Recent Catalyst Development Results and the Observed Affects on CO, LOI and Slag

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Introduction

This paper discusses recent results gained from testing a catalyst at two different test locations currently burning coal. The design of experiment and test protocol was developed to test the effectiveness of injecting a catalyst formula into the flue gas for controlling:

1. Slag/Fouling
2. Loss on ignition (unburned carbon) -- LOI
3. CO
4. NOx
5. CO_2

The first test location was a boiler located at a major University whose primary function is providing heat for their campus. The second test location was a major coal burning Utility boiler. This paper examines results from primarily the first test location with the main focus on slag/fouling, LOI and CO reduction.

The key technologies necessary for accomplishing the test results will be discussed as well as the sample collection methodology.

Key Technologies

History of Targeted In-Furnace Injection™ TIFI™ Technology

TIFI was originally designed primarily as a slag and fouling control program that involves targeting areas of the radiant and convection sections of a boiler. By targeting the problem areas of the furnace instead of targeting the fuel, performance and cost effectiveness has been significantly improved. By adding a catalyst to the same chemicals designed to control slag/fouling the question is how has performance been further enhanced. Chemicals are mixed with air and water and then injected into the flue gas stream. The areas that are "targeted" are based on Computational Fluid Dynamics (CFD) to ensure maximum coverage where the problem areas are known to exist. This has allowed excellent slag, fouling or SO_3 abatement performance previously thought to be resistant to chemical programs, including utility and other boilers firing coal.

With the chemical being added to the flue gas and "aimed" at either the problem heat transfer surfaces or at chemical reactions (catalytic combustion), greater than 90% of the injected material goes to the problem areas. This causes the additive to react with slag as it is forming and penetrate existing deposits to affect its physical crystal characteristics in areas where this is required. It is also what gives the technology its enhanced combustion performance which is the main thrust of the catalyst test protocol.

The Art of Computational Fluid Dynamics (CFD) Modeling

TIFI technology involves using two different forms of fluid dynamics modeling and a virtual reality engine. Together, these create a running duplicate of a given furnace with injection overlays and dosage maps to predict where the chemical is going and to ensure as close as possible to 100% coverage of the targeted zones.

Process Design Modeling, in effect, involves simulating the operation of a particular furnace in a high performance computer and then testing various “what if” problems and solution scenarios at various power settings. A great deal of detail goes into running this “plug flow” model.

All size and design dimensions, fuel and heat rates, fuel chemistry details, details of air usage and boiler or duct geometry as appropriate are programmed into the model.

The data set output from this model is complex and difficult to visualize. Recent advances with virtual reality visualization techniques, coupled with fluid dynamics modeling, have yielded new insights into how complex dynamic systems behave in real time.

After all of this data is programmed, a temperature and gas velocity gradient is calculated for the entire furnace or duct. In furnace applications, the results generally show small imbalances in heat release and gas flow pattern, which is considered normal. If the variations are excessive, a notation is made in a report indicating that the abnormal condition exists, along with recommendations on how to deal with the situation.

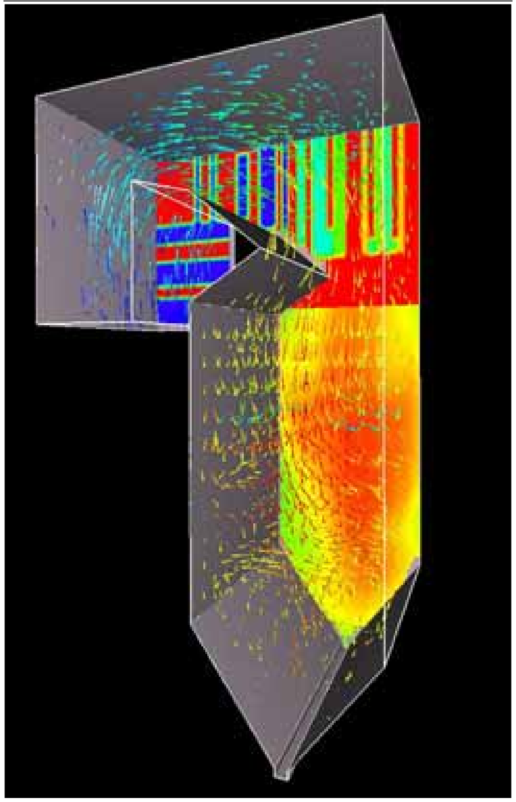

Figure A

Treatment programs can then be designed for the specific boiler or duct application. A customized injection scenario is then built inside the computer and tested under varying program conditions, and results are calculated. For example, complexities that present challenges to operating and maintaining the furnace/convection section can be highlighted and accounted for or minimized through this visualization technique.

Figure A details the gas flow fluid dynamics using flying vector arrows that are coded for velocity (length), temperature (color) and direction.

Understanding is enhanced by looking at one-half real time models running in the virtual reality environment. Eddy currents, dead spots and high gas flow areas are all highlighted and can be avoided or used to carry the chemical to desired areas. This depends on the strategy chosen and the requirements of the program.

The next phase of the model deals with setting up the injectors and their predicted performance within the model. How well the various injector scenarios perform at covering the targeted critical gas path is calculated.

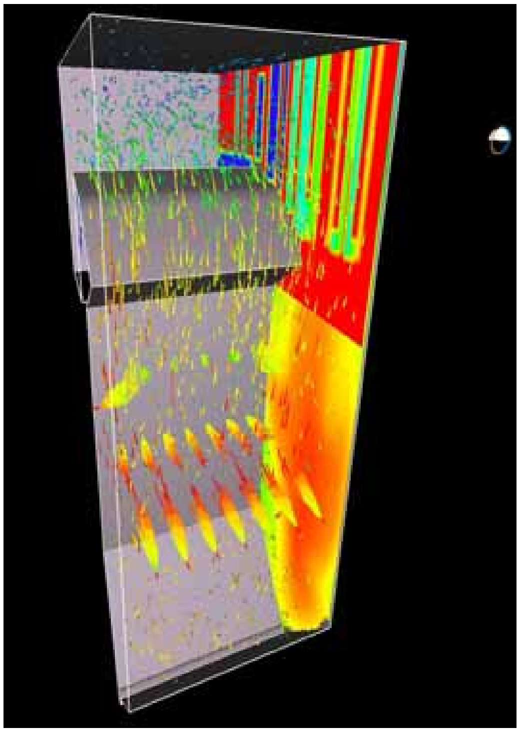

Figure B

Figure B shows how the boiler gas path from the radiant section through the superheaters and the reheaters is targeted for chemical application and the associated injection strategy.

This technology makes it possible to have high chemical activity in several places at the same time. This is thought to be a key point for the catalyst technology that is currently in development.

This process continues until the result is judged satisfactory for solving the problem. A custom feed and control system is engineered and constructed, based on these results.

In this manner, the treatment covers all the areas that need the most attention. The program uses this sophisticated "aiming" ability to ensure that the correct dosage is applied everywhere it is required.

The most common application of TIFI technology utilizes magnesium hydroxide slurry diluted with water and then atomized with air. In this particular application a metallic catalyst is also suspended in with the mixture. This mixture is then sprayed into the furnace at computer-determined ports that allow for complete coverage of the problem areas. In order to understand how this is done, it is necessary to look at the injection process itself.

Injection Technology

The injectors are set up to feed the required air, water and chemical as determined by modeling. The injectors produce a range of droplets that the computer program has calculated and/or taken into account. The smallest droplets evaporate very close to the injection point. The chemical activates, and thus covers the zones nearest the injectors.

Each successively larger set of droplets goes deeper and deeper into the furnace before evaporation is completed and chemical is activated. This provides coverage successively further into the furnace until all the droplets have been evaporated and all chemical has been activated. Furthermore the distance travel and time needed to allow for the catalyst to "collide" with the carbon particles is taken into account. The number of injectors, placement, injector design and performance settings are all critical for this process.

The program overlays all injection calculations on the fluid dynamics model. The result is chemical distribution calculations that merge into a map of how much chemical goes where; i.e., a dosage map of the targeted areas in the furnace. This targeted area can be as small as a dedicated problem heat exchanger or as broad as the furnace water walls, the convection sections and the platen areas combined.

Reagent Chemistry and Catalyst Theory

A metallic catalyst is mixed in with the reagent to form a chemical slurry with high reactive ability owing to its large surface area per unit weight ratio (approximately 530,000 sq.ft. /cu.ft.). This high activity results in better performance at recommended treatment dosages while its high stability eliminates many of the handling and feeding problems associated with unstabilized compounds. The mixture is designed to provide 100 ppm to 200 ppm catalyst at reasonable levels of magnesium hydroxide feed rates.

The levels required for good performance are based on chemical reactions in the combustion gases which allows for the catalyst to attach itself to the carbon particles. The larger carbon particles are then broken down into smaller particles and the combustion process essentially occurs sooner rather than later as a result. Furthermore the $Mg(OH)_2$ is also activating as described in the previous section. By synergistically combining slag/fouling control with more efficient combustion the overall boiler operation becomes more efficient. For example when properly treated, deposition from acid and ash reactions is significantly reduced, allowing the air pre-heater to remain clean and free of corrosive deposits as will be discussed later in this paper. The cooler temperatures further up the boiler also allows for efficiency gains that normally could not be obtained without the chemical treatment. Simply stated the predicted results per the design of experiment are reduced LOI, reduced CO, reduced NOx and reduced CO_2.

The following Figure (C) is a pictorial of the desired catalytic effect. The data to follow demonstrated this phenomenon.

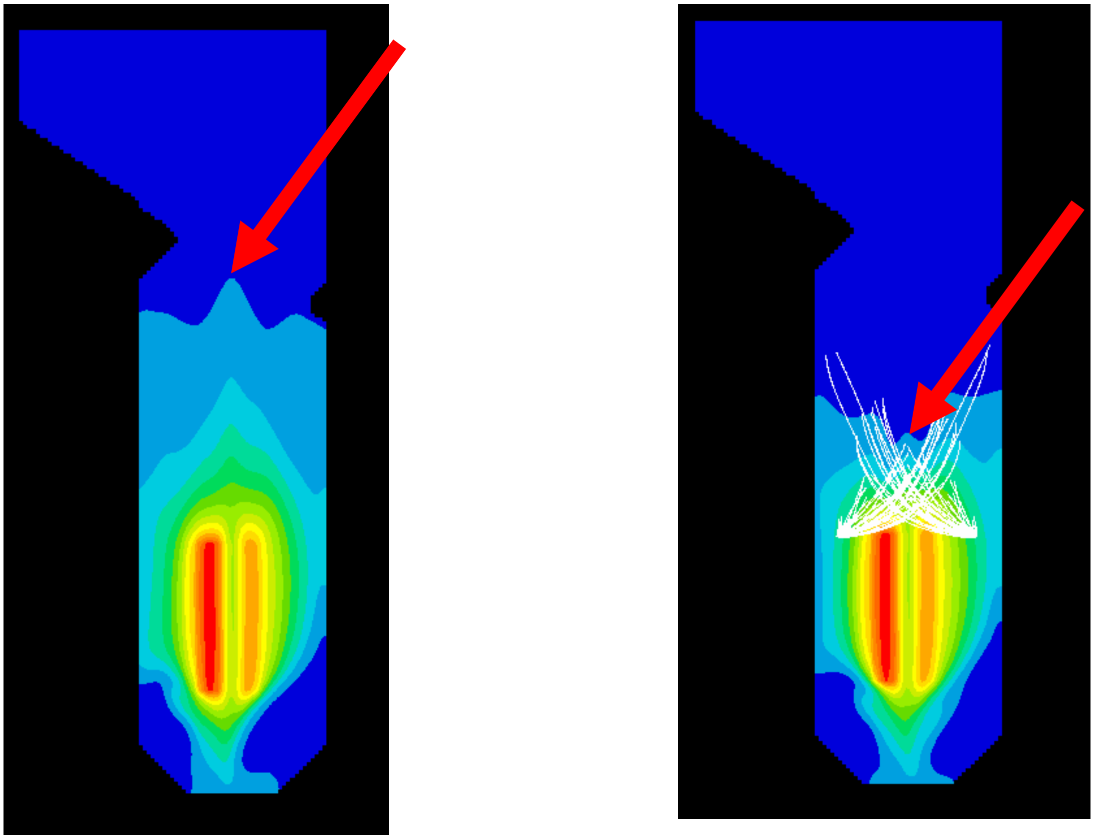

Figure C - Red Arrows indicate where combustion is complete

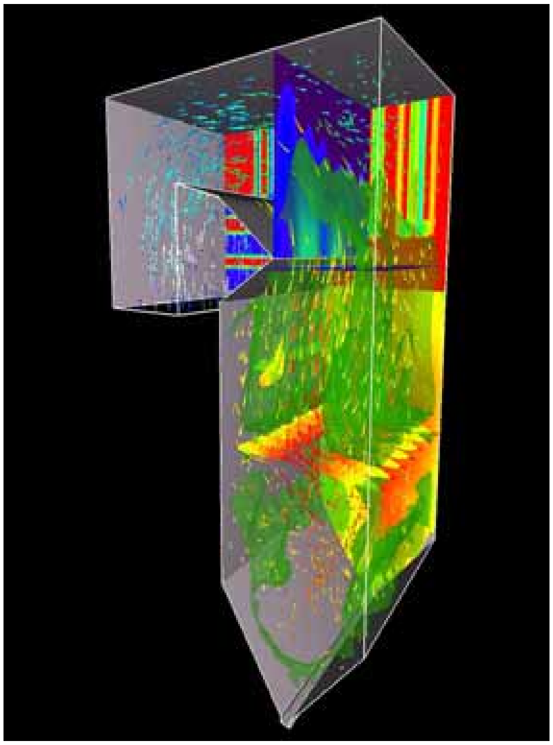

Figure D

The special formulated chemical reagent used was in the form of suspended slurry of 5–8 micron sized particles with an additional 10% by weight metallic catalyst. Atomization takes place in accordance with the model output and the kinetic activity of the catalyst is the key to the more efficient combustion.

Figure D depicts a unique capability for users of this technology. The model can also calculate iso-contours of temperature, such that any spot at a given temperature in the boiler can be visualized and linked to form a surface of the same temperature. In this example, the translucent green shape represents 2,150 degrees Fahrenheit. This, in itself, is not unique. However, when matched to the ash fusion temperature for the fuel being burned in the subject boiler, it becomes an accurate predictor of the slag and fouling front. It essentially shows the operator where the slag and fouling are likely to first show up. Assuming that the catalyst is working properly the cooler operating temperatures enhance the slag/fouling control in these areas.

When targeted with slag controlling chemical injection using the proper catalytic formula, a unique and powerful synergistic technology is formed that can be used to control the slag and fouling to a degree not possible before.

Injection Strategy

At the original test site the boiler was experiencing very high LOI (30% unburned carbon) and CO levels around 200 ppm. After reviewing the CFD model the decision was made to feed the chemical through the existing ports even though these ports were too high in the boiler to be considered ideal. Figures E and F are snapshots of the predicted coverage based on these penetration points. This boiler is relatively small at roughly 25Mw and the temperatures run a little cooler than normal. Data indicated that the temperature at the injection points was around 1500˚ F.

After reviewing different injection scenarios the decision was made to use the strategy indicated in figure E with the strategy indicated in figure F as a back up pending initial results. It should be noted that the color coded coverage was not significantly different between the two scenarios. Light blue indicates adequate coverage, green more than adequate and purple less than ideal coverage, but not necessarily void.

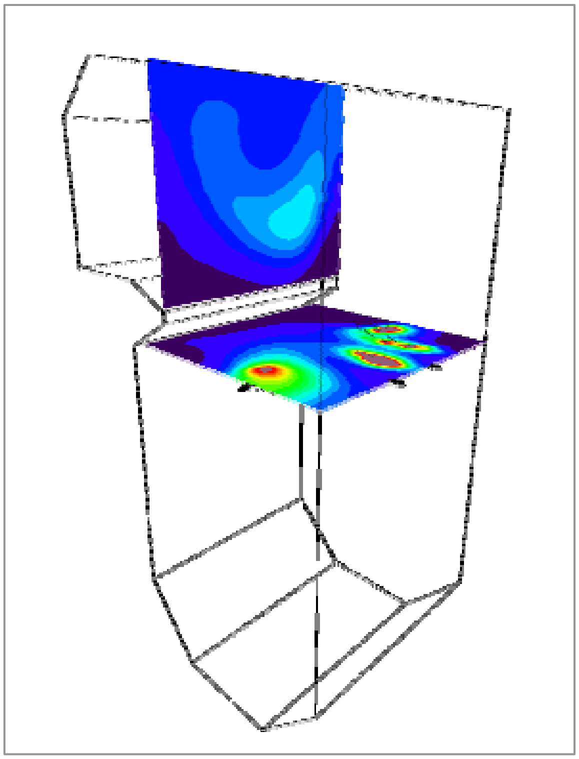

Figure E - Injection array with predictive chemical coverage

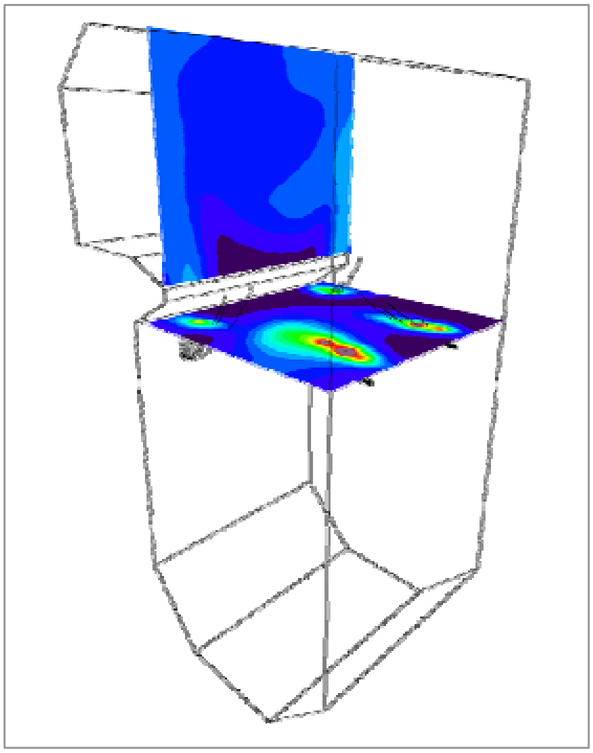

Figure F - Secondary CFD Model using Through the Web (TTW) injectors

Sampling and Testing Methodology

There were three methods used for collecting ash samples to be tested for LOI. A Cegrit ash sampler, a Storm ash sampler and samples taken directly from the ash hoppers were the three methods. The Cegrit ash sampler used was designed to obtain samples iso-kinetically and was expected to be the most accurate sampling method. As noted later in the analysis this proved not to be the case. The Storm ash sampler is not iso-kinetic and the reason it was used was to try and correlate the data per the Design of Experiment. The third method of obtaining samples (from the ash hoppers) turned out to be the most accurate. There were eight hoppers that were emptied and purged every time samples were obtained. The samples were collected every 2 to 5 hours in a manner such that equal amounts were obtained from each hopper and then mixed together to form one homogeneous test sample. Although this too was not ideal it was considered a valid test, whereas the hoppers were consistently purged after each sampling and the data considered relative rather than absolute. The ash samples were sent to an independent lab and tested for unburned carbon using a bomb calorimeter.

The data for CO was obtained using a portable CEMs (Testo 350) at 15 minute averages. The CO in the duct was measured by traversing the duct both vertically and horizontally.

Other data, such as dP across the Air Pre-Heater (APH) was obtained from the Plant supplied CEMs.

Results and Observations

The original test site data collection started 23 Oct with feed starting on 25 Oct. All samples and data collected for the first couple days is considered baseline information. Figure G is a compilation of the two weeks of testing for LOI.

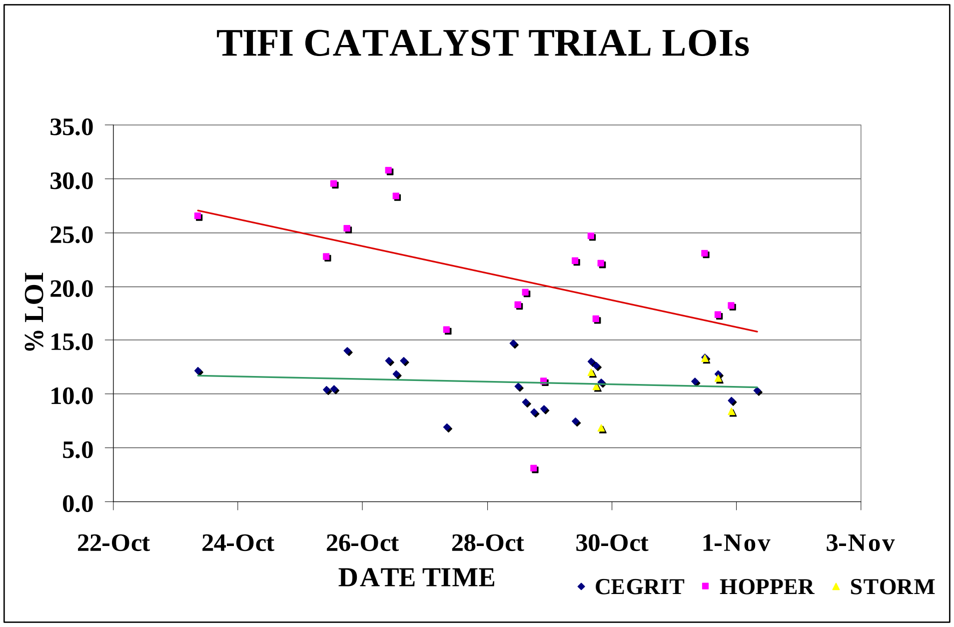

Figure G

The ash hopper data indicated that the LOI started out around 30% as expected and trended down to around 15%. The cegrit ash sampler did not show such a dramatic downward trend and the storm ash sampler was discounted, whereas the samples were taken too late and infrequently during the test cycle. Feed rate started at 3.6 lbs of reagent per ton of fuel consumed which equates to 99 ppm metal catalyst. The feed rate was increased to 4.5 lbs of reagent per ton of fuel consumed on 29 Oct which equates to 124 ppm metal catalyst.

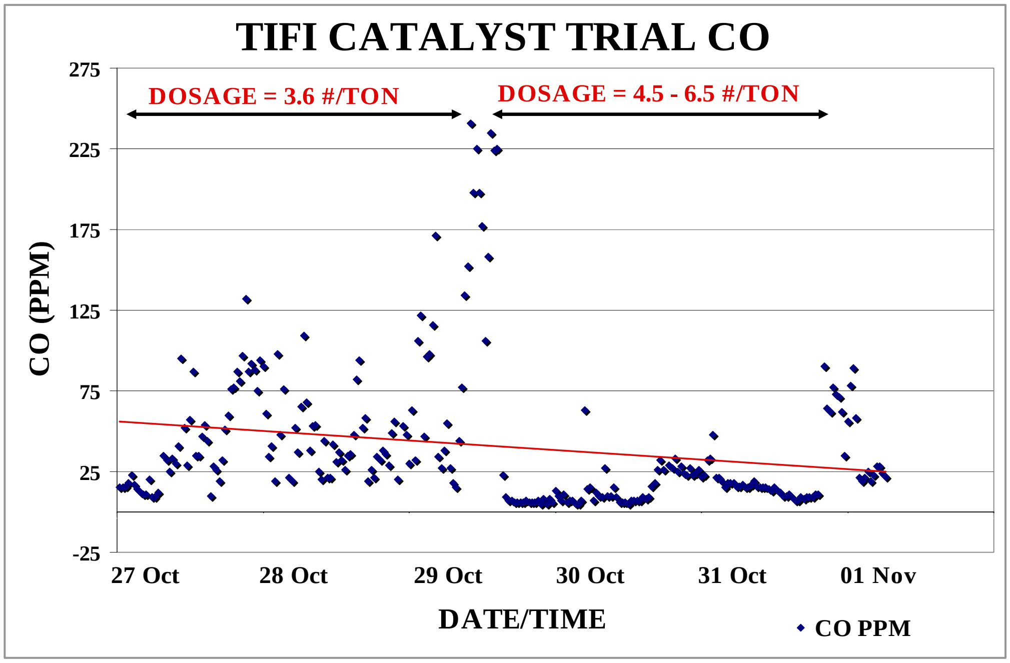

Figure H

The CO levels were initially observed to be around 200 ppm as expected. During the first week of treatment the CO data had a high standard deviation; however the trend was also noted to be downward.

Figure H is a compilation of the CO readings. Note that the variation changed dramatically when the feed rate increased. (from 3.6 lbs/ton = 99 ppm catalyst to 4.5 lbs/ton = 124 ppm) It can also be observed that the overall CO concentration was lower shortly after the feed rate increased.

Previous data indicated that the APH, once clean, had a tendency to stay clean when treated with $Mg(OH)_2$, however the feed rates for most TIFI applications are generally much lower. (i.e. < 2 lbs/ton)

Figure I - (Untreated)

Figure J - (Treated)

Figure I is a picture of an air pre-heater (APH) taken out of service during an outage at a different facility. Note the black sticky appearance of the deposits. Analysis suggests that these deposits are black due to the iron sulfate corrosion deposits, and are mixed with condensed sulfuric acid on the baskets. This combination is a problem for a number of reasons.

First, these deposits are corrosive and will significantly degrade the baskets through oxidation. Second, sulfuric acid is sticky and will cause corrosion products and ash to form a hard crusty deposit that fouls the baskets and limits gas flow through the APH.

During ozone attainment season, ammonium bisulfate deposits from SCR operations make the matter worse and can cause unscheduled outages during ozone attainment season when the cost of replacement power is at its highest. Clean up for an air heater in this condition is difficult and costly. When magnesium hydroxide is injected using Targeted In-Furnace Injection™ TIFI™ treatment, based on CFD modeling, the results are dramatic but not necessarily immediate. It has always been surmised that it takes some time and initially a relatively high dosage plan to condition and remove the deposition from duct and pre-heater surfaces.

The APH shown in Figure I was no longer fouled and corroded as indicated in Figure J. This photo shows a clean set of air baskets, free of ash, fouling and corrosion.

The dP across the APH was measured during the TIFI catalyst testing. It can be observed that the APH actually started to “clean up” so to speak. Note that the following Figure (K) actually indicated a downward trend in the dP across the APH.

Since the trial was only two weeks long the data is not conclusive, however it does suggest that at relatively high TIFI feed rates the APH does in fact start to become cleaner as earlier surmised.

There are two more areas that were briefly investigated during the first TIFI Catalyst test; that being the effects on NOx and CO_2. As previously stated the main thrust of this paper was the affects that the catalyst formula has on LOI, CO and slag/fouling. However the following two graphs are also noteworthy and encouraging.

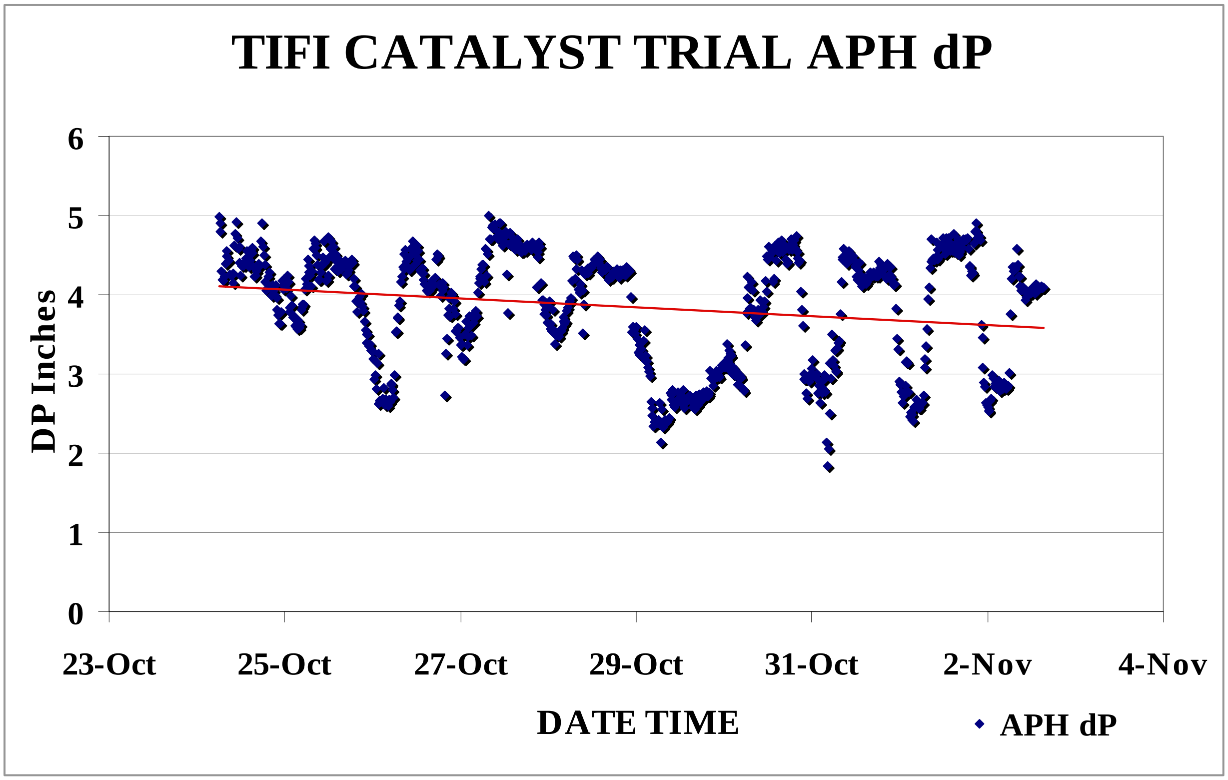

Figure K

Both NOx and CO_2 levels were trending down, albeit ever so slight, during the two week test period. This data was obtained from the plant Cems and the variation was noted to be higher than statistically ideal.

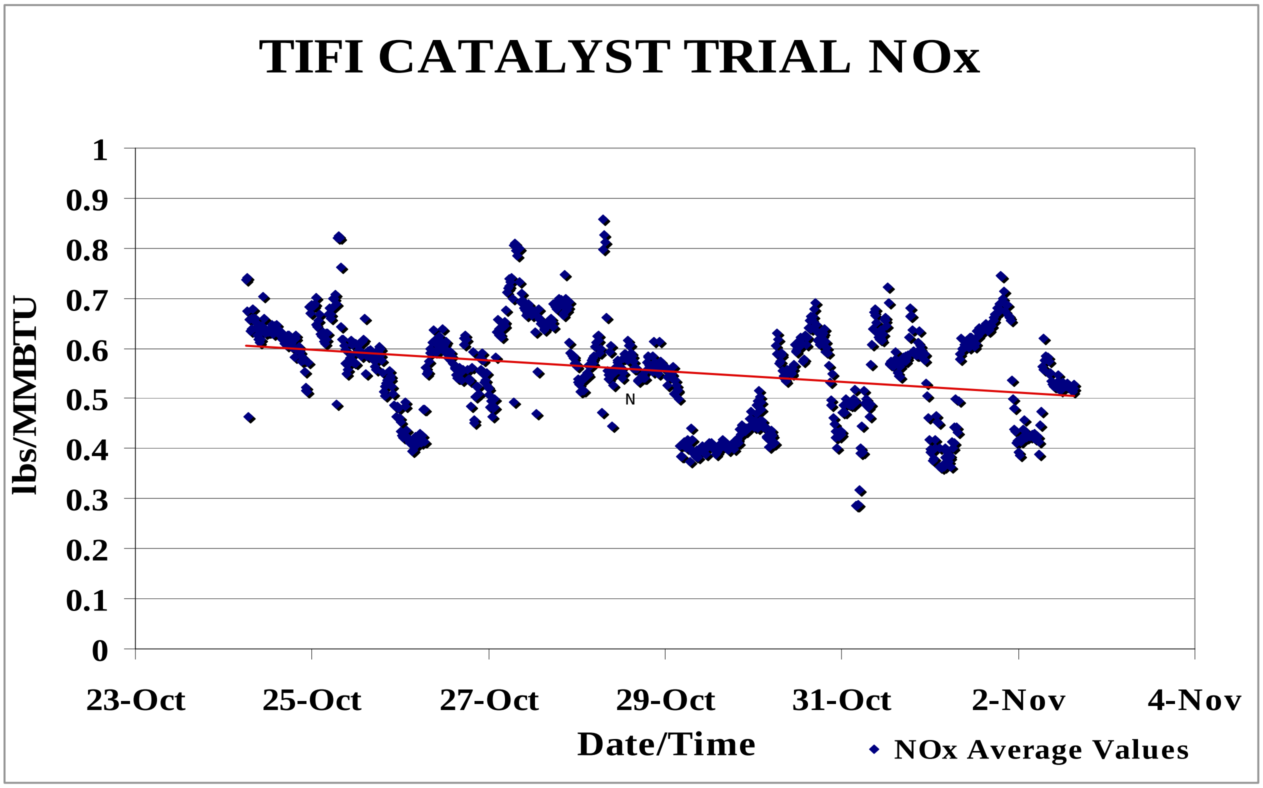

Figure L

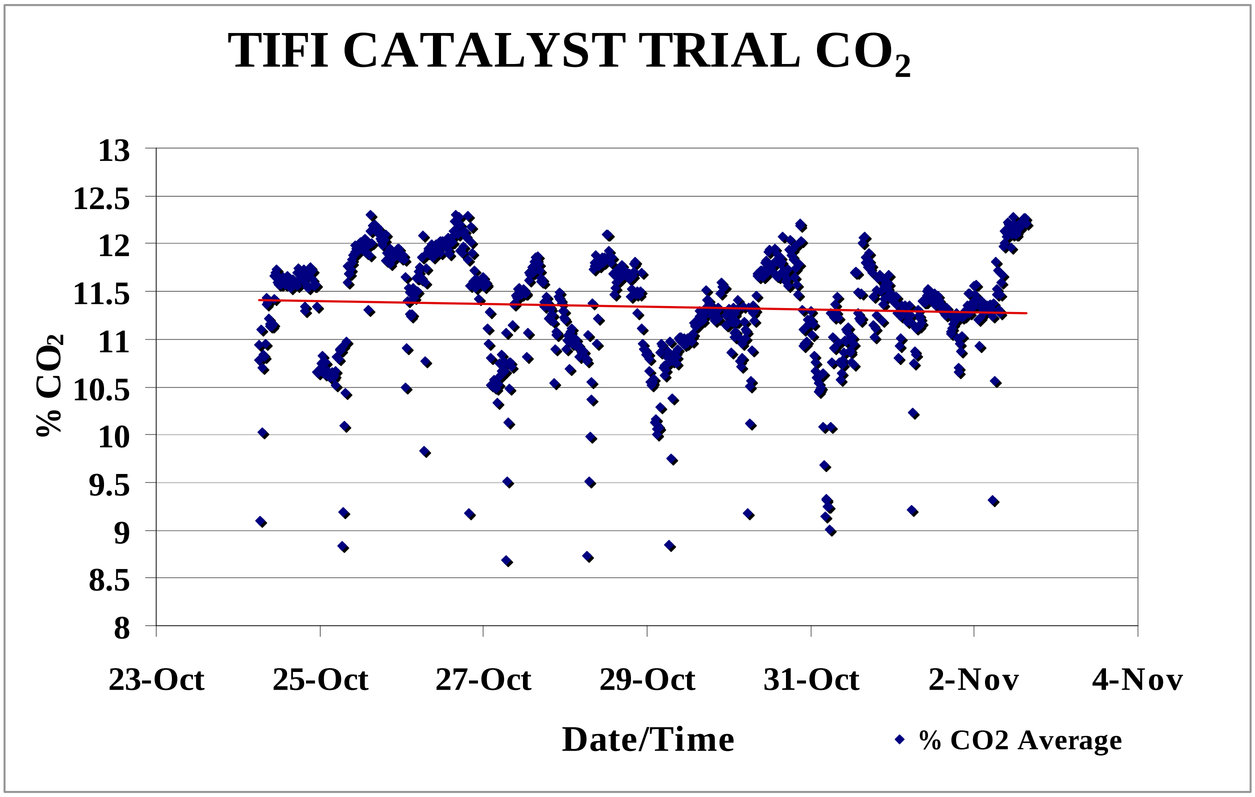

Figure M

Conclusions

The evidence supports that more efficient combustion and enhanced slag/fouling control can be obtained by synergistically combining TIFI technology with a catalyst.

The injection strategy chosen was less than ideal, because it was too high in the boiler. Therefore the distance – travel and time for the catalyst to work was also less than ideal. This was compensated for by increasing the chemical feed rate resulting in higher catalyst concentration. (99 ppm to as high as 179 ppm) The boiler was experiencing secondary and post combustion as evidenced by the relatively high CO concentrations in the duct. The high variation in the CO concentrations was indicative of the "hide out" effect of CO. Traversing the duct at one level would yield very low concentrations as well as very high CO concentrations. By saturating the boiler with a higher catalyst concentration this "hide out" phenomenon went away indicating that combustion was subsequently more complete and lower in the boiler. This was corroborated with the significantly lower LOI percent. (from 30% to 15%)

Regarding the three methods of collecting fly ash samples the method of collecting samples from the ash hoppers yielded the most accurate data. It was fortunate that the hoppers could be dumped and purged on a schedule to accommodate the sampling schedule otherwise this would not have been possible. Baseline samples taken from the ash hoppers were close to the predicted LOI value of 30%. The cegrit ash sampler, although hyper – kinetic, did not yield the same "absolute values" as was expected. (15% baseline) It appears that the cegrit ash sampler was "screening" out the larger carbon particles therefore skewing the data results. This could be fixed by redesigning the cegrit sampling probe to accommodate a more random distribution of particle sizes so as not to screen out the larger carbon particles. No conclusions could be drawn from the proposed correlation study between the storm ash sampler and the cegrit ash sampler. Due to equipment problems at start up, samples from the storm ash sampler were obtained late in the test cycle without the opportunity to develop a baseline.

The relatively high chemical feed rate has shed some light on the effects of highly reactive $Mg(OH)_2$ on slag/fouling, in particular regarding the APH. This may be beneficial for units with SCRs that are using or considering on using the TIFI technology during the ozone season.

The observed lower trend on NOx and CO_2, although encouraging, requires additional testing to definitively make any conclusions. The second test site was chosen to gather additional information in this area and will be the subject of another paper.

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