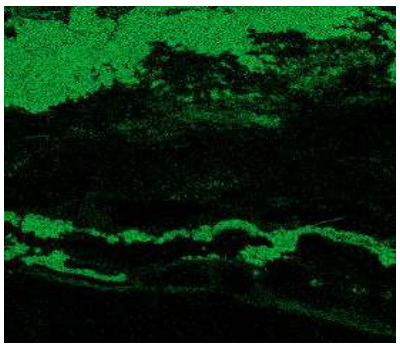

Figure 10. Chloride Color Coded Green

In Figures 9 and 10 the tube surface is at the bottom and both potassium and chloride have been color-coded. Note that the structure looks similar. There is a reason for this.

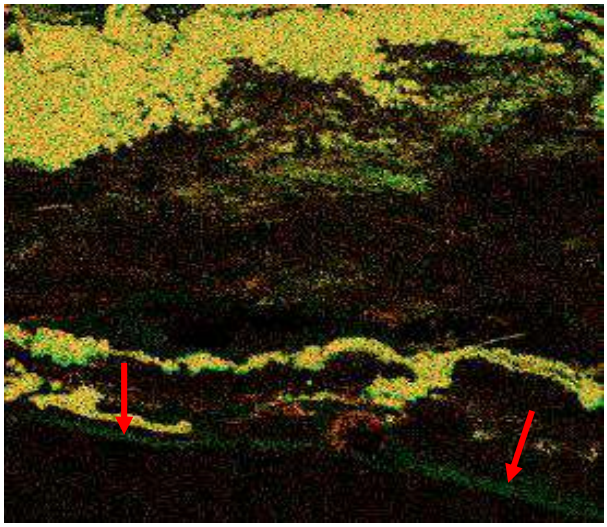

Figure 11. Potassium and chloride combined (KCl)

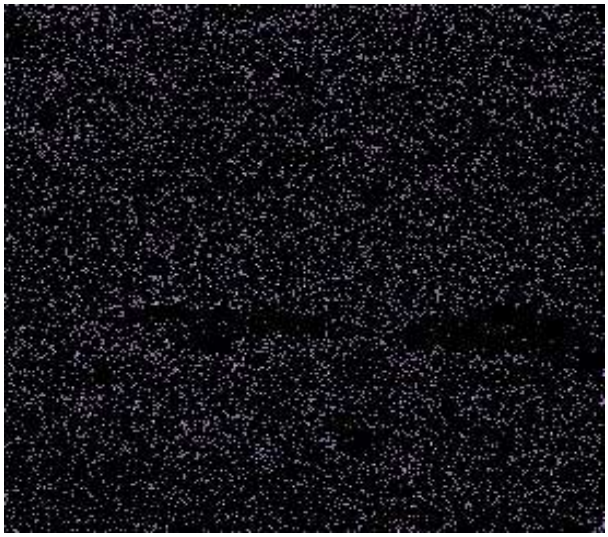

Figure 12. Magnesium Color Coded Purple

The reason why the two structures between potassium and chloride are so similar is that this is the potassium chloride compound that XRD measured. Note that when the two are layered on top of each other the color turns from orange and green to yellow. Under close examination there are streaks of green, where the chloride is no longer combined with the potassium. These green streaks lie right on the metal surface and/or have been observed below the metal surface. There is an explanation for this that will be discussed in the next section.

In Figure 12 the magnesium is color coded purple. Note the pattern that the magnesium has formed is uniform throughout the sample. This is one of the reasons why magnesium, which is one of the elements used in TIFI, is so effective for controlling slag and fouling. By properly controlling slag build up with magnesium the melt point is higher (due to the different eutectic) and the deposits ultimately more friable. Does the magnesium disrupt the chloride corrosion cycle? The evidence indicates that at a minimum it slows down the corrosion rate, and in one case study it appears to have slowed it down to the point that it appears that only erosion was wearing away the metal. (From 80 mils per year to 4 mils per year)

Unique Slag/Fouling and Corrosion Environment for Biomass Burning Industry

Burning biomass as an energy source has its unique set of issues, especially for units that were initially designed to burn coal. Interestingly enough the ash fusion temperature for most biomass is extremely high. (>2800°F) One would think that slag and fouling wouldn't be an issue. This could not be further from the truth.

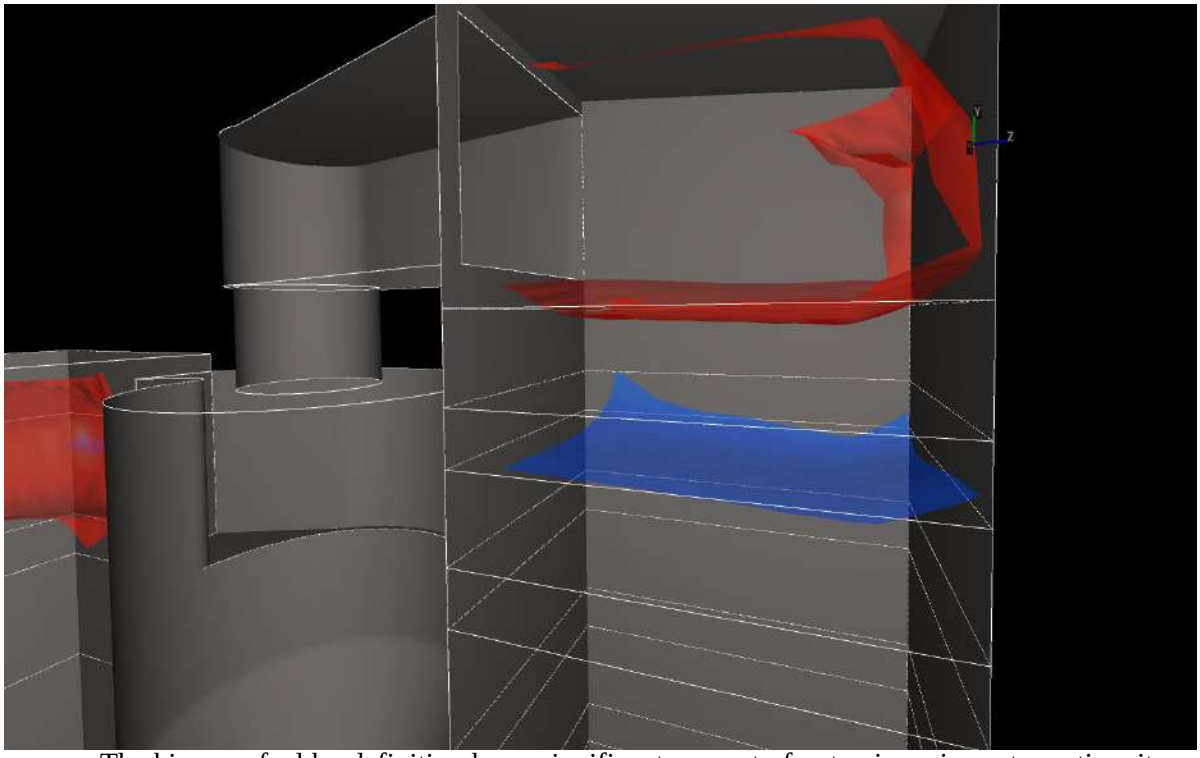

Figure 13. Red is where temperature is 1500°F and blue is where the temperature is 1200°F

The biomass fuel by definition has a significant amount of potassium since at one time it was living. And potassium, like all other alkali earth metals will precipitate out at somewhere between 1500°F and 1200°F (Refer to figure 13) depending on reducing verses oxidizing conditions and the eutectic that has formed with the deposit. Furthermore as previously indicated, in the layered analysis approach, potassium chloride (KCl) is a predominate compound. KCl is the mechanism whereby the chloride anion is deposited on the surface of the slag deposit. There are two electrochemical processes that cause the chloride ions to migrate through the slag toward the heat transfer tube's surface. These processes are electrophoresis and thermophoresis. Together, these two processes cause the Cl ions to migrate at variable speeds (~ 1 cm/hour). The speed increases with temperature (thermophoresis). Once the ions get to the white layer of the slag (this is the molten layer that actually acts as the glue that sticks the slag mass to the tube), the ions concentrate and begin a corrosion cycle that removes metallic iron from the tube. Look back at the green layer of chloride ions that have aligned along the tube surface. This is why chloride induced corrosion is so aggressive and also why when it comes to chloride induced corrosion, temperature trumps concentration.

Summary

In summary, the biomass industry has its own set of unique problems. In case study after case study the problems associated with slag, fouling and corrosion are oftentimes underestimated and/or discovered too late to reverse the damage done to entire banks of heat transfer tube bundles. These problems can be improved significantly by applying a chemical feed program. TCI® Targeted Corrosion Control™ and TIFI® Targeted In-Furnace Injection technology programs are two programs that have been successfully utilized for controlling slag/fouling and corrosion. The corrosion rate measuring system is part of the TCI or TIFI programs that have been adapted in the industry and are currently being utilized to help alleviate chloride induce corrosion.

REFERENCES

1 Federal Energy Regulatory Commission (FERC) Biomass Magazine article dated 31 Jan 2013 by Erin Voegele

2 Effects of Chlorine in Coal on Boiler Superheater/Reheater Corrosion by Chou, Lytle, Kung and Ho