

*Tips from experience*

## Unexpected FGD Safety Issues

By Melissa A. Allen, Tennessee Valley Authority (WPCA Advisor)

An unexpected safety issue exists with any open top scrubber slurry tank. If the scrubber slurry tank overflows, solids can build up on the sides of the vessel. Over time or during an outage, the solids can dry on the sides of the tank and break loose. When doing any work near open top scrubber tanks, special consideration should be taken to ensure there is no dried slurry overhead. The dried slurry is a safety concern. It could break loose at any time and seriously injure those working below. A dried chunk of scrubber slurry can weigh nearly 30 pounds. If it were to fall approximately 20 feet and hit someone below, the blow could cause compression of the neck, cause the victim to lose balance and fall, or a serious injury could result, such as a broken bone.



Figure 1: Solids Build up on Tank and Top of Piping

This same principle of dried slurry falling can be applied when inspecting scrubber ductwork and absorber towers. Dried slurry can also accumulate outside on scrubber equipment (Figure 1) as a result of piping and ductwork leaks.



Figure 2: (Top arrow) Dried Slurry Fell from Tank. (Bottom arrow) Manhole Entry

Always be aware of dried slurry and its potential to fall on you or someone else. Point this potential hazard out specifically in pre-job briefings where workers could be at risk. All identified areas where dried slurry is determined to be a safety hazard should be washed down at a safe distance with high pressure water before any work begins. Figure 2 demonstrates an area where this unexpected scrubber safety issue could exist. 🌐

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*Buy one ... get one free*

## SO<sub>3</sub> Removal as a Novel Mercury Control Strategy

By Jim Jarvis and Sterling Gray, URS Corporation

### INTRODUCTION

The U.S. utility industry is faced with the need to significantly reduce mercury emissions. Depending on location, individual power plants may be required to reduce existing mercury emissions by 90 percent or greater. To respond to this challenge, the industry has been engaged in research to quantify mercury emissions as a function of fuel type, determine the effectiveness of existing or planned emissions control equipment, and to develop and optimize new innovative control processes. In many cases, utilities are counting on their Flue Gas Desulfurization (FGD) scrubbers and Selective Catalytic Reduction (SCR) systems to control mercury. However, recent EPRI studies show that only 4 of 20 plants equipped with

SCR and FGD are actually achieving 90 percent mercury removal. Given the “overturn” of the Clean Air Mercury Rule (CAMR), even more stringent emission limits may be phased in, forcing utilities to implement supplemental measures such as Activated Carbon Injection (ACI) to further reduce their emissions. *continued on page 9*

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### Collection made easier

## The KNX™ Coal Additive Technology: A Simple Solution for Mercury Emissions Control

by J Buschmann, ALSTOM Environmental Control Systems, Dr. L Lindau, ALSTOM Environmental Control Systems, Prof. Dr-Ing B W Vosteen, Vosteen Consulting GmbH

### BACKGROUND

KNX™ coal additives and systems, available exclusively from ALSTOM, utilize a proprietary process wherein a bromine-containing chemical is added to the fuel in a coal-fired boiler. The KNX coal additive technology is operated to enhance mercury oxidation, which in turn results in an augmentation of mercury collection in downstream air pollution control equipment.

The KNX™ coal additive can provide reliable and consistent oxidation of mercury in the flue gases, without any known secondary effects. In many cases, this process significantly facilitates the collection of mercury from coal-fired boilers.

### NATURALLY OCCURRING BROMINE IN U.S. COALS

Bromine (Br) is a relatively sparsely occurring element, second to chlorine (Cl) among the halogens. The natural mass abundance ratio of Cl/Br is about 600 in the whole universe, whereas in the ocean the ratio is about 250. Based on the chemical similarity of the two elements, one could guess that since the Cl content of U.S. coals range from close to zero to 2000 ppm, the Br content would range from close to zero to merely some tens of ppm.

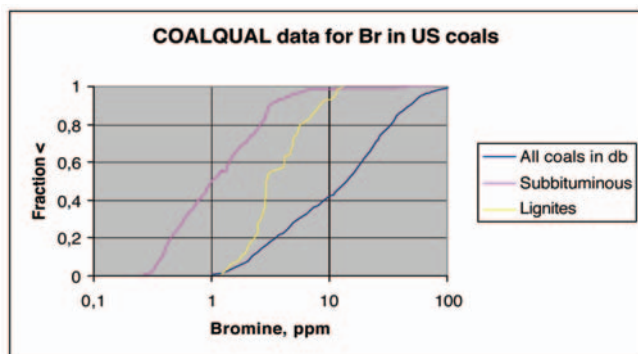


Figure 3: Distribution of Br in ppm in the coals listed in the COALQUAL database, <http://energy.er.usgs.gov>

The U.S. Geological Survey database COALQUAL gives Br data from analyzed coal specimens. The corresponding distribution of Br in the coals in the database is given in Figure 3.

According to this data, U.S. coals have Br contents between 0 and 100 ppm and the mean and median Br concentration of the coals are 20 and 14 ppm respectively. It is

moreover noted that the lignite coals (median 3 ppm) and the sub-bituminous (median 1-2 ppm) coals are significantly and systematically deficient in bromine as compared to average U.S. coals, and that the bituminous coals are systematically higher in Br than the lower rank coals.

The data in Figure 4 illustrates that there appears to be some correlation between Br and Cl in U.S. coals, at least to the extent that high Br levels are uncommon among the low Cl coals.

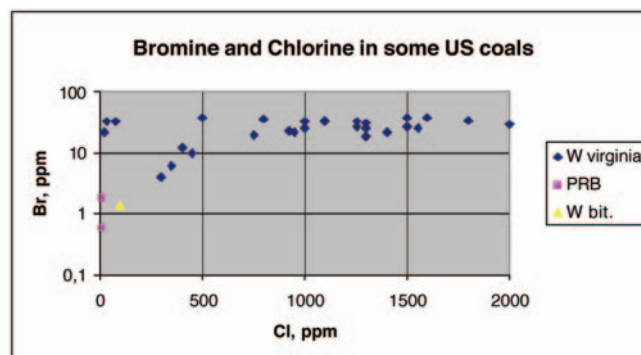
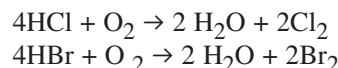


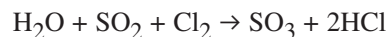
Figure 4: Chlorine and bromine in mainly W. Virginia coals (based on [www.wgs.wvnet.edu](http://www.wgs.wvnet.edu)).

### MERCURY HALOGENATION IN FLUE GASES

When coal is combusted, its content of mercury is volatilized and, at the combustion temperature, the stable species is metallic mercury. The stable form of the halogens at the high combustion temperature is the formation of acids (HCl, HBr). On cooling of the gases, the diatomic, molecular form of the halogens become stable according to the Deacon type of reactions:



The conversion of bromine starts at a higher temperature than the corresponding conversion of chlorine, so the kinetics of the Deacon are more favorable. Moreover, molecular chlorine (but not molecular bromine) is consumed during boiler passage by  $\text{SO}_2$  in the chlorine Griffin reaction:



Molecular bromine, on the other hand, is not consumed by  $\text{SO}_2$  within the boiler temperature range:

*continued on page 12*

## *Change can be for the better*

# Fuel Switching Effects on Coal Fired Units

by Scott Williams, Duke Energy (WPCA President)

Fuel property changes can have an effect on the performance of coal fired units. Due to economic conditions, plants are requested more and more to burn fuels outside the regular design basis of the equipment. Also, following the installation of scrubbers, fuels may be changed due to chloride and fluoride limitations, to name a few.

Ash property changes, associated with the changing fuels, can have dramatic effects on the performance of precipitators. It is often required to originate a precipitator performance model in order to analyze the effects of these fuel switches, in order to ensure that the appropriate emissions and opacity are maintained. The fuels analyzed very often have a wider range of properties/resistivities than currently burned.

### AN APPROPRIATE PROCEDURE WOULD BE AS FOLLOWS:

- ✓ Determine the required restrictions of both opacity and emissions. Understand that new downstream scrubbers may require additional particulate collection to properly function and make sale quality gypsum.
- ✓ Duplicate the existing functionality of the precipitator as close as possible based on years of PET data.
- ✓ Gather operating data for the unit in question. For example, LOI, fineness, flue gas temperature, gas flow, flue gas temperature stratification, particle size distribution, are all important parameters.
- ✓ Understand how much conservatism is required for transient conditions, such as boiler trips, mill blowback, sootblowing, etc.
- ✓ Model fuels that are a best estimate of future fuel properties. Many utilities are starting to blend fuels, and these too need to be modeled in the analysis.
- ✓ Include any limitations caused by SO<sub>x</sub> and NO<sub>x</sub>.

The final analysis should conclude with defined limitations on the fuels purchased for the existing precipitator.

### TYPICAL LIMITING FACTORS INCLUDE:

- ✓ The maximum amount of alumina plus silica.
- ✓ The maximum amount of calcium oxide plus magnesium oxide.
- ✓ Then minimum amount of iron oxide.
- ✓ High SO<sub>3</sub> fuels often lead to particulate reentrainment issues.

*It should also be noted that changes in fuel can also have notable effects on other portions of the plant.*

For example:

- ✓ Increase in ash content and/or increase alumina and silica can cause backpass erosion of the boiler.
- ✓ Hardness changes of the coal can cause mill grind issues.
- ✓ Fuel changes can also result in a change in boiler furnace slagging and boiler backpass fouling.
- ✓ Air heater pluggage can increase due to higher sulfur fuels and SCR operation
- ✓ Changes in fuel will require conditioning injection rate changes for both SO<sub>3</sub> and ammonia injection.
- ✓ More acid corrosion in duct and equipment
- ✓ "Blue Plume" from the FGD stack
- ✓ Higher ash coals can exceed the capability of the existing ash systems
- ✓ The expected life of an SCR catalyst can change.

In summary, it is important to evaluate the effects of any fuel change on the plant equipment. 🌐

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## *When getting rained out is a good thing*

# Making "Rain" in a Wet ESP Has Many Benefits

by Hardik Shah and John Caine, Southern Environmental, Inc.

A recent article, in WPCA News, Fall 2007, by Patrick Doonan, Buzz Reynolds, et. al., "An Old Technology For New Plants – SO<sub>3</sub> Control and Wet ESP Technology," presented an excellent discussion on how Wet ESPs are becoming the technology of choice for new boiler applications to remove fine particulate and H<sub>2</sub>SO<sub>4</sub> mist. In addition, Croll-Reynolds (now part of Siemens Environmental

Systems & Services) and others have demonstrated that by reducing the saturated gas temperature in a Wet Precipitator, using the "Condensing Wet Precipitator" concept, the metal plates can be kept clean in a gas upflow configuration. Also metal plate corrosion is reduced, and collection efficiency is enhanced.

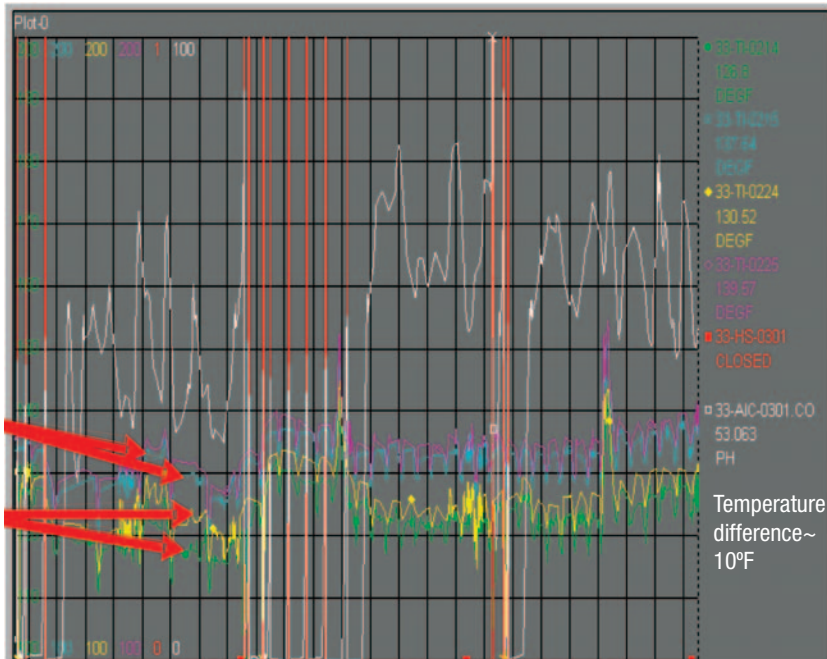


Figure 5: 24-hour PI chart of two-module membrane WESP at SSCC, Stevenson, AL  
(NOTE: Top 2 arrows at left show inlet gas temperatures;  
Bottom 2 arrows show outlet gas temperatures.)

Building on these concepts, the recently commercialized Southern Environmental Membrane Wet Electrostatic Precipitator achieves the advantages of a condensing WESP during its normal operation. This new type of wet precipitator, in which fabric membranes replace traditional metal collecting electrodes, has been developed/improved over the last six years. Extensive testing demonstrates that these membranes, made from materials that transport liquid by capillary action, are effective collecting electrodes. This capillary flow promotes well distributed water-flow over the membranes which is necessary for particle collection removal and transport. This solves a major historical problem in Wet ESPs which is to keep the collecting electrodes continuously clean. **The membrane Wet ESP operates in a condensing Wet ESP mode** - by creating a temperature difference of 30° - 40° F between the saturated gas stream and the cooled membrane irrigation water, the unit can easily reduce the saturated gas temperature by 5° to 10° F. The reduction in saturated gas temperature will condense water droplets out of gas stream. As seen in Figure 5, this has been demonstrated for the last three years in the commercial size unit at Stevenson, AL.

#### BENEFITS OF REDUCING SATURATED GAS TEMPERATURE OF GAS STREAM

- ➔ Particulate collection efficiency is enhanced: Like raindrops, the condensing water droplets form around the dust particle and H<sub>2</sub>SO<sub>4</sub> mist nuclei making them larger, therefore easier to collect.

- ➔ Supports lower cost materials of construction: A "raining" precipitator allows lower cost materials of construction for the casing.

A 1991 patent (No. 5,039,318) by Harry Johanson, describes how a "...condensing Wet Precip... cools the inner surfaces of the (metal) collector electrodes. This condensation of water from the gas stream essentially dilutes any acid build-up and effectively results in a lower concentration of corrosive substances in the condensate. This enables the collector electrodes to be made of steel which has relatively low alloy content."

Since the Membrane Wet ESP lowers the saturated gas temperature and condenses water out of the gas stream, this "washing/dilution" phenomenon occurs "naturally." In the absence of chlorides, this can significantly reduce the rate of corrosion. We have seen for example at the Unit in Stevenson (shown in Figure 6), handling ~ 20 PPM H<sub>2</sub>SO<sub>4</sub> mist, that after 3 years of continuous operation, there is no detectable corrosion on the 316L SS metal casing.

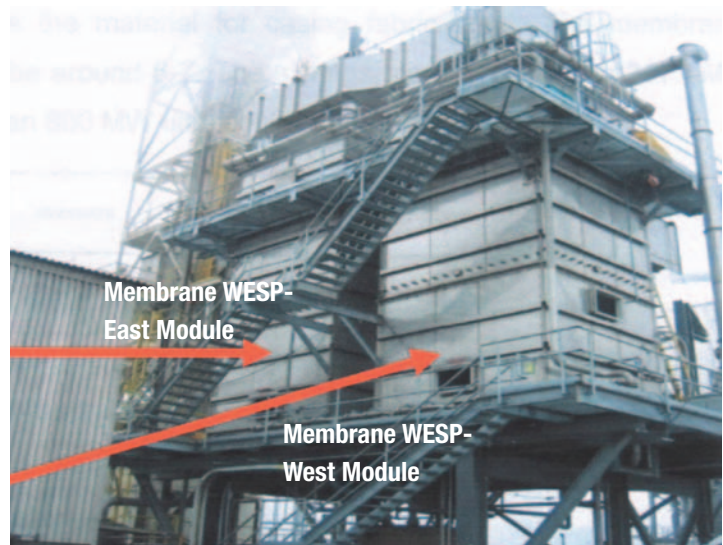


Figure 6: Picture of two-module membrane WESP at SSCC, Stevenson, AL

#### NO MAKE-UP WATER NECESSARY

The WESP system generally requires blow-down to get rid of suspended solids, and minimize any potential build-up of solids within the system. The blow-down requires an addition of make-up to maintain the system water balance. If make-up water comes from the plant, then it brings with it the down side of possibly adding chlorides to the system, which would then require costly alloys for construction for the WESP. Operation of the Membrane Wet ESP has demonstrated that by maintaining a temperature difference of 30°-40° F between the saturated gas stream and the irri-

		130F - 150F								
		MILD		MODERATE		SEVERE		VERY SEVERE		
CHLORIDE ppm		100	500	1,000	5,000	10,000	30,000	70,000	100,000	200,000
MILD	pH 6.5	TYPE 316 L STAINLESS STEEL		TYPE 317 LMN		DUPLEX STAINLESS STEEL 22% Cr		SUPER AUSTENITIC STAINLESS STEEL	NICKEL ALLOY 9% Mo	
MODERATE	pH 4.5			STAINLESS STEEL		SUPER DUPLEX STAINLESS STEEL 25% Cr		6% Mo	NICKEL CHROMIUM ALLOYS 13/16% Mo	
SEVERE	pH 2.0	TYPE 317 LMN STAINLESS STEEL						7% Mo		
VERY SEVERE	pH 1.0	TYPE 317 LMN STAINLESS STEEL		SUPER AUSTENITIC STAINLESS STEEL 6/7% Mo		NICKEL ALLOY 9% Mo				

Figure 7: Guidelines for selection of material in corrosive environment  
(Source: "Selection of Alloys for Air Pollution Control Equipment" by William L. Mathay)

gation water, the saturated gas stream can be cooled. Therefore, sufficient make-up water can easily be condensed out of the saturated gas stream to operate the WESP. In a full size utility unit, this could have quite a beneficial effect. By eliminating the need for plant make-up water; the only chlorides would be those coming over from the scrubber, which are estimated to be no more than 1 to 4 PPM, by saturated gas volume. This means that by reducing the saturated gas temperature by only 5° F, the recycle loop could be operated with no more than 100 PPM chlorides. As seen in Figure 7, this suggests that 316 L SS could confidently be used as the material for casing fabrication. The membrane irrigation liquid pH will be around 6-7. The savings, compared to say 317 LMN stainless steel alloy for an 800 MW unit, could exceed \$2,000,000.

#### NO BUILD-UP ON MEMBRANES:

There appears to be no need for a mist eliminator between the Wet FGD Scrubber and the downstream Membrane Wet ESP - An article in WPCA News Spring 2007, by Ron Richard, RE Consulting, entitled "Keeping a Mist Eliminator Clean," describes the problem of build up in a typical mist eliminator as caused by calcium sulfate crystals precipitating out of the saturated liquid on the mist eliminator blades:

*"A thin film of slurry tends to stay on the surface of the blades. Some of the water in this film can evaporate over time causing the calcium salts in the film to become more concentrated. If the concentration reaches the saturation point, calcium compounds will begin to precipitate out as crystals adhered to the blades."*

In the Membrane Wet ESP, however, since the membranes are irrigated continuously with relatively clean recycle water; it is not possible to have build-up of these CaSO<sub>4</sub> crystals on the membranes since the liquid will never reach the crystallization point. Therefore, no mist eliminator will be necessary.

We demonstrated this in a six-month test at Xcel's Sherburne County Generating Station by draping membranes over the metal plates on a side-by-side basis. As seen in Figure 8, the metal plates built up after six-months with calcium sulfates (as expected) and the membranes did not build up.

#### CONCLUSION:

These operational advantages and cost savings of the Membrane WESP change the perception of Wet Electrostatic Precipitators to the point where they can be considered a cost effective multi pollutant control device.



Figure 8: Membrane build-up test at NSP's Sherco Station

#### ADDITIONAL NOTES:

After 3 yrs. of continuous operation at ~103,000 ACFM Smurfit Stone Plant there appears to be no degradation of the membranes. In October '08, a new Membrane Wet ESP Unit will be started up on an Acid Plant. 🌐


For more information, contact Hardik Shah or John Caine at [hshah@sei-group.com](mailto:hshah@sei-group.com) or [jcaine@sei-group.com](mailto:jcaine@sei-group.com)

## *Everything under one roof* **Argillon Delivers Turn-key Plant for Unigra**

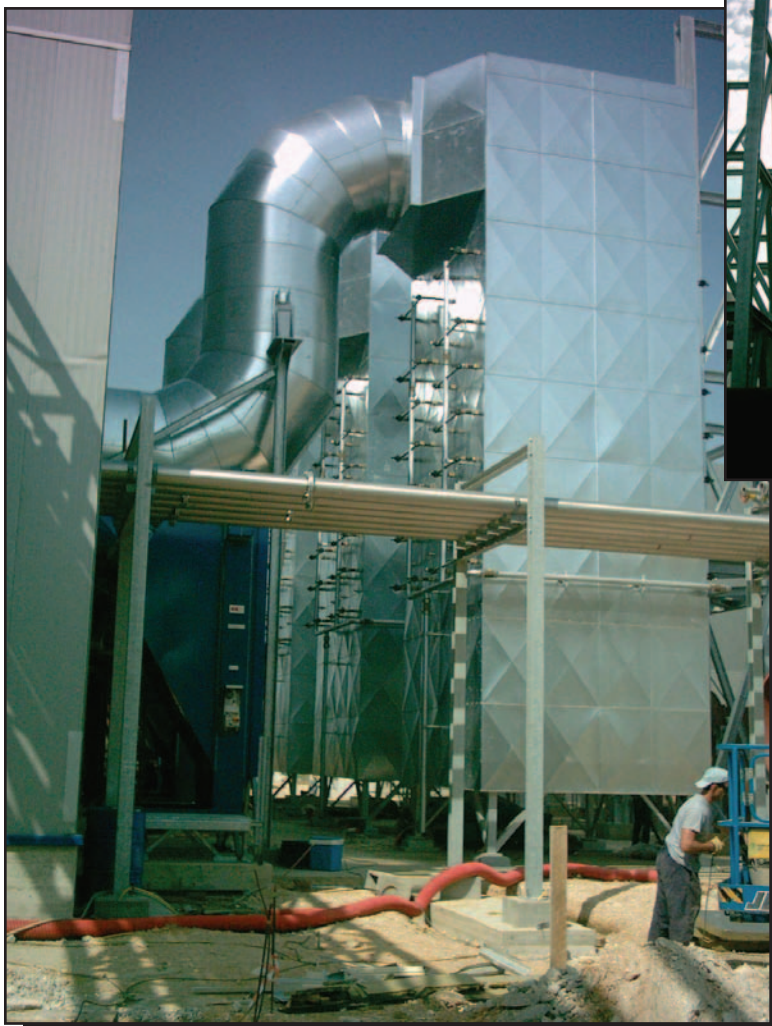
by Bahram Dormichian, Argillon

At the beginning of 2008, Unigra s.p.a., based in Conselice, Italy, assigned Argillon GmbH with the planning, delivery, assembly and commissioning of a turn-key full-scale plant incorporating the Argillon SINOx<sup>®</sup> system. Since October, assembly of the plant has been completed and is now awaiting the release for commissioning. (See Figures 9, 10, 11)

The plant has nine treatment stages. Powered by bio oil, the power generation plant consists primarily of three vegetable oil-powered Wärtsilä motors each producing 18 megawatts of electrical power, a corresponding turbo alternating current generator and a transformer. This is joined by a recovery boiler and waste heat boiler.


Argillon delivered three reactors in temperature-resistant steel, equipped with corresponding catalysts and soot blowers for the plant. Pumping and dosing stations for the ammonia water solution enable the addition of the reducing agent in dual fluid nozzles. In addition, Argillon is also responsible for the complete supply of controls and other electrical, measurement and control equipment for the power plant. 

*For more information, contact Bahram Dormichian, Argillon, at [Bahram.Dormichian@argillon.com](mailto:Bahram.Dormichian@argillon.com)*



Figures 9, 10 and 11: Partial Views of Reactor

## ICAC Releases Guidelines for Evaluation and Selecting Wet Electrostatic Precipitators Equipment

**Release Date: 2/26/08 at Washington DC:** The Institute of Clean Air Companies, Inc. (ICAC), the national association of stationary source air pollution control and monitoring technology companies, released guidance on how to purchase and compare bids of wet electrostatic precipitator (WESP) equipment for electric power and industrial applications. This guidance will improve the industry-accepted understanding of engineering principles and options for WESP designs, and support technology considerations in the bid-purchase process. Although wet electrostatic precipitator technology has been applied since the early part of the 20th century, an increasing number of electric power and industrial applications are now requiring the installation of emissions control systems to address fine particulate and sulfuric acid mist emissions. This document was prepared by WESP manufacturers to help end users collect the necessary data to solicit bids from vendors, prepare bid documents, and evaluate bids received. Explanations and commentary are also included to aid the purchaser in writing complete specifications and properly define parameters needed for WESP design. The document furthers the contents of ICAC Bid Evaluation Form for Dry Electrostatic Precipitators, ICAC-EP-10, adopted in 1995, to focus on the requirements for wet electrostatic precipitator technology. 

Contact ICAC at 202-457-0911 or [icacinfo@icac.com](mailto:icacinfo@icac.com) to request a copy of the document. The document is available at no charge to ICAC members and government officials or for \$20 to others.

*Get the most from what you have*

## Optimizing Electrostatic Precipitator Rapper Operation

by Peter Aa, Redkoh Industries

Modern electrostatic precipitator microprocessor based rapper controls provide a large number of control parameters in order to allow a high degree of flexibility in optimizing rapper settings (and minimizing opacity base line and excursions.) This high degree of flexibility does, however, produce some confusion when trying to program the controller for timing, and cleaning energy.

### GENERAL THEORY OF RAPPER OPTIMIZATION

In an ideal world, the gas and particulate would enter a precipitator in a completely uniform manner. That is, the gas flow and particulate loading would be exactly the same from top to bottom and from side to side. That being the case, the collection of the particulate would also be uniform, and knowing the particulate loading (gr/acfm), the volume (acfm), and the square feet of collecting and discharge are per electrical field, we could calculate how long it would take to collect a given depth of particulate build-up on the surfaces. Knowing this we could easily determine the rapping cycle to keep build-ups below a desired level (say 1/4" to 1/2"). It would also be easy to determine how much energy is required to keep the internals clean since all areas would require the same energy.

Unfortunately, we do not live in an ideal world, so things become a bit more difficult. Trying to calculate build-up lev-

els and cleaning energy is basically fruitless. A trial and error approach becomes the most efficient means of optimization.

### HOW TO JUDGE IF RAPPING IS OPTIMIZED

The best way to optimize rapper operation, and the precipitator efficiency, is to perform programmable parameter changes while observing the instantaneous readings obtained from the flue or stack opacity meter. If an opacity meter is not presently installed on the stack or flue, it is strongly recommended that one be installed. It is also recommended that a strip chart showing instantaneous opacity levels be used. Where two or more precipitators feed a common stack, separate opacity meters should be installed in the outlet flue from each precipitator. Without an opacity meter it is extremely difficult to judge when the rapper control, and the rappers, are optimized. Opacity meters installed in flue work do not have to be EPA compliant since they are being used for tuning and not reporting. These non-compliant opacity meters are fairly inexpensive and provide excellent response to fine tuning activities. Without opacity meters, visual stack observations will have to be made.

*The optimum rapper program will produce the smoothest opacity strip chart reading at the lowest opacity level, with the fewest "spikes".*

## WHERE TO START OPTIMIZING

There are probably as many theories of where to start as there are precipitator consultants. Here is one procedure to get started.

- If you are not sure of the state of the cleanliness of your internals, put the rapping system into a maintenance or sequence mode. Let the system perform a cleanup as best as it can.
- If you believe you have a clean Precip, the above step can be left out.
- Turn the rapping system off for a few minutes to obtain a base level. (Figure 12). The opacity trace obtained is the best you will achieve for the existing process conditions (this is now your target).

We can't leave the rapping system this way because particulate will start to build-up on the precipitator collecting plates and discharge electrodes and eventually cause sparking and re-entrainment that will reduce operating levels and cause the base opacity level to rise, eventually to unacceptable levels. So we must eventually turn the rapping system back on.

For rappers where the plunger lift can be measured, start by setting the lifts for all rappers, except the outlet field rappers, at a 6-inch lift. The outlet field rappers should be set for a 3-inch lift (Some installations have rapper rod insulators that require the lift on the high tension frames to be limited. If this is the case, make sure that the control is never programmed to exceed the manufacturer's recommended maximum lift). For cleaning devices where plunger lift can not be measured, set the energy level to about 50% for all fields except the outlet, and set the outlet to about 25%.

Program the cycle clock for progressively longer cycle times from the inlet field to the outlet field. A typical initial setting would be:

- 1st field cycle time 3 minutes (each device is rapped once every 3 minutes)
- 2nd field cycle time 8 minutes
- 3rd field cycle time 13 minutes
- 4th field cycle time 18 minutes
- 5th field cycle time 23 minutes

If the opacity level initially drops but starts to climb back up with time, the cycle times are probably too slow. If the opacity initially increases and does not come back down, the cycle times are probably too fast. When setting the cycle times consider that the time between raps should be long

enough to allow particulate collection to occur to a "nominal" build up that will not promote sparking before the particulate is rapped off the electrodes. It is not desirable to try and keep the collecting or discharge electrodes "metal" clean.

The optimum cycle time setting for each field is obtained by trying both longer and shorter cycle times on each precipitator field until the lowest opacity that remains constant over time is reached. It is recommended that one field be optimized at a time. Work from the inlet to the outlet and complete optimization of one field before moving to the next.

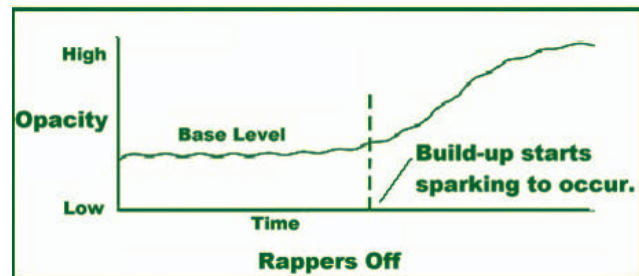


Figure 12 Opacity with Rapping System Turned Off

Try to do the evaluation of your changes under reasonably constant and similar process conditions. Allow at least an hour after changes have been made before evaluating the effects of your work.

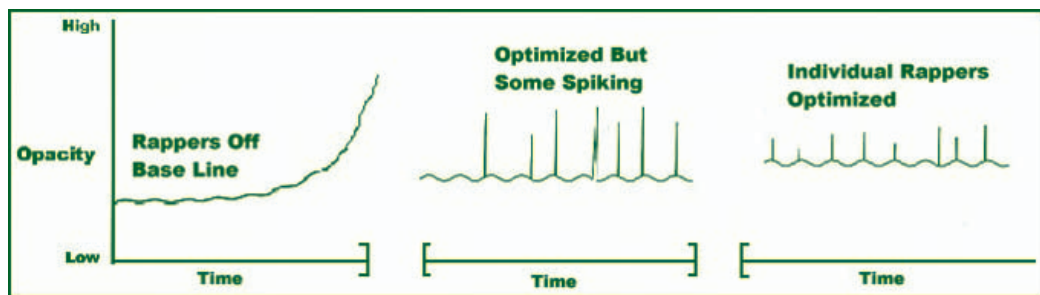


Figure 13: Reduction in the Rapping Intensity May Cause the Baseline Opacity to Rise

Once the lowest opacity base line has been established, any remaining rapping spikes can be reduced in size, or eliminated, by adjusting individual rapper intensities. By careful observation of the timing of the opacity spikes, the rapper that causes a spike can be identified.

As a consequence of trying to reduce spiking, reduction in the rapping intensity may cause the baseline opacity to rise. Balance the relationship between the spiking and the baseline as best you can. See Figure 13.

## OUTLET FIELD SENSITIVITY

The outlet field rappers were initially set for a lower plunger lift for two reasons:


- ① The outlet field is the last field of charging and collection of particulate. Any particulate that gets out of this field goes past the opacity meter. Some of the particulate that is cleaned off the collecting plates is re-entrained into the gas stream and carried out of the precipitator causing an opacity spike.
- ② The outlet field typically contains the smallest particle size of collected particulate. This fine particulate, if not allowed sufficient time on the collecting plates to agglomerate into larger particles, will easily re-entrain and be carried out of the precipitator causing an opacity spike.

Rapping energy greater than the minimum required to dislodge the particulate from the collecting plate will also cause the particulate to be re-entrained into the gas flow and create an opacity spike.

*Extra time spent on optimizing the outlet field rappers is well worth the effort.*

### HIGH VOLTAGE FRAME RAPPERS

Very little has been said about optimizing high voltage frame rappers. The same theory applies to the HV rappers as to the collecting plate rappers except the timing of the HV cycle is typically much faster (maybe 3 minutes in the inlet increasing 30 seconds for each field towards the outlet).

Since the surface area of a discharge electrode is so much less than that of the collecting plate, re-entrainment from them is of far less concern. 

*For more information, contact Peter Aa, Redkoh, at [peter.aa@redkoh.com](mailto:peter.aa@redkoh.com)*

## SO<sub>3</sub> Removal as a Novel Mercury Control Strategy

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However, SO<sub>3</sub> could foul this strategy and potentially jeopardize the ability of some coal-fired power plants to achieve compliance.

There is a growing consensus among emissions control engineers and researchers that the presence of SO<sub>3</sub> in the flue gas from coal-fired boilers reduces the capacity of fly ash and/or activated carbon to adsorb gaseous mercury species. Indeed, recent full-scale testing has confirmed the impacts of SO<sub>3</sub>, including testing where SO<sub>3</sub> was removed with alkali sorbents and testing where SO<sub>3</sub> was injected into the flue gas for particulate conditioning. If SO<sub>3</sub> threatens the feasibility of low-capital-cost approaches involving activated carbon, utilities will be forced to explore other more costly options. One example is the use of catalytic oxidation of the mercury, with catalysts either within the SCR or elsewhere along the flue gas path, to boost mercury removal efficiencies in wet scrubbers. However, catalytic oxidation of mercury using SCR catalysts may have unintended consequences such as the formation of additional flue gas SO<sub>3</sub>, which can increase air heater plugging and downstream corrosion, and may lead to visible emissions (a “blue” sulfuric acid mist plume).

A better alternative may be to remove the SO<sub>3</sub> so that it doesn't interfere with the removal of mercury via the fly ash and/or activated carbon. This approach has the further advantage of avoiding the SO<sub>3</sub>-related operational problems listed above. Further, removing SO<sub>3</sub> can allow a reduction in the air heater outlet temperature, which can improve heat rate and further increase the capacity of sorbents to capture

mercury. But how much of the SO<sub>3</sub> must be removed, and are there unanticipated consequences? This article addresses these questions based on recent research results and over five years of commercial operating experience removing SO<sub>3</sub> from boiler flue gas.

### DEFINING THE MERCURY CHALLENGE

The mercury control challenge is complicated by the fact that mercury in flue gas can exist in more than one form. Specifically, mercury can exist in the gas phase in either the elemental state (Hg<sup>0</sup>) or in the oxidized state (Hg<sup>2+</sup>). Research has shown that for low-sulfur, low-chloride coals, the majority of the mercury tends to be in the elemental state. In high-sulfur, high-chloride situations, a significant fraction of the mercury exists in the oxidized state. Furthermore, it has been found that SCR catalysts and other catalysts can, to varying degrees, convert elemental mercury to the oxidized state. Oxidized mercury can be removed effectively in wet FGD systems (in contrast, elemental mercury is not soluble and simply passes through the scrubber). Consequently, many utilities are relying on the combination of SCR and FGD to control mercury emissions.

Unfortunately, the SCR/FGD strategy may not be as widely applicable as it might seem. For example, many smaller boilers are not equipped with both SCR and FGD equipment. In addition, mercury removed by the FGD may be re-emitted from the scrubber (reducing the control efficiency) due to the chemical reduction of some of the absorbed oxidized mercury. Finally, the presence of mercury in the scrubber waste and byproduct materials is an area of increasing concern. The fate of mercury in the gypsum byproduct is

also an issue, and there are concerns regarding mercury emissions during gypsum wallboard production.

As a consequence of the limitations of the SCR/FGD approach, other technologies are being evaluated and developed to provide the industry with a wider range of alternatives. Activated carbon injection has been found to be effective in removing both the elemental and oxidized mercury species. This technology removes mercury upstream of the scrubber (decreasing the mercury contained in the gypsum byproduct), and has lower capital costs than other alternatives. Although ACI has emerged as the currently preferred technology for the low-sulfur, low-chloride coal situations, it may also see an application on boilers firing high-sulfur, high-chloride coals to assure compliance with more stringent mercury emission limits.

### SO<sub>3</sub> FOULS THE COMPLIANCE STRATEGY

SO<sub>3</sub> is an important consideration for compliance strategies based on both ACI and SCR/FGD. Conceptually, it is important to recognize that oxidation of SO<sub>2</sub> to SO<sub>3</sub> is also promoted by SCR catalysts, and designing a catalyst for both low oxidation of SO<sub>2</sub> and high oxidation of mercury may be challenging, especially if extremely high mercury oxidation rates are desired. One option is to use SO<sub>3</sub> control to help optimize the SCR/FGD approach. Specifically, the catalyst could be designed for high mercury oxidation, and then an SO<sub>3</sub> control process could be used to remove the additional SO<sub>3</sub> produced by the catalyst.

SO<sub>3</sub> will play an equally important role in the application of ACI technology. Research results from multiple test programs are now clearly showing that SO<sub>3</sub>, present in higher-sulfur flue gas or added to enhance particulate control, interferes with the ability of the carbon to adsorb mercury. In simple terms, SO<sub>3</sub> and mercury compete for the active adsorption sites on the carbon particle (and for that matter, on the carbon contained in the fly ash itself).

Several years ago, URS and Codan Development LLC observed that the retention of mercury on fly ash was strongly affected by the presence of SO<sub>3</sub>. These results were developed based on the analysis of ESP fly ash samples obtained from five different units where a high-efficiency SO<sub>3</sub> control process (SBS Injection™) was in operation. The SBS Injection™ technology involves injection of a sodium-based solution such as soda ash into the duct either upstream or downstream of the air heater. The sodium-based particulate reacts to remove the SO<sub>3</sub>, and is then removed in the ESP or fabric filter with the fly ash. By turning the SBS technology on and off, and by varying the reagent feed ratio, correlations were obtained at all of these units for the amount of mercury retained on the ash as a function of the SO<sub>3</sub> concentration in the flue gas.

As illustrated in Figure 14, the amount of mercury retained on the native fly ash increased substantially when the amount of SO<sub>3</sub> in the flue gas was significantly reduced. When very low levels of SO<sub>3</sub> were achieved (less than 3 ppmv), the amount of mercury retained on the fly ash increased dramatically. In one case, the projected mercury removal increased from less than 10 percent to greater than 50 percent.

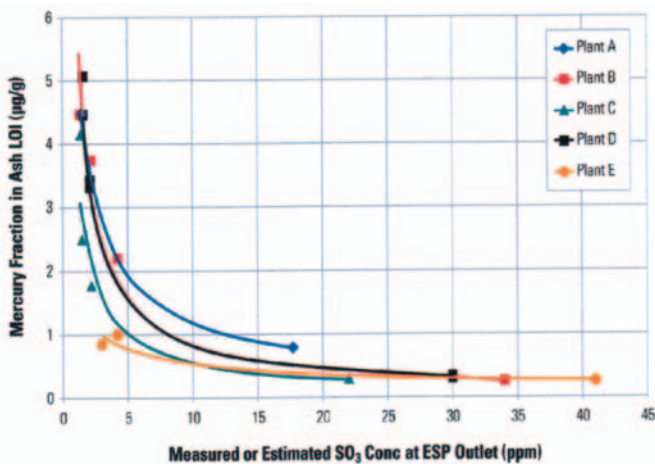


Figure 14: Mercury removal by carbon in ash with SBS Injection™

These results described above provided the impetus to conduct additional testing to explore the relationships between SO<sub>3</sub> concentration and mercury adsorption. In a recent project, a systematic evaluation of the impact of SO<sub>3</sub> on ACI performance was conducted at Southern Company's Mercury Research Center (MRC) located at Gulf Power's Plant Crist in Pensacola, Florida. The testing made use of the MRC's unique capability to manipulate key process variables such as SO<sub>3</sub> concentration, activated carbon injection rate and air heater outlet temperature over wide ranges, and the work was sponsored, in part, by the Electric Power Research Institute (EPRI) and Southern Company. The testing demonstrated the dramatic effect of SO<sub>3</sub> on mercury

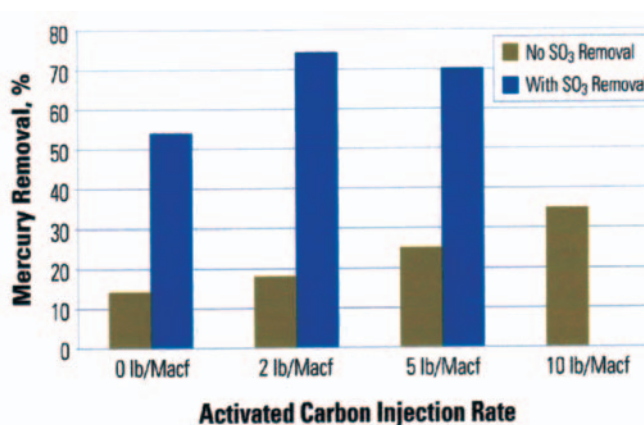


Figure 15: Effect of SO<sub>3</sub> removal on mercury removal efficiency

capture, and the beneficial impact of SO<sub>3</sub> removal on the mercury removal capability of both the carbon in the native fly ash and the activated carbon. Indeed, when high-efficiency SO<sub>3</sub> removal (SBS Injection™) was employed, the mercury removal capability of the native ash alone was greater than that with activated carbon and no SO<sub>3</sub> controls.

Utility	Plant	MW	Injection Location	Design SO <sub>3</sub> ppm	SO <sub>3</sub> Removal	Operating Season	Startup Date
FirstEnergy	Mansfield 1-3	3x860	Air Heater Inlet	80	90-98%	Year-round	March 2003
TVA	Widows Creek 7	550	Air Heater Inlet	54	90-95%	Ozone	April 2003
NIPSCO	Bailey 8	365	Air Heater Outlet	59	90%	Ozone	April 2004
Vectren	Culley 3	287	SCR Outlet	48	90-96%	Year-round	July 2004
PPL	Montour 1/2	2x765	Air Heater Outlet	42	90%	Ozone	August 2004
Cinergy	Gibson 1-5	5x650	Air Heater Outlet	90	90-98%	Ozone	April 2005
DPL	Killen 2	635	Economizer/SCR Outlet	30	>90%	Year-round	October 2007
IPL	Harding St. 7	465	SCR Outlet	58	>90%	Year-round	November 2007
NIPSCO	Bailey 7	175	SCR Outlet	58	>90%	Year-round	April 2008

Figure 16: Summary of Commercial SBS Injection™ System

A summary of key MRC tests results is shown in Figure 15. The data summarized in Figure 15 include 28 tests where the initial SO<sub>3</sub> concentration in the flue gas was elevated (to between 35 and 50 ppm). ACI rates ranged between 0 and 10 lb/Macf, and mercury removal efficiencies shown in the figure represent the removals measured between the ACI location (just upstream of the ESP) and the ESP outlet. With no SO<sub>3</sub> control, the mercury removal efficiency remained below 35%, even at the relatively high 10 lb/Macf carbon injection rate. On the other hand, by removing the SO<sub>3</sub>, mercury removal efficiencies were over 50% with no activated carbon injection at all (mercury removal in this case resulted from adsorption of the mercury onto the carbon in the fly ash). Mercury removal efficiencies rose to above 70% with SO<sub>3</sub> removal and as little as 2 lb/Macf of activated carbon.

For a large, coal-fired power plant, a mercury control strategy involving SO<sub>3</sub> removal could reduce activated carbon costs by several million dollars per year or perhaps even eliminate the need for ACI entirely. As an example, the annual carbon costs for a 500 MW boiler at an injection rate of 10 lb/Macf would be about \$3.4 million while a combination of SO<sub>3</sub> control and 2 lb/Macf of carbon would be about \$1.3 million.

### SO<sub>3</sub> CONTROLS PROVIDE A SOLUTION

The test results presented above, along with a growing body of data collected by other investigators, show that SO<sub>3</sub> is an important consideration in the use of ACI. Reducing the SO<sub>3</sub> concentration to very low levels can boost mercury removal by increasing the sorption capacity of activated carbon, as well as the unburned carbon in the native fly ash. But how low do you have to go - and how do you get there?

Research has shown that only when the SO<sub>3</sub> concentration

is reduced to 1 - 3 ppm at the ESP does mercury removal increase dramatically. Researchers also believe that it is important to remove as much of the SO<sub>3</sub> as possible prior to the air heater, or at least prior to activated carbon injection. The SBS Injection process, applied to more than a dozen boilers, has been demonstrated to reduce SO<sub>3</sub> levels to less than 5 ppm prior to the air heater, less than 3 ppm at the ESP outlet, and to about 1 ppm after the FGD system. Commercial installations of the SBS Injection technology are shown in Figure 16.


The removal of SO<sub>3</sub> upstream of the air heater offers additional benefits with respect to mercury reduction and unit efficiency. Specifically, low air heater inlet SO<sub>3</sub> concentrations allow a reduction in the air heater exit temperature and a corresponding increase in unit efficiency. Flue gas temperatures at the air heater outlet must be kept above about 320°F for units firing medium- to high-sulfur coals. At lower temperatures, excessive sulfuric acid condensation results in air heater fouling and corrosion.

High efficiency SO<sub>3</sub> removal allows air heater outlet temperatures to be reduced to as low as 250°F. In addition to improving unit heat rate, the adsorption capacity of activated carbon increases at lower temperatures. Thus, high-efficiency SO<sub>3</sub> removal, employed upstream of the air heater, allows further reductions in mercury removal together with the opportunity to improve efficiency and reduce CO<sub>2</sub> emissions.

### SUMMARY

The effective removal of SO<sub>3</sub>, upstream of the air heater and activated carbon injection, has the potential to achieve a number of benefits, including the following:

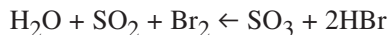
- ◆ A reduction in the activated carbon rate needed to achieve a specific mercury removal efficiency;
- ◆ An increase in the amount of mercury removed by the fly ash carbon;
- ◆ A reduction in the air heater exit temperature, which will improve mercury removal and increase boiler efficiency;
- ◆ An effective means to remove mercury upstream of the FGD system, which will reduce mercury levels in the FGD gypsum and wastewater stream; and
- ◆ A reduction in mercury re-emissions from the FGD system.

Given these benefits, SO<sub>3</sub> removal may become a critical and cost-effective strategy for many plants to consistently achieve greater than 90 percent mercury removal, and thus compliance with anticipated mercury regulations. 

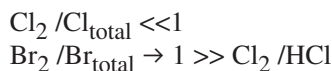
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## A Simple Solution for Mercury Emissions Control

continued from page 2



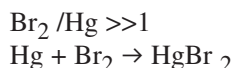
The net effect of these reactions is that after the combustion zone, there is much more molecular bromine as compared to the corresponding quantities of molecular chlorine:



So although for practically all coals, the chlorine in the coal is far higher than the bromine in the coal, the amount of molecular bromine ( $\text{Br}_2$ ) in the flue gas may many times be higher than the amount of molecular chlorine ( $\text{Cl}_2$ ) in the flue gas downstream the combustion zone. It is also observed that in practically all combustion processes, almost all the chlorine exists as HCl at the boiler back end.

When the gases have been cooled down below approximately 1300° F, and direct halogenation of the metallic mercury is becoming thermodynamically favorable, there will be a very small supply of molecular  $\text{Cl}_2$  in the flue gases.

Whereas if the bromine content of the coal is high enough, there will be ample supply of  $\text{Br}_2$  (typically 1 to 10 ppm in coal) to oxidize the typical amounts of mercury prevailing in coal flue gases:



It has been observed that the inherent (in the existing air pollution control equipment) collection of mercury from U.S. power plants burning Eastern bituminous coals is significantly higher than in the plants burning sub-bituminous and lignite coals. In the ICR data collected by the U.S. E.P.A. in 1999, the average mercury collection efficiency for existing plants without any dedicated measures for mercury control equipped with cold-side ESP's was 16% and 46% for the plants burning PRB and Eastern bituminous coals respectively. And in the plants equipped with spray drying absorption and bag filter, the figures were 25% and a surprising 98%, respectively.

It is generally, but incorrectly, believed that this is due to the effect of the higher chlorine of the bituminous type of coals. An alternative explanation first advanced by Vosteen (B. Vosteen, Air Quality IV, 2003) and supported by the above reasoning, is that the critical species for the halogenation of mercury is not chlorine (at the level of some

1000 ppm in the coal) but rather bromine (at the level of some tens of ppm in the coal) is the crucial factor.

This notion has the important practical corollary that for coals that show low mercury oxidation, this can be changed by the addition of small amounts of bromine compounds to the hot side of the boiler, whereby a predictable halogenation of mercury will be achieved at the cold end of the boiler. This change is an important step to solve the challenging problem of mercury control on most of the coal-fired boilers burning the lower rank coals in the U.S.A. The addition of bromine to PRB and lignite coals renders the problem of mercury control similar to that of boilers that are operated with the high halogen, Eastern bituminous coals.

### EXPERIENCE BASE

The process of bromine addition to improve mercury control has been applied since 2001 to four different chemical waste incinerator plants in Germany (equipped with ESP, scrubbers and SCR,) and since 2004 to two sewage sludge incinerators. The experience to date with bromine addition is that there has been reliable mercury oxidation and collection, and no side effects.

The process was recently tested, full-scale, on coal fired utility boilers under U.S.-D.O.E. contract No. DE-FC26-03NT41986 at three different sites burning PRB coals:

- Holcomb Station in Kansas, equipped with spray-drying absorption and bag filter as air pollution control
- Laramie River Station Unit 3 equipped with spray-drying absorption and ESP
- Meramec Station Unit 2 equipped with ESP only

The KNX coal additive technology is operated to promote mercury oxidation. To collect the oxidized mercury, some active collection mechanism is also needed. In the first two cases, this has been accomplished by the addition of modest amounts of pulverized activated carbon (PAC). In the case of the Meramec unit, the UBC (UnBurnt Carbon) content in the ash was sufficient, without the need to inject any additional PAC, to provide high mercury collection efficiency, in one case > 90%.

The addition of KNX coal additive in these units was done either by spraying on the coal, on the coal conveyor during silo charging, or in the coal feeders upstream of the mills. The KNX additive must be evenly distributed on the coal to provide uniform distribution of the active chemical of the KNX additive throughout the flue gas - the global mix-

ing in a large coal-fired boiler is limited. Because a comparatively small flow of the active chemical of the KNX additive was required - even on a large plant - metered pumping from 50 gal drums of bromide compound in solution was sufficient.

The results from the Holcomb unit indicate that the use of the KNX additive increased mercury oxidation at the air preheater outlet: from 20% without addition of the KNX coal additive to more than 80% with only a modest addition of the KNX additive. The fly ash from the Holcomb unit has a very low UBC and very low native mercury collection efficiency. To get high mercury collection efficiency, a small amount of activated carbon injection was necessary. At an addition of 1 lbs/MMacf of ordinary PAC, the mercury collection efficiency was measured between 40 and 60% without the addition of the KNX additive. Under the same conditions, with the addition of the KNX additive, the mercury removal efficiency was measured at 86%. The data indicates that the application of the KNX coal additive combined with injection of common activated carbon achieved results similar to those obtained when injecting the newly developed impregnated activated carbons.

The results at the Laramie River station were comparable. But, the results were achieved with higher injection rates of PAC, since the ESP is considerably less efficient in the mercury control aspect than the fabric filter.

At the Meramec plant, the UBC in the fly ash is rather high for a PRB firing case with figures varying between 2 and 4%. This carbon material is relatively effective for controlling oxidized mercury. Prior to parametric testing of the Meramec unit, the baseline native mercury removal was measured at around 40%. With the addition of the KNX additive and the natural carbon in the fly ash, the mercury collection efficiency varied with UBC but was typically 80% and was measured in one parametric test as high as 91%.

Further utilization of the KNX technology in different applications is currently being planned in conjunction with different ALSTOM customers. The results of these future uses of the KNX technology are expected to enable to refine and optimize mercury control for a variety of the back-end air pollution control configurations currently being applied for both green field and brown field projects in development.

#### **POSSIBLE SECONDARY EFFECTS OF COAL Br CONTENT ADJUSTMENT**

The secondary effects of retrofitting the KNX technology to a system normally operating with a low bromine coal are basically the same as switching to a coal with higher native

bromine content. Very few, if any, negative effects of higher Br as compared to lower Br coals are known.

In examining this matter, the first obvious question is where does the bromine go in the system? The literature is sparse regarding this matter, since bromine in connection with coal-fired power plants has rarely if ever before been an issue. Some data regarding the fate of Br and the other halogens in Dutch power plants equipped with SCR, ESP and wet flue gas desulphurization are known:

	<b>F</b>	<b>Cl</b>	<b>Br</b>
Coal (back-calculated), ppm	20	470	10
Flue gas, mg/nm <sup>3</sup>	2	47	1
<b>Mass streams in the system:</b>			
Collected in flyash, % of total	15	1	13
Gypsum, % of total	35	1	0.2
Sludge, % of total	24	1	0.7
Water discharge, % of total	0.4	88	82
Stack, % of total	25	9	4

(Source: R Meij: "Mass Balance Study...", presented at IEA Trace Element Workshop, University of Warwick Sept. 6, 1999.)

On the cold side of the boiler, one can then say that in the ESP, the Br behaves like F, and in the scrubber, it behaves like Cl. Consequently, the ultimate fate of the Br is the discharge thereof from the system, via the WFGD wastewater stream.

When it comes to possible effects in the boiler, nothing has been found in the literature pertaining to effects of Br concentration levels that are of relevance in this context. The very high bromine levels that can occur in chemical waste incinerator boilers are accounted for in the waste incinerator industry by combining the Br and Cl (and F) levels when designing for high temperature corrosion effects. The rationale for doing so is that both Br and Cl exist as the acids HBr and HCl at boiler temperatures. This is supported by the work in the Netherlands: (<http://www.ebfrip.org/statements/TNO-AKZO-corrosion-study2002-Final.pdf>)

Halogen-induced high temperature corrosion of superheaters is a known and potentially serious issue for fuels having a high Cl/S ratio like in waste-incineration boilers and in bio-fuel boilers, where it is primarily managed through the use of conservative steam temperatures. For coal-fired boilers, page 3-27 of the *Combustion- Engineering Handbook* begins a discussion on the subject of Chloride As a Factor in Corrosion by referencing a 1970 ASME study that "the research establishing the mechanism of the liquid-phase-deposit high-temperature corrosion has not shown any significant corrosion at the chloride levels of

0.1 to 0.2 percent (~1,000-2,000 ppm) normally encountered in coal firing" (A.L. Plumley, "Incinerator Corrosion Potential," ASME Incinerator Division Corrosion Symposium, New York: American Society of Mechanical Engineers, 1970.) More recent research has been largely based on results from the UK, as well as on the conclusions in an EPRI report (B Dooley (1993), "Boiler Tube Metallurgical Guide," Vol. 1 EPRI Report TR -102433-V1). According to these sources, there appears to be a threshold Cl concentration of 2,000 ppm Cl in the coal, and above that the corrosion rate increases approximately linearly with Cl content. These conclusions are supported by ALSTOM's experience over many years in designing coal-fired boilers. The vast majority of U.S. coals have less than 2,000 ppm Cl. Thus, in most cases, the life of the boiler materials is rarely limited by the halogen (Cl+Br+F) content of the fuel.

The high temperature chloride corrosion mechanism is generally explained as the effect of: (a) alkali halide eutectic melts; or (b) release of the halogen from tube deposits by sulfation attack. The melting point difference between the sodium and potassium bromide and chloride is a mere 46° C such that the eutectic temperatures of mixtures with other salts normally will be similar. Sulfation will occur of both bromide and chloride salts. Based on this, it can be inferred that the corrosion effect from an increase of Br at the level of some 10 ppm will be similar to the effect of an increase in coal Cl by the same amount. Thus, this is of no importance below a 2,000 ppm halogen level, while above that limit an insignificant amount of additional corrosion is to be expected during the life of the boiler.


To summarize: The effect of adjusting the Br content of the coal by levels less than 50 ppm is that the corresponding amount will be mainly discharged through the stack in plants having no FGD, and will be discharged with the waste water discharge in the plants with WFGD. As such, no significant effect on boiler corrosion is thus to be expected.

### CONCLUSIONS

Bromine is active in oxidizing the mercury emitted from the boiler flue gas, and the simple addition to the boiler of small amounts of bromine compounds can provide reliable oxidation of the mercury, which substantially facilitates the problem of mercury collection.

This patented method, invented by Prof. Vosteen of Germany, has been in commercial operation in Germany on chemical waste and sludge incineration and has been successfully demonstrated on a commercial scale on U.S. coal-fired boilers in U.S.-D.O.E. projects with considerable success. This technology is now available in KNX coal additives and systems that are marketed exclusively by

ALSTOM in the United States and Canada.

The addition to the boiler of small amounts of bromine compounds for the purpose of improved mercury control has basically the same secondary effect as changing from a coal with low native bromine content to a coal with a higher bromine level. Such changes are not expected to have any significant negative effects on the boiler. 

The technology (discussed here,) invented by Prof. Bernhard Vosteen in Germany, has been commercially applied in some German waste incineration plants and is the subject of patents and patent applications in countries throughout the world. ALSTOM has been granted an exclusive marketing rights license from Vosteen Consulting GmbH for joint exploitation and commercialization of this technology for fossil fueled boilers, thermal waste treatment units, and other thermal processes in the United States and Canada.

For more information, contact Robert J. Broglio, Alstom Power, at [robert.j.broglio@power.alstom.com](mailto:robert.j.broglio@power.alstom.com)



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