

CONTROLLING OPACITY, SO₃, FOULING, AND SLAGGING IN OIL-FIRED UTILITY BOILERS: TECHNOLOGY & EXPERIENCE

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SYNOPSIS

This paper discusses a method to control opacity, SO₃ generated blue plume and fouling and slagging in oil and coal fueled boilers. This method entails the injection of certain chemicals through special injection systems guided by both CFD fluid dynamics modeling and virtual reality visualization techniques. Included is a description of the processes and methods of use, an explanation of how the technology works and plant experience.

Examples of data from use of the technology on operating boilers is also discussed and analyzed. The theory behind mechanisms of operation is covered. Graphics showing how the modeling and the virtual reality visualization are employed are also included.

HISTORY & BACKGROUND

History of Targeted In-Furnace Injection Technology

TIFI, which stands for Targeted In-Furnace Injection, is based on technology that was originally developed by Fuel Tech Inc. for the air pollution control market for Selective Non-catalytic Reduction (SNCR) of nitrous oxides in the 1980s. In 1993, an attempt was made to apply the technology to slag control agents and was found successful enough to warrant further development. This effort proved so successful for Fuel Tech Inc., that a new division was formed to handle the technology.

The process involves sophisticated models run on high performance computers to predict chemical performance in a given furnace. The models were later validated in field measurements using suction pyrometry for temperature and gas species data. Guarantees of performance could then be made based on the model.

This technology base developed into hundreds of applications throughout the U.S. and the World. The slag and fouling control program involves targeting areas of the radiant and convection sections of a boiler with chemicals designed to control these

problems. Further refinement of this technology has demonstrated capability to control corrosion, fouling, and opacity problems related to SO₃ in the flue gas.

By targeting the problem areas of the furnace instead of targeting the fuel, performance and cost effectiveness are significantly improved for each of these technologies. Chemicals, mixed with air and water to aid in distribution and control are injected and targeted to cover the critical gas path area.

This has allowed excellent performance in systems previously thought to be resistant to chemical programs, including utility and other boilers firing oil, coal, pet coke and other solid fuels.

With the chemical being added to the flue gas and "aimed" at the problem areas, 90% of the injected material goes to treating those problem areas. This causes the additive concentration in the combustion gas to become high enough to positively affect the problems caused by the gas chemistry in areas where this is required, without excessive overfeed. This is what gives the technology its added boost in performance.

PROCESS DESCRIPTION

TIFI technology involves using two different forms of fluid dynamics modeling and a virtual reality engine. Together, these simulation methods 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 to 100% coverage of the targeted zones as possible.

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

Droplets Key

The calculation of furnace interior fluid dynamics is discussed in the section on computational fluid dynamics, or CFD for short. Once the temperature profiles, velocities and currents are all calculated, it is then necessary to calculate how to get the prescribed chemical into the furnace, taking into account all the fluid dynamics of the gases as they flow through the furnace and heat transfer zones of the boiler.

One module of this complicated software deals with the injection of the chemical itself. The whole process uses the evaporative qualities of water as a driving force to help assure that the chemical is distributed in the concentrations needed for good performance, without wasting anything.

To maximize effectiveness, the equipment atomizes a mixture of chemical and water with a certain quantity of air. The model determines how much chemical, air, water and both the number and placement of injectors in the furnace that will be required to get full coverage in the trouble spots.

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 taken into account. The smallest droplets evaporate very close to the injection point. The chemical activates and this covers the zones nearest the injectors.

Each successively larger set of droplets goes deeper and deeper into the furnace before evaporation completes and chemical is activated. This provides coverage successively further out into the furnace until all the droplets have been evaporated and all of the chemical has been activated.

The program overlays all of these calculations on the earlier fluid dynamics calculations. 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.

In-Body vs. TIFI

In comparing Targeted In-Furnace Injection with other methods of chemical based slag, fouling, corrosion, and emission control, there are numerous differences and limitations that arise.

The most common method of treatment before the advent of TIFI was In-Body, or in-fuel treatment technology. This technology was and is still a

popular method for treating furnaces burning No. 6 residual fuel oil. This in-fuel treatment works well for lower furnace slag mainly because the oil burners act as injectors and the fuel bound ash component is so small, typically about 0.15% or less.

With Targeted In-Furnace Injection, the whole issue of being in close to the burners and subject to limitations of the fuel and air mixing is answered. Instead, the injection takes place with what is happening to the burn zone, taking advantage of fluid dynamics in that zone and avoiding pitfalls identified during modeling.

The result is entirely different from an in-body treated furnace. Injectors are located where they can best access gases to carry the chemical to the needed zones after first mixing, then activating and spreading to all the areas that need it.

This methodology is effective on opacity, radiant section waterwall slagging, convection pass fouling, plugging of platens and cold end corrosion control when high sulfur fuels are in use.

At typical usage rates, the In-Body technology follows stoichiometric guidelines of three to one (3:1, Mg:V) for the most common contaminants.

The limitation of the in-body approach, while effective for lower furnace slagging and the SO₃ produced in the flame area, is that it is not very effective for upper furnace and convection section problems. Overfeeding to the fuel may help with some of the convection section fouling, but will not help much at all for SO₃ produced in the convection section. That is why no in-fuel program ever achieves ash pH's much higher than 4.0.

With solid fuels, things have to be done differently to be cost effective. Consider that with a solid fuel that is ten percent ash by weight, adding fuel slag conditioner to the fuel will result in a huge quantity of the material remaining with the bottom ash.

TIFI Technology

TIFI

TIFI technology actually has three different types of application. One type of application deals with fouling and involves generally only one array of injectors.

TIFI Hybrid

The second type deals with either injectors in the lower furnace waterwalls or feed of a slag inhibitor directly into the fuel. This Hybrid program enables control of both lower waterwall slagging problems and convection section fouling simultaneously.

Hybrid technology is also highly effective in SO₃ abatement. Using this technology lowers opacity, drops SO₃ levels and raises ash pH higher than any conventional program on a consistent basis.

TIFI Hybrid Plus

The third evolution of the technology involves using Hybrid technology plus use of catalyst technology, either fed into the fuel or into the furnace in reducing conditions. The advantage of this technology is even greater reductions in opacity due to the reduction of LOI, loss on ignition, which is essentially unburned carbon. Also, for units with low LOI, reductions in excess O₂ may be possible with the use of a catalyst. This will improve boiler efficiency and reduce flame generated SO₃ and NO_x. This is in addition to control of slagging, fouling and other SO₃ related problems. Reductions in total stack opacity utilizing this technology approach 75 to 80%.

CFD Modeling & Virtual Reality Visualization

Process Design Modeling, in effect, involves duplicating the operation of a particular furnace in a super computer and then testing various "what if" problem and solution scenarios at various power settings. A great deal of detail goes into running this "plug flow" model.

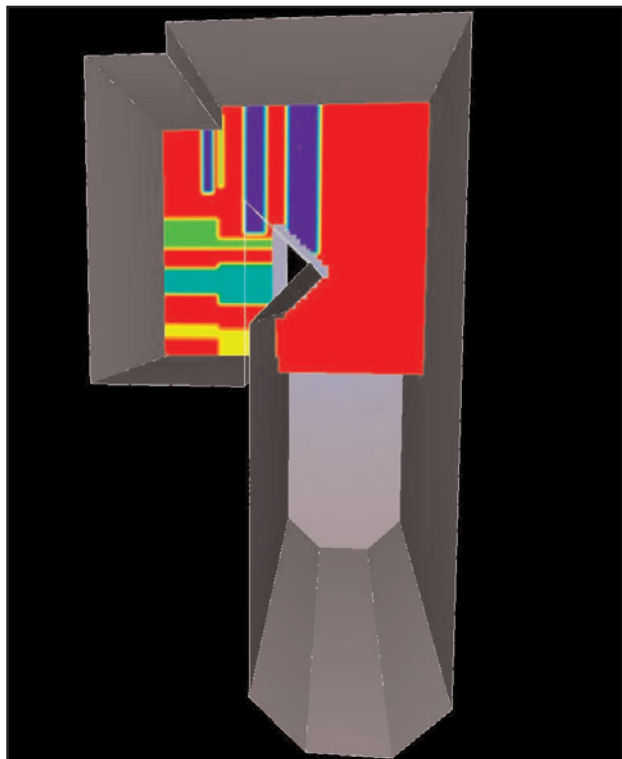


Figure A

All size and design dimensions, fuel and heat rates, fuel chemistry details, details of air usage and boiler geometry 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 like coal burning utility boilers and other furnaces, behave in real time.

Figure A shows a virtual reality simulation snapshot of a 400 MW No. 6 oil fired boiler. This "semi-solid" view depicts how the unit is modeled to simulate what goes on in the furnace.

In this view, (Figure A) with only the heat transfer equipment visible, one can see that the resistance created by that equipment to the gas flow and its concurrent heat transfer are accounted for.

After all of this data is programmed, a temperature and gas velocity gradient is calculated for the entire furnace. The result here generally shows small imbalances in furnace heat release and gas flow pattern, which is normal. If the variations were excessive, a point would be made in the report that the abnormal condition exists, along with some recommendations on how to deal with it.

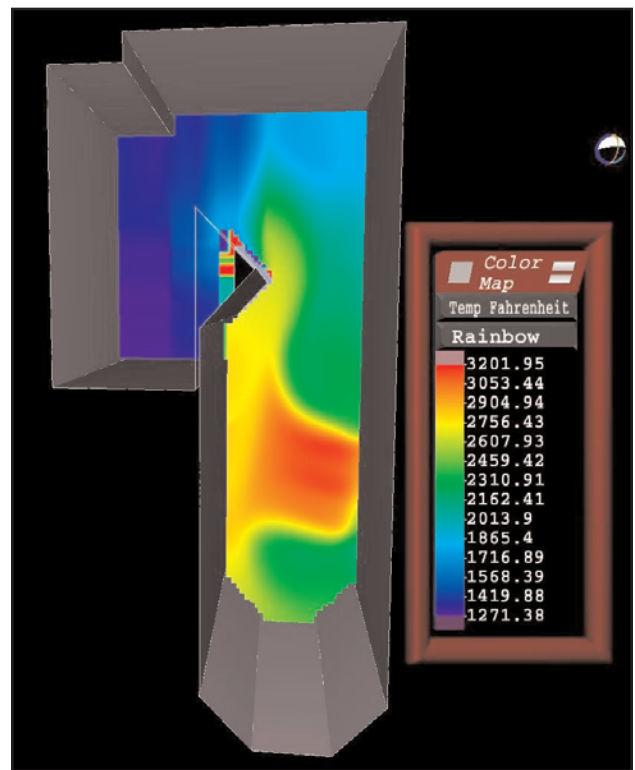


Figure B

Figure B shows the temperature gradient or profile in the furnace in the vertical plane. This particular view shows a cutaway of the furnace, looking in from the left side of the boiler at the vertical temperature contour of the boiler.

Treatment programs can then be designed for the specific boiler or furnace situation. A customized injection scenario is then built inside the computer and tested under varying program conditions and results calculated.

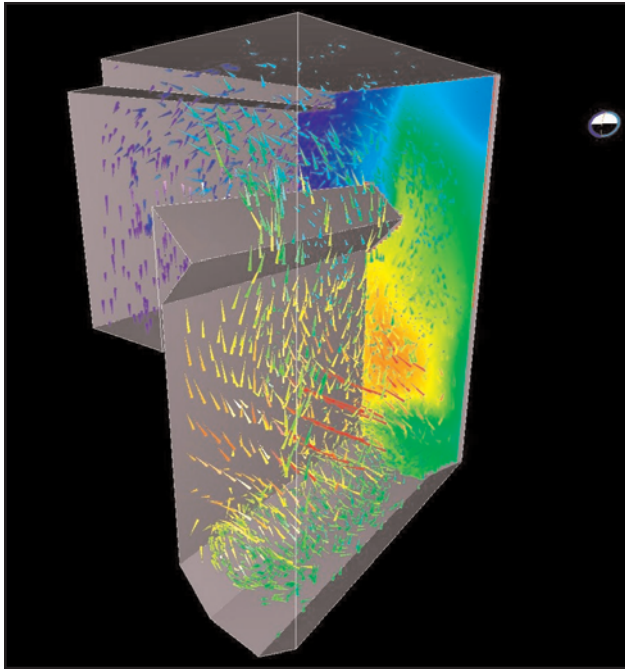


Figure C

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 C details the gas flow fluid dynamics using flying vector arrows that are coded for velocity (length), temperature (color) and direction. Problem areas are now easier to spot and any needed corrective action can be taken.

Understanding is further 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 D shows how the entire gas path from the radiant section through the superheaters and the reheaters is targeted for chemical application by adjusting the number of injectors, placement, design

and performance settings. This technology makes it possible to have high chemical activity in several places at the same time.

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 it the most. The program uses this sophisticated "aiming" ability to ensure that the correct dosage is applied everywhere it is required. Figure E depicts the chemical dosage map that was judged best to control the problems associated with SO_3 and slugging in the critical targeted areas.

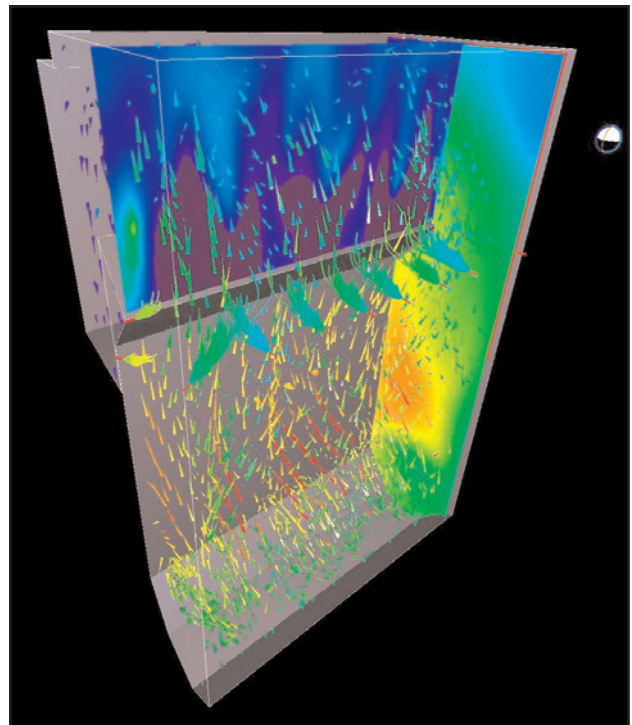


Figure D

Colors now change to representing chemical concentration with red being very high concentration (near injectors) and dark purple being very low concentration (further away from injectors).

Figure E also depicts a unique capability for users of this technology. The model can 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. The translucent maroon shape represents 2,150 degrees Fahrenheit. This, in itself, is not unique. However, when matched to the ash fusion temperature for the fuel blend 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 show up.

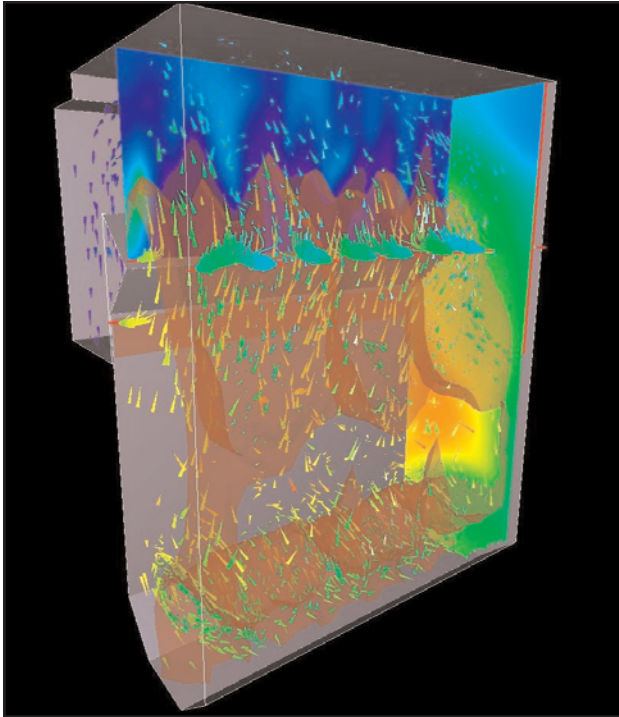


Figure E

Reagent Chemistry

The reagent is a specialty chemical slurry with high reactive ability due to its large surface area per unit volume ratio (approximately 530,000 sq.ft./cu.ft). This high activity results in reduced treatment dosages while its high stability eliminates many of the handling and feeding problems associated with unstabilized compounds.

The low levels required for good performance are based on modification of the crystal structure of the slag as it is formed and adheres to tube surfaces. Finished crystal strength is significantly reduced, allowing sootblowing to remove the deposits with little difficulty. Chemical feed rates are much less than stoichiometric requirements and ash fusion temperatures are unaffected.

The chemical reagent arrives at the customer site in the form of a suspended slurry of 5-8 micron sized particles. Atomization takes place in accordance with the model output.

Opacity Discussion

Components of Opacity

There are four basic drivers to the formation and control of opacity. These are listed and discussed below. By addressing each of these components, opacity, corrosion and acid fallout can be reduced.

NO_x

NO_x is a polluting gas caused by two different mechanisms in combustion. The first one is thermal NO_x and is caused by the 3000 degree Fahrenheit flame temperature during combustion. The second NO_x component is so-called fuel bound NO_x and is a function of the organic nitrogen content found in the fuel.

NO_x escapes to the atmosphere as a non-condensable gas from the stack of a fossil fuel plant. Its brownish appearance contributes to stack opacity, but is one of the lower contributors to opacity.

LOI (Unburned Carbon)

LOI, or unburned carbon is a significant contributor to stack opacity. LOI typically occurs in boilers fitted with low NO_x burner technology and in heavy residual fuel oil boilers as well as those burning Eastern bituminous coal, which is high in fixed carbon content.

Regardless of the source, LOI contributes to opacity because the particles absorb light and register as opacity on the stack opacity monitor. LOI is also a problem because it represents lost fuel and lost efficiency up the stack. Despite this, it is not the worst contributor to opacity.

Ash

Ash represents a component of opacity that can only be controlled by purchasing fuel with lower ash content, or installing solids capture equipment on the back end at very high cost.

Since this is the least controllable component of opacity without resorting to expensive fuel changes or back end retrofits, the focus here will remain on lowering opacity by controlling LOI and sulfuric acid mist control.

Sulfuric Acid Mist

Sulfuric acid and the mist it generates on condensing, either in the back end of the flue gas system somewhere, or outside the stack in the atmosphere is the biggest contributor to stack and visual opacity. It is also the most expensive in terms of damage to the local environs and to the equipment itself.

Sulfuric acid mist has an environmental cost, a regulatory cost, a mechanical cost, and an operating cost. Added together, the case for treating to prevent and/or control the problem becomes cost effective.

The reason this acid mist is so damaging and expensive has a lot to do with how it is generated and what form it appears in. Sulfuric acid mist is the

result of SO_3 , which comes from catalysis of SO_2 to SO_3 in two different areas of the boiler. These SO_3 molecules, which represent anywhere from 1-4% of the SO_2 generated in the furnace during combustion, combine with moisture, a by-product of fossil fuel combustion, present in the flue gas of every fossil fuel fired boiler.

This moisture and the SO_3 combine to form pure sulfuric acid. This acid forms, for a variety of reasons, into droplets so small, they are almost impossible to control. Droplet sizes, on average, are about 0.1microns in diameter. This is so small, that these droplets behave as if they are gas molecules.

Since these droplets behave this way, they are very difficult to capture. Any type of scrubber is going to generate droplets of water that are hundreds of times too large to collide with the acid mist particles and react with any reagent present in the scrubber. Even wet precipitators can have difficulty in dealing with these small droplets.

TIFI Hybrid technology addresses this major limitation by avoiding these droplets altogether. TIFI Hybrid technology functions by capturing the SO_3 molecules in the hot furnace and reacting directly with the SO_3 molecules to form magnesium sulfate. In the same vein as slag and fouling control, the extremely small MgO particles are just the right size to react with the SO_3 molecules to capture these gas molecules, react and form a solid material that can be captured more easily. Acid formation is avoided altogether.

NANO TECHNOLOGY DISCUSSION

Nano Technology and Fractal Geometry

It is here, in the physical aspects of the chemical reaction that controlling opacity, SO_3 , slag and fouling problems takes place. The reagent actually functions in two ways. First, it alters the crystal structure of the slag and fouling that originates in the boiler fuel as ash, and is entrained in the flue gas of the upper furnace. Second, it reacts directly with SO_3 as it is being formed in two different areas: the fireball and the convection section.

This technology changes the molten slag to a more friable material that does not adhere as tenaciously to the tube surfaces and is therefore easier to remove during sootblowing. This minimizes the catalytic impact of vanadium bearing fuels on SO_3 production by limiting vanadium deposits. The particles of MgO also are small enough to collide and react with the SO_3 molecules in the gas.

Until recently, the exact mechanism of how this was accomplished was not well understood. Recent research results have revealed some striking new

ways to explain what the mechanism of function appears to be.

Current theory suggests that nano technology is at work in the way the TIFI program functions. For the use of the term "nano" in this discussion, it is defined as "the ability to synthesize, manipulate and characterize matter at the sub-100nm level." To simplify, 100 nm = 0.1 micron.

In order to comprehend what was happening to the magnesium hydroxide particles after they were injected into the boiler, an indirect measurement method had to be devised to test the theory that the nominal 5-8 um particle sizes had to become much smaller. This was surmised because performance of the technology suggested that far smaller particles had to be at work to explain the activity observed in real life conditions.



Figure F

The experiment selected consisted of a Dean Stark distillation apparatus (Figure F) which would be used to synthesize an organo-metallic magnesium compound using a solvent based sulfonation method. This scenario was selected because in the synthesis of this material, several things would happen:

- The temperature at which things happened could be measured.
- The reaction process produces about 10% soluble material, and the rest remains as insoluble particles.
- The size of these particles in suspension could be accurately measured and a distribution established.

- If a change in particle size and distribution were to occur, it could all be accurately measured, even down well into the nano-particle range.
- Other methods were more complex, costly and did not increase the accuracy over this set-up.
- The soluble material generated was deemed within the margin of error and acceptable, due to the difficulty of trying to measure these things in-vitro.

Tests were conducted on a number of magnesium sources to determine which ones were the most suitable for TIFI technology. Two different particle size measuring technologies were selected and used to make the determination.

1000xSEM Baseline Untreated Slag

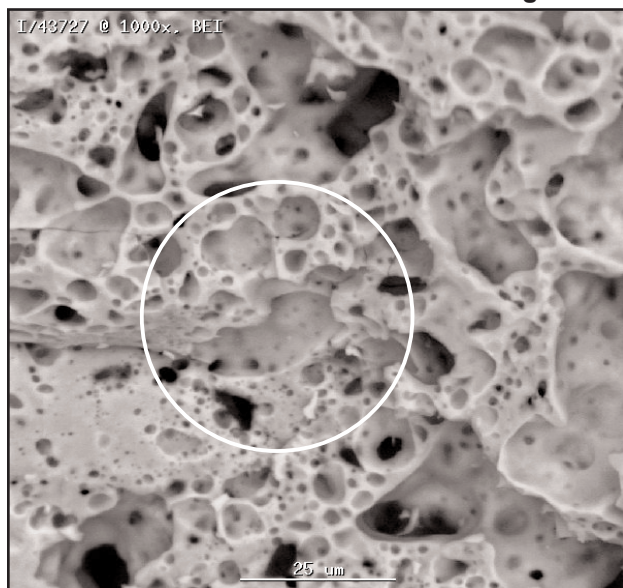


Figure G

Scanning electron microscopy photos of different parent magnesium hydroxides showed observable differences in crystal structure that could account for differences in reactivity and performance. Crystal structures that prevented the venting of steam caused by the water of hydration being heated until it flashed to steam appeared to have higher reactivity than crystal structures that were open and allowed steam to escape without disrupting the particle structure.

Particles in the sub-100 nm level, in effect, become like a gas and have properties of gases. This property of Brownian motion is important for particles penetrating deeper into the boiler to be small enough to react with molecules in the gas (i.e., SO₃ molecules) and the ability to penetrate existing slag and fouling deposits, loosening them and enabling removal of pre-existing deposits.

The TIFI process operates by using droplets of varying size ranges to allow particles to travel to

varying depths in the furnace and convection section, dependent on the initial droplet size. When the water evaporates, there is a brief period of travel as the 5.0 micron particles heat up to about 325 degrees Celsius. At this point the particles explode into varying sizes from 0.03 to 0.3 microns.

1000x SEM TIFI Treated Slag

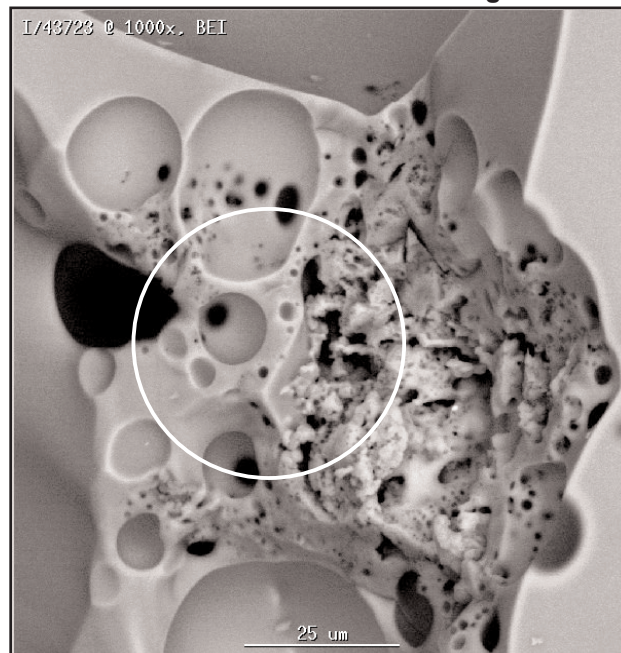


Figure H

Results from all the studies showed that, in the case of the brine manufactured material, which is what is used in TIFI, particles which started at nominal sizes of 5-8 microns, were converted at 325 degrees Celsius to particles in the size range of 0.03-0.3 microns.

This is significant, because this testing proved that TIFI is, in fact, an in-vitro nano technology. That is, TIFI becomes nano technology inside an operating furnace. These two events, targeted in-furnace technology, and the in-vitro creation of nanoparticles of high reactivity and performance are unique.

When these tests and theories were paired with SO₃, opacity and particulate testing done on baseline untreated, in-body injection and TIFI-Hybrid treated furnaces, a theory of function and operation began to emerge that is quite different from previous explanations of chemical based SO₃ and opacity control technology for oil fired boilers. Other evidence indicates this is also true for slagging and fouling in both oil and coal fired furnaces.

Crystal Morphology of Slag Control

Testing and scanning electron microscope photomicrographs were taken as a continuing part of slag

control research. This part of the study was undertaken at a customer site in which in-situ slag samples were taken during baseline untreated runs and after TIFI treatment was switched back on. The results of this study can be seen below.

Figure G shows a 1000x magnification scanning electron microscopy image taken from a fractured surface of a sample of untreated slag removed from the furnace exit of a large utility firing coal. This sample is dense, hard and relatively heavy for its volume.

Here the slag appears to be perforated by pores that, at the smallest, are about 0.1 micron in diameter, and range in size up to 25 microns. This fact is important to the ability of the TIFI technology to penetrate existing slag and fouling deposits.

This is typical of hot plastic slag and fouling seen in furnaces firing western coals. Inside the highlighted area a typical slag structure can be observed. Bubbles and inclusions are relatively small and packed tightly together. This is the structure that is responsible for the tenacious slag and fouling that create problems with firing these types of fuels in utility boilers.

Figure G depicts a sample of slag removed from the same part of the boiler as the sample obtained in Figure H. It was removed while the unit was firing and after switching the TIFI chemical system back on for 8 hours

The structure of this material, although the same chemically as that in Figure G, is much lighter, softer and is easy to crumble. Structurally, the material, as seen in the highlighted area, has holes (pores) that are noticeably larger than those in Figure G.

This explains why the material is much weaker and lighter than the baseline untreated material.

The structural differences in this photo are noticeable. The smooth dense (and strong) areas are replaced with surfaces that are irregular, broken up and have numerous inclusions and other particles that break up the unified crystal structure. In the highlighted area of Figure H it can be observed that the surface has a wider distribution of larger pores present than in the structure of Figure G.

Smooth and dense areas can still be seen, but the pores are generally larger and add to the lightness and friable nature of this sample. The walls between the largest pores have thinned considerably.

MECHANISM OF FUNCTION

In this section, the theories of how the TIFI program works are discussed in detail. This is based on the evidence presented above in addition to other evidence not presented here.

Pore Distribution in Solids: Slagging & Fouling

Most slag and boiler convection section fouling have structures similar to the structure seen in Figure G. The material consists of a network of pores in a solid glassy material that also comprises some crystalline matter. The pore distribution is from about 25 microns on the high side to about 0.1 microns on the low side.

The material in between forms walls between the pores that are thick, dense and quite strong. It is important to realize that this structure is NOT monolithic, not of uniform composition, and is in fact perforated with so many pores as to be permeable. That is, the material can absorb fluids

Percolation and Diffusion of Fluids

The non-monolithic slag with the pore distribution discussed earlier is not immune to absorption of fluids. Physicists refer to this phenomenon as percolation.

The fluid in this case is the combustion gas and the media is the slag itself. The gas diffuses throughout the slag due to the permeability of the slag material, created by all the pores distributed throughout the material.

In the case of a TIFI treated boiler system, the gas now has particles of magnesium oxide, in the range of 0.03 to 0.3 microns in size, 30 to 300 nanometers. These particles are almost as small as the gas molecules, and behave as if they were gas molecules, exhibiting Brownian motion.

Plasticity and Nucleation

The mag oxide particles undergo this migration, or percolation, because these particles now behave as if they are the fluid. The particles' size is so small, they act as a fluxing agent, helping the now plastic slag material to flow more easily internally.

The pores mentioned before now migrate to merge and become larger pores in the process known as nucleation. These larger pores continue to merge and form even larger pores. The rules governing the strength and physical properties of the slag change

Fractal vs. Integer Geometry

Fractal geometry governs the behavior of the untreated slag and fouling. As the treated slag and fouling undergo the changes described above, this fractal behavior shifts to integer geometry. In this

case, the large pores cause the density, rigidity and structural strength to change.

Where thick walls between many small pores occurred before, you now have fewer much larger pores with much thinner walls between the pores. These walls become so thin that crack propagation starts and the walls fracture, fostering the destruction of the whole structure. Normal soot blowing temperatures and pressures are now sufficient to remove the friable material from heat exchanger tubes

EXAMPLE CASES

For decades, the addition of magnesium-based compounds to various furnace/boiler systems has been employed as a strategy to raise the back end fly ash pH. This is done with the understanding that neutralizing sulfuric acid has two valuable functions.

First, it changes the nature of the fly ash from acidic to alkaline, and in so doing, reduces corrosion to ductwork, economizers and air heaters. Secondly, the conversion of liquid, sticky H_2SO_4 to a dry salt ($MgSO_4$) will reduce or eliminate ash accumulation and eventual pluggage of the narrow gas passages generally seen in the colder back end regions of a furnace.

Fly ash pH is the easiest (and subsequently most common) means of measuring the efficacy of chemical addition to a steam generating facility. Typically, fly ash samples are captured in-situ in the back end of a furnace (air heater outlet is the most appropriate location). This fly ash is added to distilled water to form a 1% slurry, and the pH of this slurry is measured.

For facilities burning sulfur-bearing fuels, a slurry pH of 1.5 - 2.5 is not uncommon. This is because the fly ash adsorbs the sulfuric acid that forms in areas operating below the dewpoint for SO_3 concentrations seen in the furnace back end. Sometimes, as a time-saving measure, ash samples are taken from various fly ash hoppers located in the back passes of the boiler. It cannot be overemphasized that this practice is without value for the purpose of determining reagent efficacy. Hopper samples represent an historical record at best, but are generally so altered by the passage of time and exposure to atmosphere that they are without value.

Any increase in pH is considered desirable, but a neutral level of pH 7.0 is considered the minimum requirement. This is not always achievable at reasonable (economical) dosages because of the huge quantities of ash involved, and because of the

limitations of conventional chemical additive injection. It is simply difficult and expensive to inject enough reagent, properly distributed, to sufficiently elevate the fly ash pH. And while a slurry pH of 7.0 is considered a minimum, a pH of this level alone will not ensure a non-corrosive environment in the cold end of a boiler.

Experience has shown that only when a pH of 8.5 or above is achieved is one assured of non-aggressive conditions in the back pass of a boiler. This extra level of buffering is required to ensure that no localized pockets of unreacted H_2SO_4 exist. Unfortunately, without the benefit of computational fluid dynamics modeling and targeted in-furnace chemical injection, a pH level of 8.5 is extremely difficult to achieve.

Case 1

As an example of the level of fly ash pH elevation achievable through Targeted In-Furnace Injection, Figure I plots the pH of grab samples of fly ash taken in the air heater outlet gas ducting of a steam generating unit burning an off stream of non-condensable gases. In this example, there are a series of baseline pH measurements made over a period of 10 months. Over this period, the pH of a 1% slurry of fly ash measured between 1.4 and 2.0.

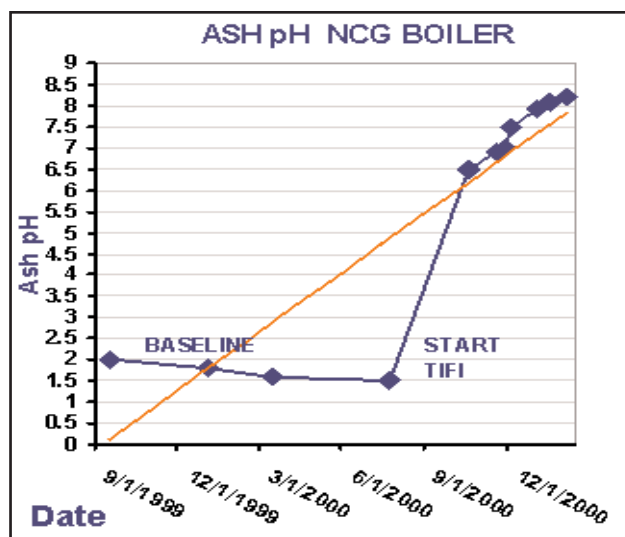


Figure I

Targeted In-Furnace Injection of a proprietary reagent was then initiated, and the first post-injection fly ash sample was taken seven days later. Because of the relative infrequency of ash sampling, it is not clear how quickly the ash pH rose. However, the first treated sample was measured at pH 6.5, and ranged from 6.5 to 8.1 for the remainder of the period plotted (roughly 6 months), a very significant improvement.

Case 2

The second example that will be discussed involves three oil-fired industrial boilers. In this example, three units at this plant used a magnesium-based slurry that was injected into the primary oil feed pump outlet piping. This simple In-Body chemical injection scheme had been in practice for years, and was marginally effective in raising the back end fly ash pH from an unconditioned level of approximately 1.5, to a conditioned pH of about 4-5. This represented an improvement in cold end corrosion and air heater plugging, but was far from a perfect solution. The useful life of ductwork and air heater baskets was less than desired, and air heater plugging was sometimes the cause of boiler deration and ultimately unplanned outage. Despite year round warm weather conditions, this plant was forced to preheat their air at considerable energy cost.

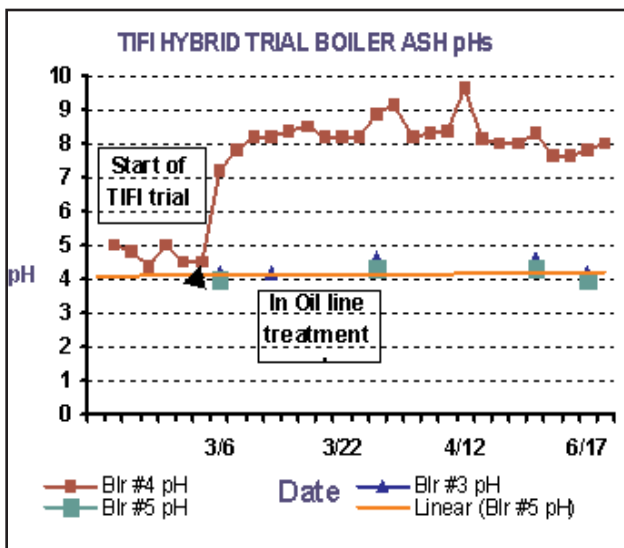


Figure J

Because of the positive results seen with In-Body injection of magnesium, this plant decided to measure what additional benefit might be gained by overlaying targeted in-furnace injection of the same Mg-based reagent. This dual approach, in-body and TIFI, is known as "Hybrid" injection, and has been shown to be effective beyond the level achievable with in-body injection alone, regardless of injection rate.

This Hybrid method is able to both reduce the conversion of SO_2 to SO_3 , as well as react with gaseous SO_3 in the flue gas. The result is a lowered acid dewpoint and, subsequently, less sulfuric acid adsorption onto the fly ash. In this way, the operator of a steam generating plant is able to raise the pH of the back end fly ash to higher levels, and this is a direct indicator of reduced cold end corrosion and plugging potential.

The results of this hybrid injection demonstration are shown in Figure J. In the days prior to hybrid injection into Boiler 4, all three boilers (3, 4 and 5) showed back end fly ash pH of approximately 4-5. Then, within a day or so of overlaying TIFI on boiler 4, the pH on this unit rose to a level 8-9, and held to this level for the remaining three months of the evaluation.

Based on the results seen during this Hybrid injection scheme, the plant has turned off their steam coil preheater to Boiler 4. Despite this, cold end corrosion has diminished to the extent that component life has been extended, and forced outages due to air heater plugging have ceased. The other boilers are expected to convert to Hybrid technology shortly.

Case 3

A third demonstration is highlighted in Figures K-N. In each of these figures the terms "base" or "baseline" or "no injection" all refer to the pre-TIFI condition, when only in-body injection of reagent was present. It is not a baseline in the sense that no chemical was being used. It is a baseline in that this utility had used in-body injection for a number of years prior to evaluating a TIFI/Hybrid scheme. The "normal" situation for this boiler was to inject chemical into the bulk oil, and so this situation is considered baseline.

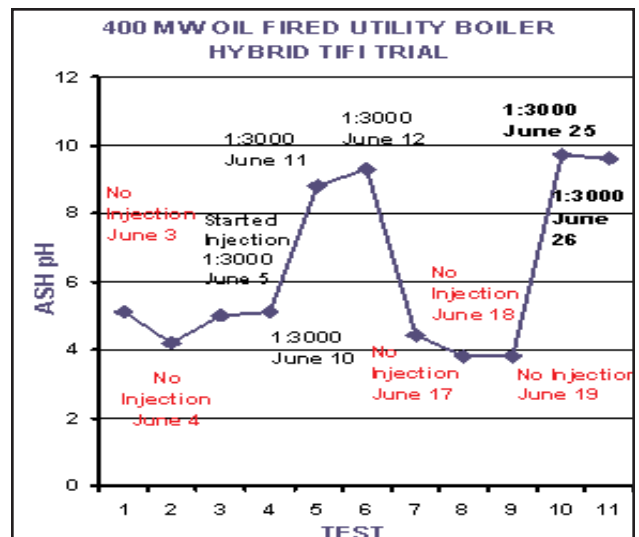


Figure K

The boiler in question is a 400 MW, front-fired B&W unit. The initial incentive for chemical conditioning was excessive slagging of the radiant portions of the boiler, brought about by the firing of low quality No. 6 fuel oil, laden with vanadium, sulfur and other contaminants. The reagent added to the fuel oil had consistently allowed for uninterrupted cycling or base-loaded operation, with no slagging or fouling of the radiant or convective passes, respectively.

However, the unit occasionally experienced a "blue plume" attributed to SO₃ emission. Also, since the installation of low NO_x burners, excessive stack opacity during periods of load ramping was often a problem. With these two issues as incentive (blue plume and stack opacity), the utility elected to try adding targeted in-furnace injection to the mix.

A very aggressive testing protocol was developed, whereby fly ash grab samples were taken and gaseous SO₃ levels were measured on a daily basis, while TIFI was overlaid upon the normal in-body addition of a magnesium-based reagent. Whenever reagent was injected into the furnace, the amount of chemical added to the fuel oil was adjusted downward so that the total addition of reagent to the furnace remained fixed at normal (or baseline) levels. This approach was chosen so that any changes in unit performance could be attributed to the application technology, rather than to absolute levels of reagent injection. No more chemical was used, but its application was altered.

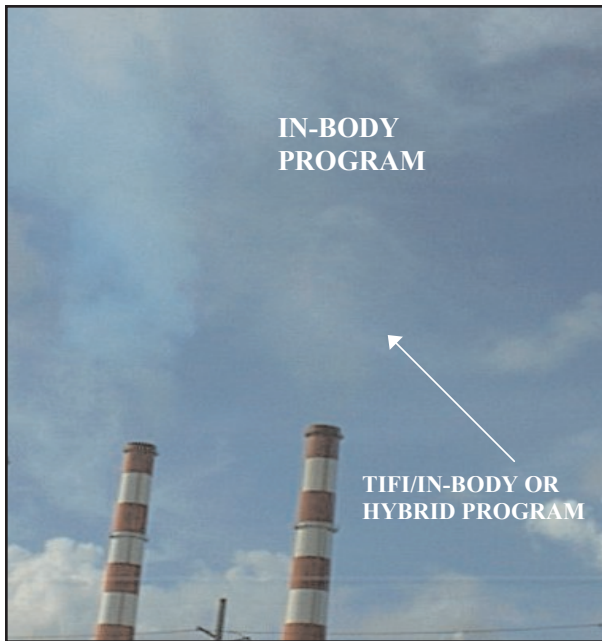


Figure L

Figure K shows the changes to fly ash pH measured during a 12 day period of variously overlaying TIFI with In-Body application. As is seen in this graph, the in-body injection alone (no TIFI) was able to achieve an ash pH of roughly 4-5. This pH was considered "normal", when compared to ash pH levels of 1.5 -2.0 seen before any reagent application to the fuel oil began several years prior.

The application of TIFI was made at a total targeted rate of 1 part chemical:3,000 parts fuel oil. What is clear from the data is that it requires several days of conditioning for the full effect of this change in

chemical application to take place. After this conditioning period, however, fly ash pH of higher than 9.0 is achieved. In other words, unconditioned fly ash in this unit has a very aggressive pH of less than 2. Injection of reagent into the fuel oil can elevate the back end fly ash to an improved pH level of 5. This same amount of reagent, split between the fuel oil and direct (TIFI) injection into the furnace can bring the fly ash pH up to the entirely safe level of 9.0.

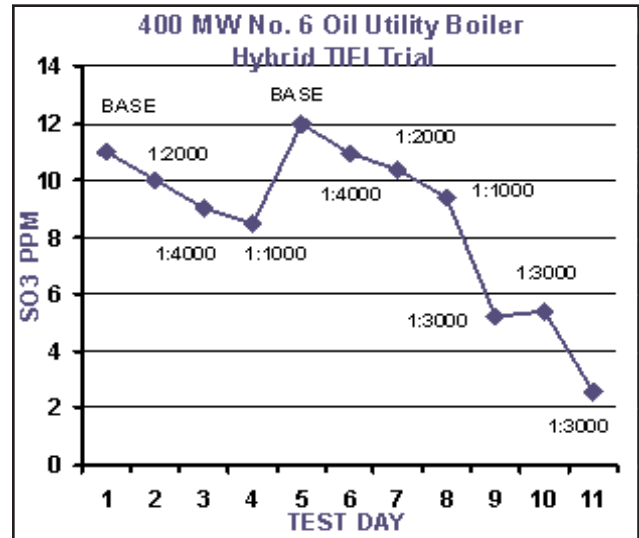


Figure M

The trial described above had the additional benefit of having eliminated the occurrence of a stack "blue plume" (see Figure L) while the Hybrid injection method was in progress. This was not unexpected, but the plant personnel were anxious to quantify the changes in SO₃ concentration that led to the elimination of blue plume. With this purpose in mind, a second trial period was arranged, with the addition of real time, in situ measurements of gaseous SO₃ made at the air heater outlet duct. These numbers are shown in Figure M.

The entire trial lasted only 12 hours; with the idea that changes in SO₃ concentration would be essentially instantaneous. In practice, the addition of reagent through TIFI application was able to reduce SO₃ levels very quickly, but not completely within the hour or two allotted to each dosage change. In fact, even after several hours of TIFI conditioning, the SO₃ levels were continuing to diminish. It is uncertain precisely how low the Hybrid combination of in-body and TIFI chemical injection could have brought the SO₃ concentration, but it is clear that after only 5 or 6 hours the SO₃ level was depressed below the 4-5 ppm level generally considered to be a minimum required to produce blue plume. It is speculated that some reduction in

SO₃ is immediate, as the conversion of SO₂ to SO₃ is interrupted within the gas stream. However, the continuing trailing off of SO₃ levels is attributed to a reduction of catalytic conversion by exposed iron surfaces, as the various super- and reheating banks of tubes are coated with magnesium.

Another benefit of the Hybrid reagent injection system can be reduced unburned carbon, or Loss on Ignition (LOI), and its effect on stack opacity. This effect is assigned to the ability of certain metals (Cu, Ca, Fe, Mg) to catalyze the combustion of carbon through a lowering of its ignition point.

This effect had been seen during the two trials examined above, and so it was decided to run a third, very short evaluation designed to measure just this effect on stack opacity. Since the plant's opacity meter is located within the stack, and blue plume forms once the flue gas leaves the stack, opacity measurements do not see the effect of lowered SO₃. Instead, they see the impact of various levels of unburned carbon adding an opaque, highly light scattering particulate to the gas stream.

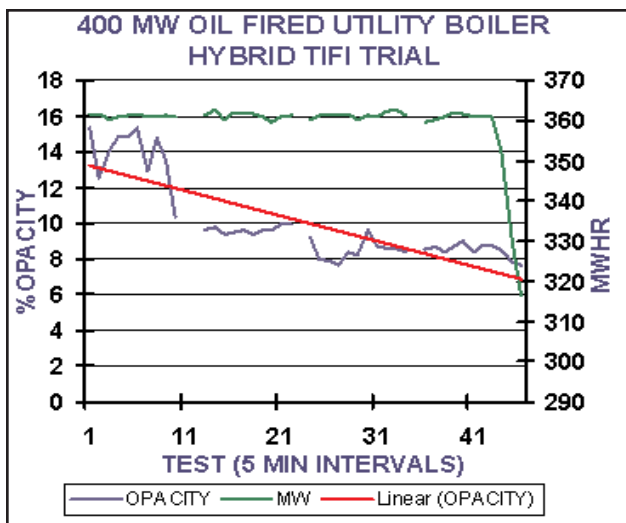


Figure N

The level of unburned carbon seen within an oil-fired boiler is impacted by a host of variables besides the introduction of a chemical agent. Understanding this, this trial was kept very short, and ran for only 230 minutes. Every effort was made to keep all operating conditions as consistent as possible, with unit load and excess O₂ being foremost among the parameters known to impact LOI levels.

With the excess oxygen at 0.2%, and the unit at 360 MW gross, the steady state baseline stack opacity ranged from about 12 to 15%. Then, targeted in-furnace injection was added to furnace, while subtracting a like amount from the in-body injection.

The total addition of chemical was at a rate of 1 part chemical: 2,000 parts fuel oil. This point is seen as first break in the opacity line in Figure N, and for the next 70 minutes the opacity is seen to hold at about 9.5%

The second break in the opacity line in Figure N signifies the point at which the total addition of chemical was increased to a rate of 1 part chemical : 1,500 parts fuel oil. For the remainder of this trial (about 60 minutes) the opacity averaged about 8.5%.

In summary, Hybrid injection of the chemical reagent was able to reduce stack opacity by about 30%, with no net increase in chemical usage. A subsequent increase in dosage of 33% was able to reduce stack opacity by nearly 40% from baseline (in-body alone) levels.

Case 4

In yet another example of the ability of a catalyst to reduce stack opacity, there is the data presented in Figure O. This data is from a series of combustion catalyst dosage changes made to a 130 MW unit located in the northeastern United States.

This unit is located on the outskirts of a suburban area, directly on the Atlantic coast. There is no electrostatic precipitator or any other type of particulate collection equipment, and small changes in boiler operation can bring the stack into non-compliance as stack opacity exceeds 10%. In particular, running the unit at maximum continuous rating can be a problem, as the excess oxygen levels must be kept low enough to keep NO_x levels in compliance, without causing smoking. This is a very delicate balance at this plant.

It was decided that a series one hour tests of baseline (zero chemical addition) and treated (1:1000 or 1:3000 parts) conditions would be conducted, with a third party testing crew performing in-situ particulate capture measurements. This is the data presented in Figure O.

The average particulate loading in the flue gas for the first one-hour baseline test period was found to be 0.093 lb particulate/mmBtu of oil burned. After this testing period, chemical injection was initiated at 1 part catalyst:3,000 parts fuel oil (volume:volume). The average particulate loading for the next one-hour period was found to be 0.062 lb/mmBtu. This is a 43% reduction from the baseline level.

Immediately following the one-hour testing period described above, the chemical dosage was increased to 1 part catalyst:1,000 parts fuel oil. Over the next

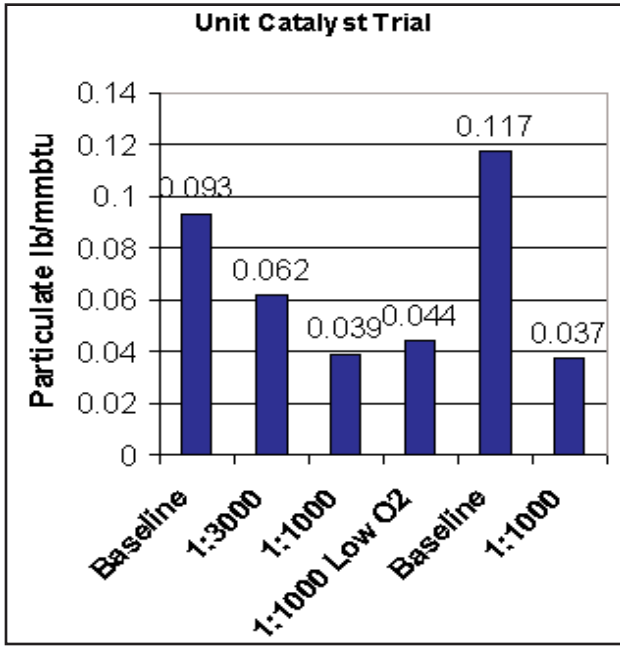


Figure O

hour, the average particulate loading was found to be 0.039 lb/mmBtu. This represents a further 37% reduction in particulate loading, or a total reduction of 58% from the baseline level. Operating conditions were kept as consistent as possible throughout this three-hour period.

Holding unit operation as level as possible, one parameter was deliberately changed for the next one hour testing period. Chemical addition was kept the same, but excess O₂ was decreased from 0.83% to 0.45%. This had the effect of increasing the average particulate loading from 0.039 to 0.044 lb/mmBtu (13%), but this new level of particulate loading remained at only 47% of the untreated level.

At this point, excess O₂ was returned to "normal", chemical injection was discontinued and baseline was reestablished at 0.117 lb/mmBtu for the next one-hour period. Catalyst injection was then reinstated at 1:1,000, and over the following one hour, particulate averaged 0.037 lb/mmBtu. This shows a 68% reduction, bringing the actual particulate loading back to a level very close to that seen previously.

IN CONCLUSION

There are a host of operational and compliance issues associated with oil-fired utility boilers that can be addressed through the addition of fireside chemistry. These include stack opacity, furnace slagging and fouling, unburned carbon (or LOI), nitrogen oxides (NO_x) and sulfur trioxide (SO₃).

Traditionally, fireside additives were added to the bulk fuel oil. Whether as a true solution, slurry, emulsion or dispersant, the various chemistries were mixed into the bulk fuel oil, and depended upon normal pumping and firing equipment to distribute the product throughout the furnace/boiler system. This In-Body injection scheme required that the chemical additive travel through the fireball, and it was assumed that equal distribution (if actually attainable) was the proper answer to all fireside conditions. There was no way to bias treatment toward the most troublesome areas, avoid areas which would not react well to the chosen chemistry, or preserve chemical efficacy for the further reaches of the boiler.

With the incorporation of Computational Fluid Dynamics modeling, Fuel Tech Inc. has been able to target chemical injection, and in so doing, achieve levels of fireside performance not previously within reach. Fuel Tech's patented Targeted In-Furnace Injection (TIFI) can subtly or dramatically alter chemical distribution to compensate for changing furnace operating conditions, and in so doing, provide levels of improvement not achievable with in-body or even alternate in-furnace technologies. Combination chemical strategies (TIFI/In-Body or Hybrid) take advantage of synergistic effects to achieve higher levels of slagging and fouling control or combustion improvement, than are otherwise possible. Additionally, this Hybrid approach can bring about in-situ reductions in gaseous SO₃ concentration, with subsequent elimination of the "blue plume" associated with acid misting.

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