Evaluation of Mercury Control Strategies in the Presence of SO_3

Abstract

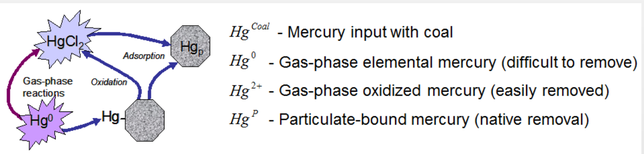
A 500 MW wall-fired boiler firing a PRB coal was evaluated to investigate how mercury control strategies may perform in the presence of SO_3. Model results showed initial baseline native mercury removal of less than 1% and co-benefit removal levels of 23%. Use of bromine boiler additive or activated carbon injection (ACI) with co-benefits (baseline configuration plus SCR and wFGD) resulted in ~94% removal; removal levels without co-benefit plant configurations were much lower than this. Increased SO_3 concentrations (~25 ppm) interfered with mercury removal when SO_3 was introduced early in the boiler process (e.g., increased SO_2 oxidation in the SCR) compared to later (e.g., flue gas conditioning for enhanced ESP performance). High mercury removal (75%+) was maintained when using fabric filters, co-benefit configuration with bromine boiler additive if SO_3 was added as FGC, and bromine boiler additive and ACI (with or without co-benefit configuration) if SO_3 was added as FGC.

MerSim™ Mercury Model

- User-friendly software package for modeling Hg behavior in coal-fired power plants
  - › Modules available
    - − Boiler, APH, SCR, hot- or cold-side ESP, Fabric Filter (FF), SDA-FF, ductwork, wet FGD
  - › Homogeneous and heterogeneous oxidation kinetics
  - › Multi-phase catalytic oxidation across SCRs
  - › Adsorption on and removal with fly ash
  - › Removal and re-emission across wFGD scrubbers
  - › Halogen and activated carbon injection
  - › Oxy-combustion conditions
- Validated against 144 data sets from 28 plants
- Uses inputs generally available to utilities
- Expected to be +/- 20% accurate

Introduction

Mercury undergoes transformations from an elemental form present in the high temperature regions of the boiler to oxidized and particulate forms as the flue gas is cooled.



Hg^{Coal} - Mercury input with coal

Hg^{0} - Gas-phase elemental mercury (difficult to remove)

Hg^{2+} - Gas-phase oxidized mercury (easily removed)

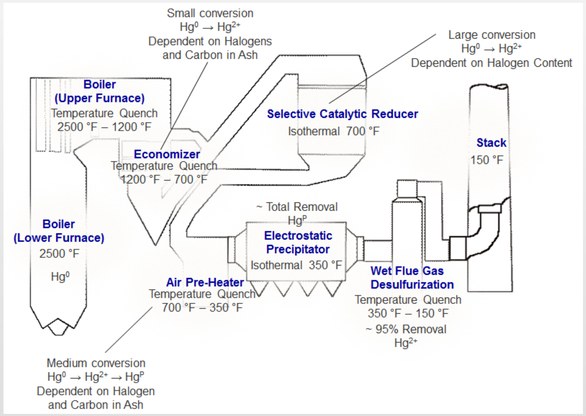
Hg^{P} - Particulate-bound mercury (native removal)

Total mercury : $Hg^{T} = Hg^{0} + Hg^{2+} + Hg^{P}$

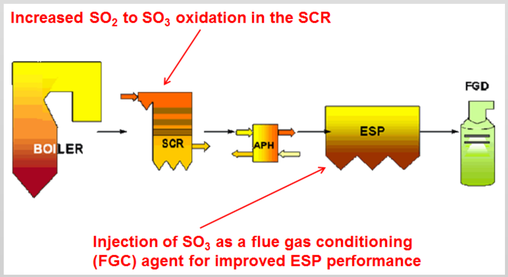
Total gas-phase mercury : $Hg^{TG} = Hg^{0} + Hg^{2+}$

Mercury removal : $1 - \frac{Hg^{TG}}{Hg^{Coal}}$

Important Factors:
- Type of coal
- Halogen speciation and concentration
- UBC in fly ash
- Flue gas temperature and quench rate
- SO_3 and other inhibitors

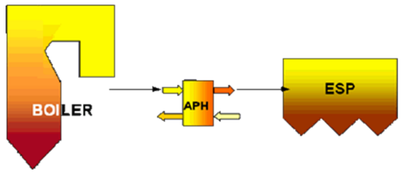


- SO_3 is known to interfere with mercury capture by activated carbon (or unburned carbon in fly ash)
- SO_3 condenses out of the gas phase as H_2SO_4 when temperatures drop below the H_2SO_4 dew point
- Most power plants operate at flue gas temperatures above the dew point to avoid corrosion
- However, many particle surfaces or equipment surfaces may be below the dew point
  - › H_2SO_4 condenses on the surfaces and on unburned carbon, removing sites for mercury oxidation and absorption



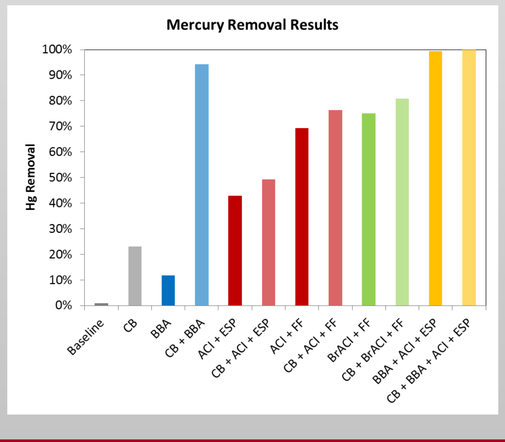
Mercury Control Strategies

Combustion system	wall-fired
Firing Rate (MW)	500
Coal	**100% PRB**
Hg in Coal (ug/g)	0.096
Cl in Coal (ug/g)	20
Br in Coal (ug/g)	0.304
Particulate control	C-ESP
Sulfur control	None
NOx Control	None
Carbon in Fly Ash	1%



Uncontrolled Configuration

Mercury Control Technologies Investigated
Co-benefit Control (CB), SCR & wFGD
Boiler Bromine Additive (BBA), KNX
Activated Carbon Injection (ACI), Darco-Hg
Brominated Activated Carbon Injection (BrACI), Darco Hg-LH
Boiler Bromine Additive (BBA), KNX & Activated Carbon Injection (ACI), Darco-Hg



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No. 18
2014 MEGA Symposium
August 19-22, 2014 Baltimore, MD

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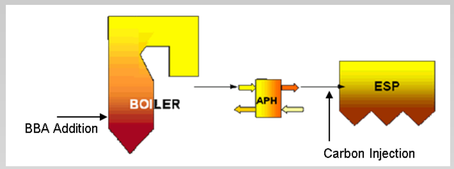
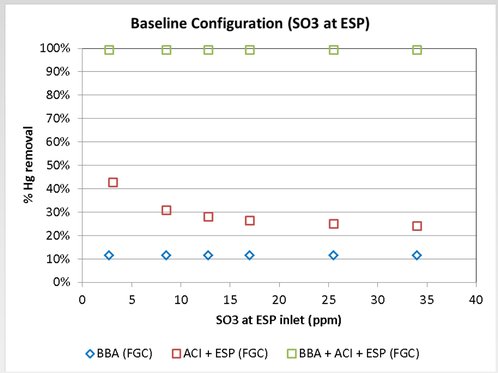
SO_3 Interference
Baseline Configuration

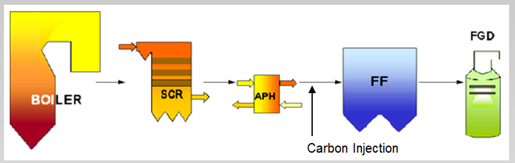


SO_3 addition for flue gas conditioning (FGC) in ESP

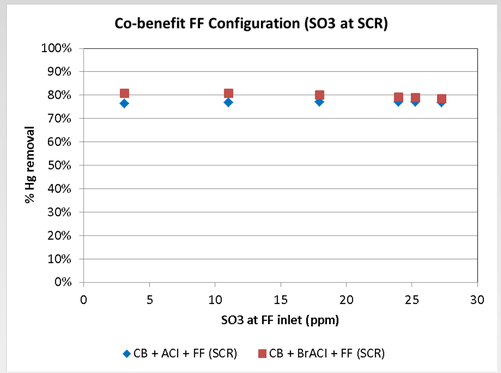


- For BBA scenarios, increased SO_3 later in the system (FGC at ESP) avoided upstream interference and had little impact on Hg removal
- For ACI, FGC in the ESP caused an initial drop in mercury removal which eventually leveled out

SO_3 Interference
Co-benefit FF Configuration

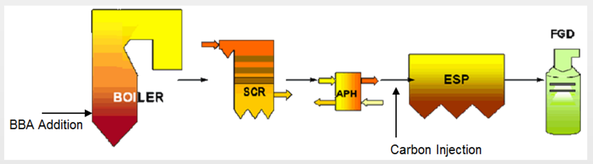


Increased SO_2 to SO_3 oxidation in the SCR

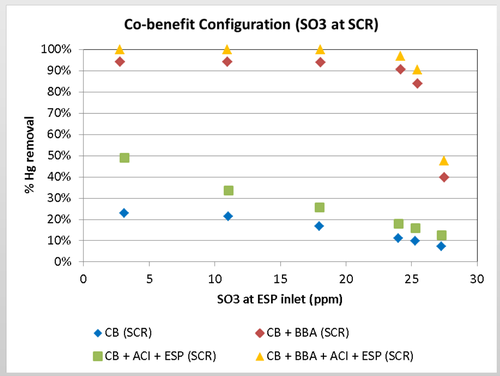


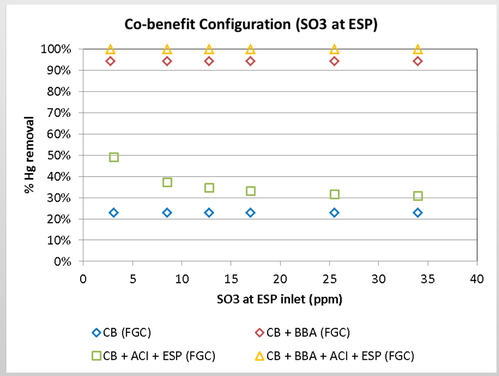
- Increased SO_3 concentration entering FF did not significantly impact mercury removal across the FF
- Filter cake and long residence time for particle-mercury contact were sufficient to overcome most SO_3 interference

SO_3 Interference
Co-benefit Configuration



Increased SO_2 to SO_3 oxidation in the SCR or SO_3 addition for flue gas conditioning (FGC) in ESP





- Increased SO_3 early in the system (SCR oxidation of SO_2) reduced Hg oxidation and reduced removal for all co-benefit scenarios
  - Cases without BBA showed a continuous drop while those with BBA exhibited some resistance to SO_3 at lower concentrations
- When SO_3 was increased later in the ESP, mercury removal dropped for the scenario with ACI alone

Conclusions

- Mercury behavior in coal-fired power plants can be predicted using:
  - Appropriate homogeneous and heterogeneous kinetic models
  - Plant combustion and air pollution control equipment properties
- When firing PRB coal with low carbon in ash and low halogen content:
  - Native Hg capture was very low
  - Bromine fuel additives produced more Hg removal with a plant configuration that included a full suite of APCD's
  - ACI was much more effective when combined with a Fabric Filter than with an ESP
  - Advanced mercury control techniques (i.e., brominated ACI, combination of fuel additive and ACI) can be used for effective Hg control for plants with limited APCD's
- High SO_3 concentrations can interfere with mercury removal
  - Interferences were larger when SO_3 was introduced early in the system (i.e., increased SO_2 oxidation in SCR) compared to later (i.e., FGC for enhanced ESP performance)
- High mercury removal was degraded for:
  - Co-benefit configuration with BBA and/or ACI if SO_3 from SCR (no FF)
- High mercury removal was maintained for:
  - Fabric Filter scenarios
  - Co-benefit configuration with BBA if SO_3 from FGC
  - BBA and ACI (with or without co-benefits) if SO_3 from FGC

Evaluation of Mercury Control Strategies in the Presence of SO_3

Paper #18
Presented at the Power Plant Pollutant Control "MEGA" Symposium
August 19-21, 2014, Baltimore, MD

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ABSTRACT

Mercury behavior in coal-fired power plants can be predicted using appropriate homogeneous and heterogeneous kinetics models with boundary conditions representative of plant combustion and air pollution control equipment. A 500 MW wall-fired boiler firing a PRB coal was evaluated to investigate how mercury control strategies may perform in the presence of SO_3. Model results showed initial baseline native mercury removal of less than 1% and co-benefit removal levels of 23%. Use of bromine boiler additive or activated carbon injection (ACI) with co-benefits (baseline configuration plus SCR and wFGD) resulted in ~94% removal; removal levels without co-benefit plant configurations were much lower than this. ACI was also shown to be more effective when combined with a fabric filter (FF) compared to an ESP. Increased SO_3 concentrations (up to ~35 ppm) interfered with mercury removal more when SO_3 was introduced early in the boiler process (e.g., increased SO_2 oxidation in the SCR) compared to later (e.g., flue gas conditioning for enhanced ESP performance). High mercury removal was degrades for co-benefit configuration (ESP, not FF) with bromine boiler additive and/or ACI if SO_3 was added across the SCR. High mercury removal (75%+) was maintained when using fabric filters, co-benefit configuration with bromine boiler additive if SO_3 was added as FGC, and bromine boiler additive and ACI (with or without co-benefit configuration) if SO_3 was added as FGC.

INTRODUCTION

Mercury exists as the elemental form (Hg^0) in the high-temperature regions of coal-fired boilers. As the flue gas is cooled, a series of complex reactions begin to convert the Hg^0 to gaseous oxidized forms (Hg^{2+}) and particulate-bound mercury (Hg_p). The extent of conversion of Hg^0 to Hg^{2+} and Hg_p depends on the flue gas composition, the amount and properties of fly ash and the flue gas temperature and quench rate. The speciation of mercury in coal combustion flue gas affects the performance of activated carbon and the removal of mercury by wet FGD scrubbers.

SO_3 is known to interfere with mercury capture by activated carbon (or unburned carbon in fly ash). SO_3 condenses out of the gas phase as H_2SO_4 when temperatures drop below the dew point of H_2SO_4. Even though the flue gas temperature may be above the dew point, surfaces within the system (particle surfaces or equipment surfaces) may be colder. It is believed that the condensation of SO_3 removes sites for mercury oxidation and adsorption.

With EPRI support, REI has developed an integrated process model, MerSim^{TM}, for predicting mercury behavior based on fundamental mechanisms that allow for meaningful extrapolation to

new situations, not merely interpolation. MerSim is a useful tool which may be used to investigate possible compliance strategies for mercury emissions control. It is a user-friendly, module-based model which uses inputs typically known by the utility. MerSim has been developed and validated using 144 data sets from 28 full-scale power plants.[1,2,3] It includes homogeneous and heterogeneous oxidation kinetics, adsorption on fly ash, oxidation across SCRs, and removal and re-emission across wet FGD scrubbers. It can represent impacts of halogen addition and activated carbon injection. Detailed SO_3 calculations are also performed in MerSim to account for interference with mercury removal.

MODELING STUDY APPROACH

The baseline plant modeling in this study was a 500 MW wall-fired boiler firing a PRB coal with an air preheater (APH) and cold side electrostatic precipitator (ESP). The PRB modeled contained 0.096 ug/g dry Hg, 20 ug/g dry chlorine and 0.304 ug/g dry bromine. The unburned carbon in fly ash was set to 1%. This baseline was chosen to show minimal mercury removal. A diagram of the baseline case is shown in Figure 1. For some parametric configurations a selective catalytic reducer (SCR) and wet flue gas desulfurization unit (wFGD) were added to the model or a fabric filter (FF) was used in place of the ESP. Diagrams of these setups are shown in Figures 2-4.

Figure 1. Baseline MerSim model.

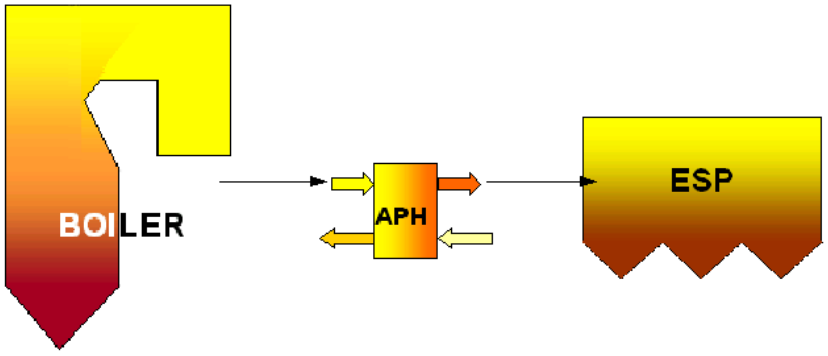


Figure 2. MerSim model for parametric cases with SCR and wFGD (co-benefit (CB)).

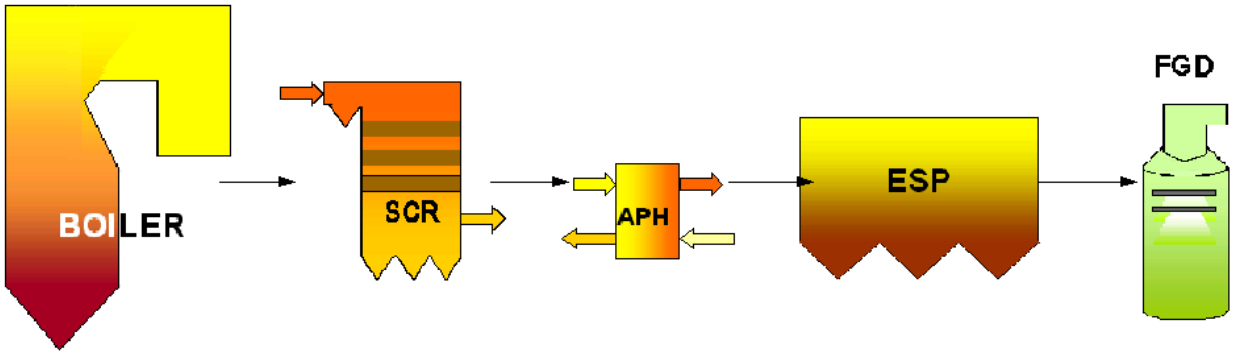


Figure 3. MerSim model for parametric cases with fabric filter (FF).

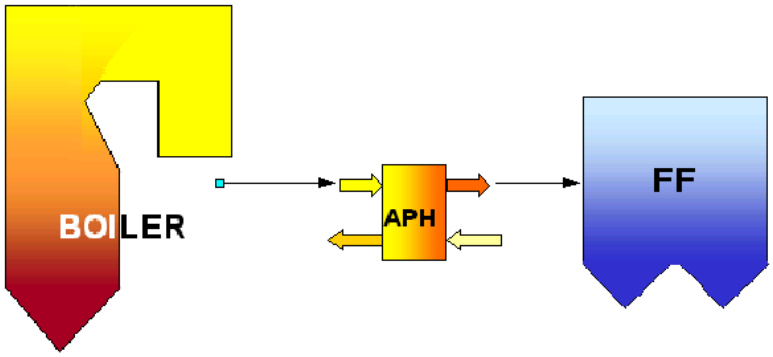
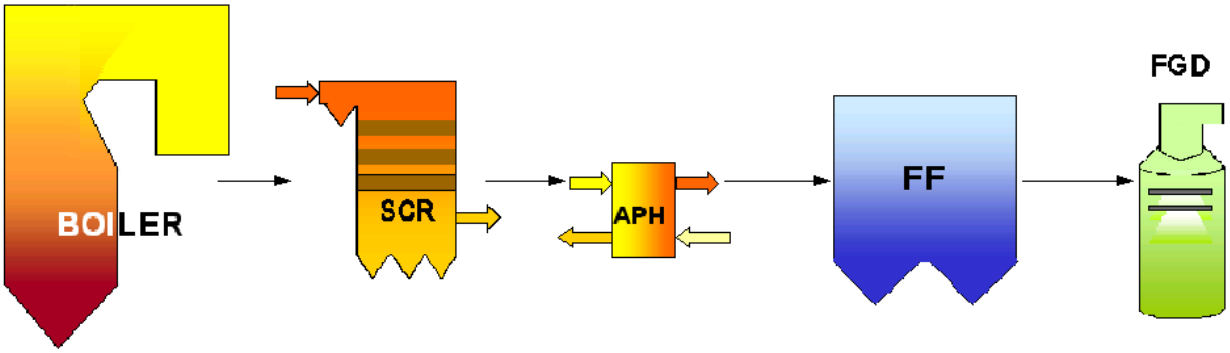


Figure 4. MerSim model for parametric cases with SCR, wFGD, and FF (co-benefit (CB)).



RESULTS AND DISCUSSION

Initially, eleven parametric cases were run to show how a utility could use MerSim to investigate the impact of co-benefit and mercury specific control strategies. A summary of the cases and the predicted mercury removal are shown in Table 1 and a plot of mercury removal is shown in Figure 5. The first parametric model involved adding an SCR and wFGD to the baseline case. This co-benefit (CB) approach increased mercury removal to 23%. Removal is achieved in this system as mercury if first oxidized in the SCR and subsequently captured in the aqueous phase of the wFGD. While oxidation in enhanced with the addition of the SCR, the halogen concentration is of key importance. Because the PRB coal used in this modeling contains very little halogens, the oxidation in the SCR is limited and mercury removal is still low. The second parametric study investigated the effect of a boiler bromine additive (BBA), KNX. This additive promotes mercury oxidation and with the baseline plant setup mercury capture was increased to 12%. When the KNX additive was added to the co-benefit model, mercury removal increased to 94%. Increased halogen concentration and oxidation promotion in the SCR were able to oxidize a significant fraction of the mercury which could then be captured in the wFGD.

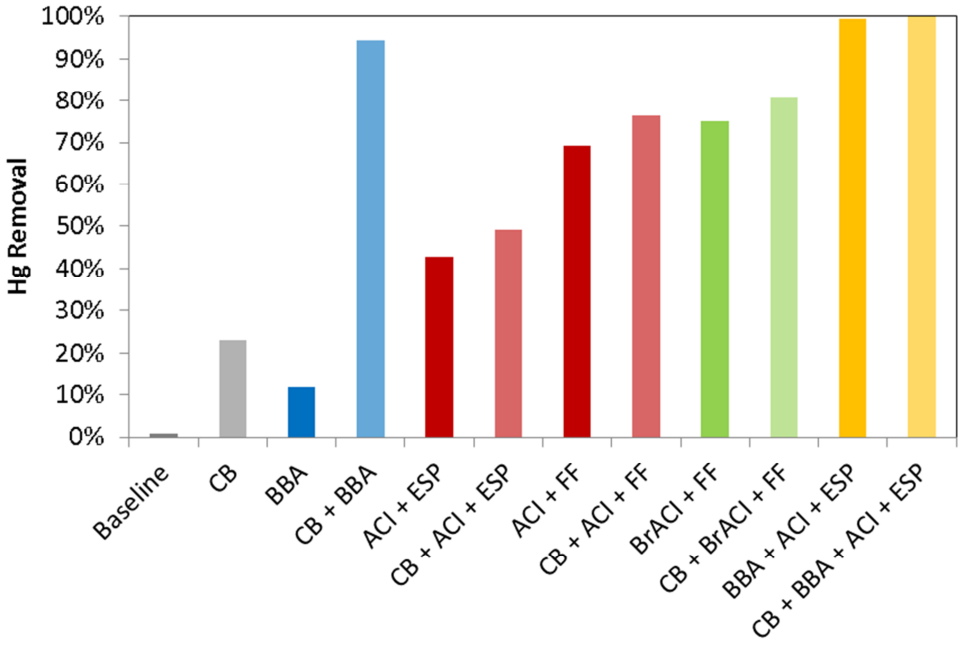
Modeling cases were also run with activated carbon injection (ACI). When 2 lb/MMacf of Darco-Hg was injected upstream of the ESP (same plant configuration as the baseline case),

mercury removal increased to 43%. Adding co-benefit (SCR and wFGD) further increased removal to 49%. When the ESP was replaced with a FF mercury removal increased to 69% or 76% (with CB). Another mercury specific control technology involves using an oxidant enhancer in combination with activated carbon. There are two approaches available that utilize this combination: brominated activated carbon injection or BBA with standard ACI. Model results predicted 75% mercury removal with brominated carbon injection upstream of a FF and 81% when in conjunction with CB. Boiler additive in combination with standard ACI upstream of an ESP was predicted to have 99% removal and 99.9% removal when used in a CB scenario.

Table 1. Summary of MerSim cases and predicted mercury removal.

Case	Network	ACI	Boiler Additive	Hg removal
Baseline	Boiler + APH + ESP	none	none	0.9%
Co-benefit	Boiler + SCR + APH + ESP + wFGD	none	none	23.0%
BBA	Boiler + APH + ESP	none	3 gal/hr KNX	11.7%
BBA + Co-benefit	Boiler + SCR + APH + ESP + wFGD	none	3 gal/hr KNX	94.3%
ACI + ESP	Boiler + APH + ESP	2 lb/MMacf Darco Hg	none	42.8%
CB + ACI + ESP	Boiler + SCR + APH + ESP + wFGD	2 lb/MMacf Darco Hg	none	49.2%
ACI + FF	Boiler + APH + FF	2 lb/MMacf Darco Hg	none	69.3%
CB + ACI + FF	Boiler + SCR + APH + FF + wFGD	2 lb/MMacf Darco Hg	none	76.3%
BrACI + FF	Boiler + APH + FF	2 lb/MMacf Darco Hg-LH	none	75.0%
CB + BrACI + FF	Boiler + SCR + APH + FF + wFGD	2 lb/MMacf Darco Hg-LH	none	80.8%
BBA + ACI + ESP	Boiler + APH + ESP	2 lb/MMacf Darco Hg	3 gal/hr KNX	99.3%
CB + BBA + ACI + ESP	Boiler + SCR + APH + ESP + wFGD	2 lb/MMacf Darco Hg	3 gal/hr KNX	99.9%

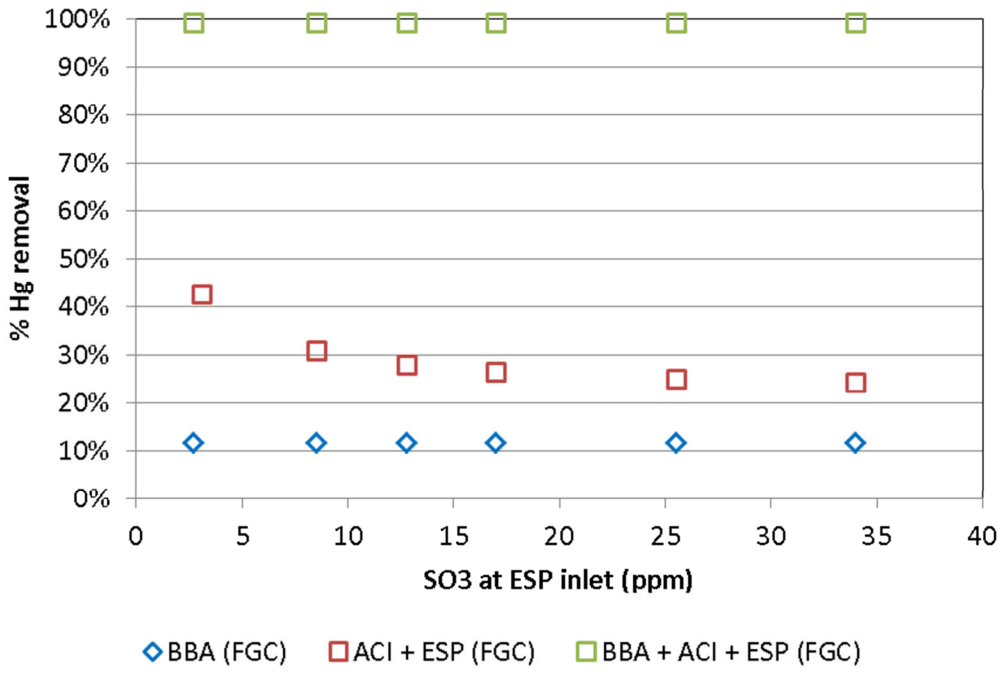
Figure 5. Model predicted mercury removal.



To investigate how these mercury control strategies may perform in the presence of SO_3, several addition cases were run with increasing levels of SO_3. There are two ways in which SO_3 may increase in a power plant: increased oxidation of SO_2 to SO_3 in the SCR or SO_3 injection as a flue gas conditioning (FGC) agent for improved ESP performance. Both of these scenarios are included in the MerSim model.

For the baseline configuration (ESP only), SO_3 can be increased through FGC. Figure 6 shows SO_3 dependence for cases with the baseline configuration. With BBA (with or without ACI), increasing SO_3 through FGC in the ESP does not have a significant impact on mercury removal. With BBA but no ACI, mercury removal is already severely limited due to lack of mercury oxidation and active surface sites. With BBA and ACI, very high levels of mercury removal are maintained. For the case with ACI alone, mercury removal drops as SO_3 is initially increased, but tends to level out at high SO_3 concentrations. The impact here is purely interaction with activated carbon sites in the ESP.

Figure 6. Impact of increasing SO_3 through FGC for baseline configuration.



For the co-benefit (CB) configuration, SO_3 can be increased by oxidation of SO_2 to SO_3 in the SCR or SO_3 injection for FGC in the ESP. Figure 7 shows mercury removal with increasing SO_3 in the ESP and Figure 8 shows mercury removal with increasing SO_3 upstream in the SCR. When co-benefit alone is the only mercury control technology, increasing SO_3 in the SCR causes a significant decrease in mercury removal while increasing SO_3 through FGC in the ESP does not. For these scenarios, mercury capture is achieved through mercury oxidation across the SCR and APH followed by subsequent removal in the wFGD. Increased SO_3 levels in the SCR and APH negatively impact oxidation, while introducing SO_3 later in the system (ESP) removes this upstream interference.

Figure 7. Impact of increasing SO_3 through FGC for co-benefit configuration.

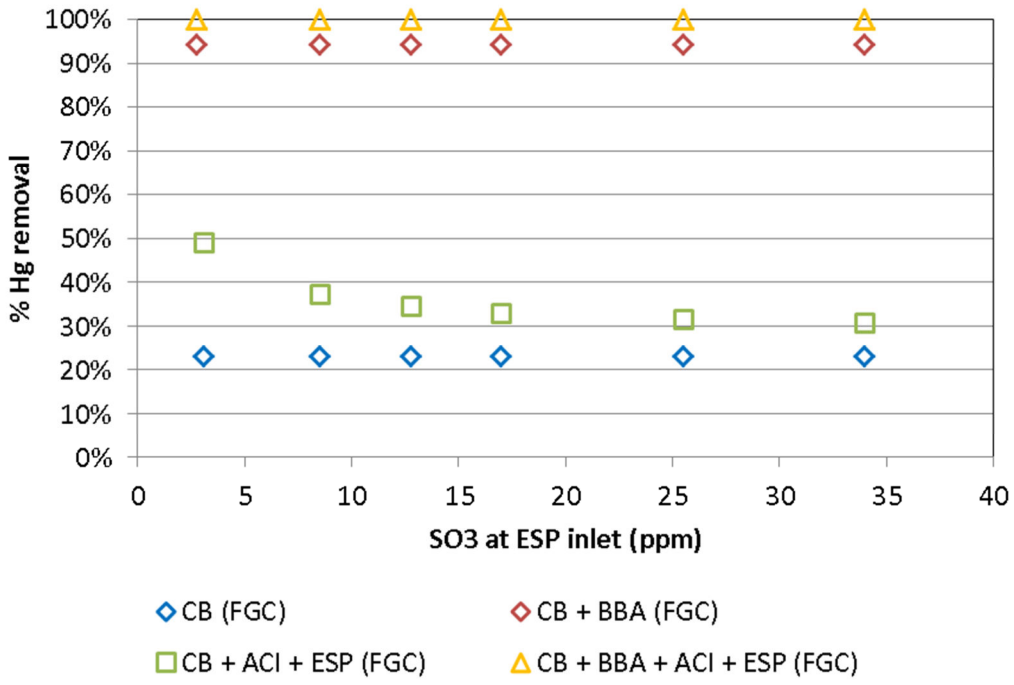
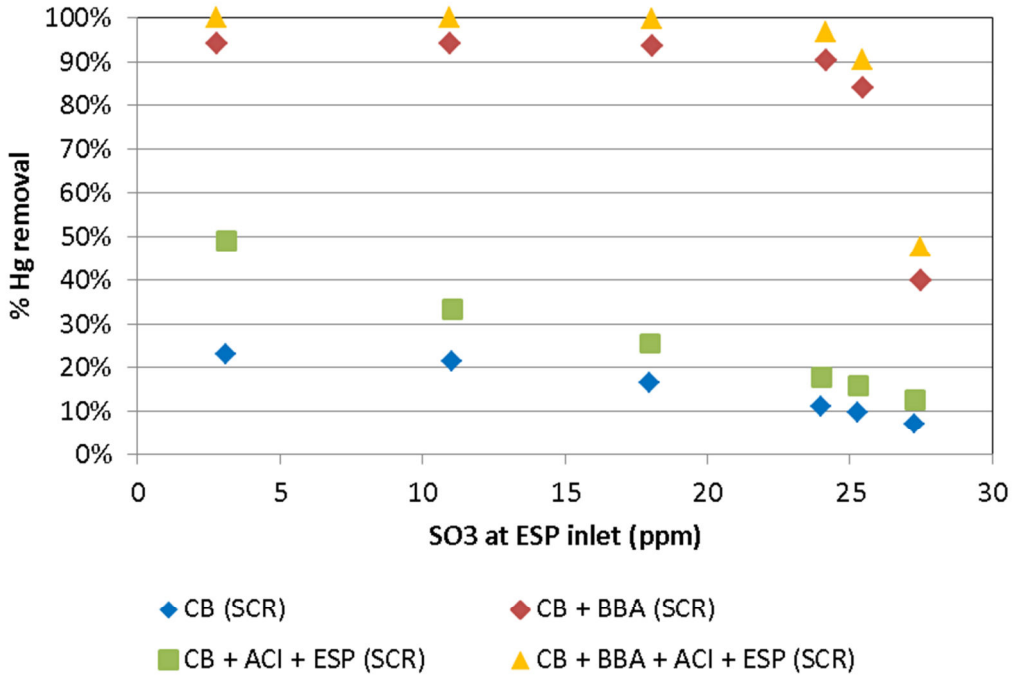


Figure 8. Impact of increasing SO_3 through increased SO_2 oxidation across the SCR for co-benefit configuration.



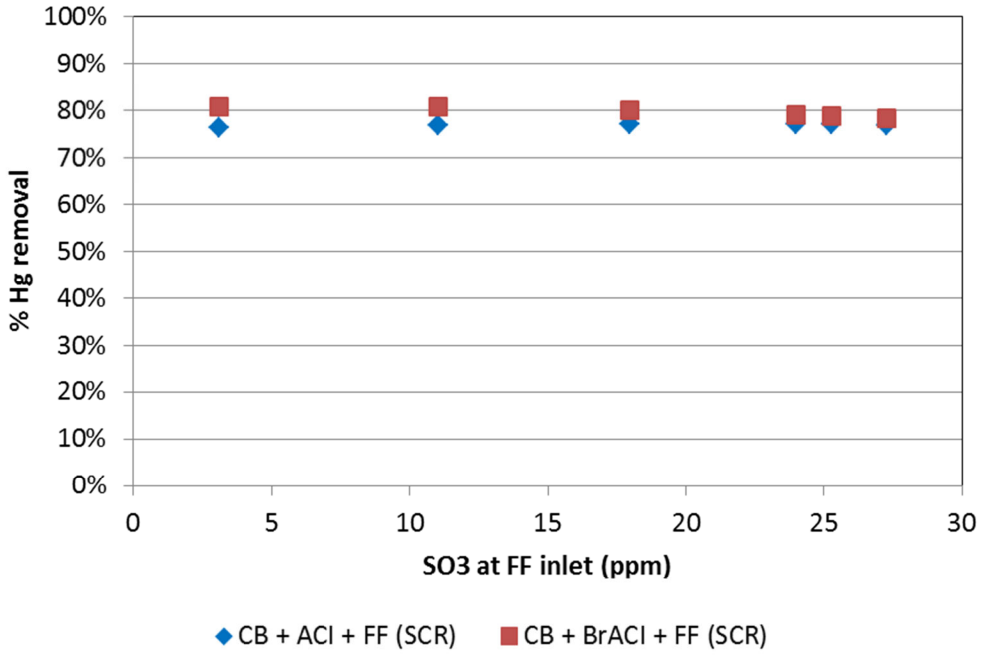
In a co-benefit scenario, the BBA is much more effective. For BBA without ACI, increasing SO_3 early in the process (through SO_2 oxidation in the SCR) severely limits mercury removal, as SO_3 interferes with mercury oxidation. Increasing SO_3 later (through FGC in the ESP) has little impact as mercury oxidation has already occurred and capture in the wFGD is successful.

When ACI alone is added to the co-benefit configuration, increasing SO_3 has an impact on mercury removal whether increased in the SCR or ESP. With FGC in the ESP, the mercury removal tends to level out at high SO_3 concentrations. The impact here is purely interaction with activated carbon sites in the ESP. When SO_3 is increased earlier in the SCR, the mercury removal shows a continuous drop as SO_3 interferes with active carbon sites as well as mercury oxidation in the SCR and APH.

The addition of BBA and ACI shows more resistance to SO_3. Increasing SO_3 concentrations only have an impact when introduced across the SCR. Here the SO_3 interferes with mercury oxidation in the SCR and APH. The combination of BBA and ACI holds up better than the BBA alone, but the curves show similar shapes. When introduced as FGC, SO_3 did not hinder mercury removal with BBA and ACI. Mercury oxidation is sufficient before the FGC (oxidized mercury is more readily absorbed on activated carbon making SO_3 competition less important).

For cases with a fabric filter, the option for increasing SO_3 in the system is to increase SO_2 oxidation across the SCR in a co-benefit situation. Figure 9 shows that the increased SO_3 concentration entering the FF does not have a significant impact on mercury removal across the FF. The filter cake and long residence time for particle-mercury contact are sufficient to overcome most SO_3 interference.

Figure 9. Impact of increasing SO_3 through increased SO_2 oxidation across the SCR for cases with fabric filter.



SUMMARY

This modeling study showed how high SO_3 concentrations can interfere with mercury removal under different control strategies. REI's MerSim modeling tool was used to investigate various mercury control strategies for specific plant configurations based on a 500 MW plant firing PRB coal. Conclusions from this study were as follows:

- Plant configuration and conditions significantly affect mercury speciation and capture as well as the impact of control technologies.
- High SO_3 concentrations can interfere with mercury removal.
- Interferences are larger when SO_3 is introduced early in the process (increased SO_2 oxidation in the SCR) compared to later (FGC for enhanced ESP performance).
- Certain mercury control strategies are more resistant to SO_3
  - High mercury removal was maintained for:
    - Fabric Filter Scenarios
    - Co-benefit with bromine boiler additive if SO_3 introduced as FGC
    - Bromine boiler additive and ACI (with or without CB) if SO_3 introduced as FGC
  - High mercury removal was degraded for:
    - Co-benefit with bromine boiler additive if SO_3 formed in SCR
    - Co-benefit with bromine boiler additive and ACI if SO_3 formed in SCR

- MerSim is a useful tool that can help utilities evaluate mercury control strategies by predicting the performance of different control technologies for specific coals and plant configurations, whether existing or planned.

REFERENCES

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2. "Understanding Mercury Chemistry via the Reaction Engineering International (REI) ProMerc™ Model," EPRI report 1014893.
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KEYWORDS

mercury, SO_3, modeling, co-benefit, bromine, activated carbon