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# Improving Capture of Mercury Efficiency of WFDGs by Reducing Mercury Reemissions

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# Reemission White Paper Workgroup

Bruce Keiser, Ph.D, Nalco, An Ecolab Company, Workgroup Leader
Sheila Glesmann, ADA Carbon Solutions, ICAC Mercury Control Division Co-Chair
Bill Taff, ICL-IP, ICAC Mercury Control Division Co-Chair
Connie Senior, ADA-ES, Inc.
Behrooz Ghorishi, Albemarle
Jon Miller, Albemarle
Richard Mimna, Calgon Carbon
Heather Byrne, Ph.D Carbonxt

## ACKNOWLEDGEMENT

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## ABSTRACT:

The U.S. Environmental Protection Agency (EPA)[1, 2] and World Health Organization (WHO)[3, 4] along with several published reports[5-8] have identified mercury as a hazardous air pollutant leading to the EPA establishing Mercury and Air Toxics Standards (MATS)[8] for coal-fired electricity generating units (EGUs) that take effect in 2015. Currently over 50% of the existing coal-fired EGUs based on capacity utilize wet flue gas desulfurization systems (WFGDs) to reduce sulfur dioxide emissions.[9] WFGDs represent existing air quality control devices (AQCDs) that as part of a mercury emissions control strategy, can facilitate EGU mercury compliance.[10-15]

This white paper focuses on EGUs that contain WFGDs and their utilization as part of a MATS mercury compliance strategy. In particular, our focus is limited to wet-scrubbed units with highly oxidized mercury flue gas entering the WFGD that are not attaining or are only marginally attaining mercury emission limitations.

Practical implementation of WFGD-based mercury compliance strategies has yielded two key conclusions.[11-17] First, the flue gas elemental mercury concentration entering WFGDs must be at or below compliance limitations, i.e., the flue gas mercury oxidation percentage at the WFGD inlet must be adequate such that efficient capture of oxidized mercury in the WFGD will achieve MATS mercury compliance. Second, EGU stack mercury emission can exceed limitations even when mercury is oxidized to adequate percentages prior to the WFGD. Failure of WFGDs to consistently facilitate compliance with mercury emission compliance limitations can be due to the phenomenon called mercury reemission.[11, 13, 18-22] Evidence of mercury reemission is seen when higher flue gas elemental mercury concentrations exist at the stack versus at the WFGD inlet. This increase in flue gas elemental mercury concentration across the WFGD can cause the EGU to exceed the MATS mercury limit, and generally indicates a need for active mercury management within the scrubber liquor circuit. This paper describes mercury reemission, its impact on WFGD mercury capture efficiency, currently available methods to reduce or eliminate it and how control of mercury reemission assists EGU mercury emission compliance.

## I.    INTRODUCTION

Mercury has been widely studied and is well known as a toxic pollutant that has widespread effects from anthropogenic emissions around the globe.[1-10] One source of anthropogenic mercury is coal-fired electricity generating units (EGUs).[2,3] As such, regulations to limit EGU mercury emissions in the US have been under consideration for some years. The Mercury and Air Toxics Standards (MATS) rule was promulgated by US EPA in December 2011 and published in the *Federal Register* on February 16, 2012 (77 FR 9304-9513).[8] The MATS rule establishes limits on mercury emission for EGUs to less than 1.2 lb/TBtu (pounds per trillion Btu heat input) for most coal-fired units with the exception of lignite-fired units which have a limit of 4.0 lb/TBtu. The approximately 1,100 units affected by the rule are faced with implementing strategies to meet the mercury emission limitations.[9] Many of these EGUs have as part of their existing air quality control strategies a wet flue gas desulfurization system or WFGD. WFGDs can

be an integral part of mercury emission control strategies.[11-13] The focus of this paper is maximizing mercury capture for EGUs with WFGDs.

The primary function of EGU WFGDs is the capture of sulfur dioxide ($SO_2$) emissions. Flue gas scrubbing with WFGDs moves water-soluble pollutants such as acid gases from the gas phase to the liquid phase of the scrubber. The water solubility and concentration of sulfur dioxide in flue gas at the WFGD inlet combine to drive efficient absorption and reduce emissions. Additionally, WFGDs can facilitate mercury emission reduction. In the case of mercury, oxidized mercury has a high solubility in water.[34] While concentrations of oxidized mercury in the flue gas are very low relative to sulfur dioxide, the solubility is sufficient to drive oxidized mercury absorption into scrubber liquor.[11-23] The first criterion required for successful use of WFGDs to meet mercury emission limitations is that the elemental mercury flue gas concentration entering the WFGD is equal to or less than the regulatory limit. The inlet flue gas mercury concentration and speciation (oxidation percentage) are dependent on coal composition and the presence of catalysts or mercury oxidants.

Coal is classified into four ranks: anthracite, bituminous, sub-bituminous, and lignite.[24] The coal rank is defined by properties such as carbon content, heat value, volatiles, and ash. As coal is combusted in the boiler, nearly all of the mercury contained in the coal is released into the flue gas, leaving an insignificant fraction in the bottom ash. Mercury is released in the combustion zone of a boiler as gaseous elemental mercury, $[Hg^0]_g$. As combustion gases cool, gaseous elemental mercury interacts with oxygen and combustion byproducts, including halogens and fly ash, leading to oxidation of mercury to form gaseous oxidized species (collectively known as $[Hg^{2+}]_g$). Particulate-bound mercury $[Hg^P]$ also forms when mercury is adsorbed by fly ash particles or activated carbon in the flue gas.[15, 25] The total mercury content and initial speciation in the flue gas depends on the coal. Other elements in coal, particularly halogens, also play a role in the speciation.[15] In general, flue gases from the combustion of low-halogen-content, sub-bituminous and lignite coals will have a higher proportion of elemental mercury or low mercury speciation, while higher rank, higher-halogen-content bituminous coals produce flue gases with more oxidized mercury. For this paper, mercury speciation at the WFGD inlet is of most interest, and the speciation can change markedly after the flue gas leaves the boiler. Besides the fuel properties mentioned above, other factors such as fly ash properties and the AQCDs in service in the flue gas path upstream of the WFGD have a significant impact on mercury speciation.[15, 16, 32]

Bituminous coals usually have higher sulfur content (0.7 to 6.1 lb $SO_2$/MMBtu) requiring WFGD mitigation and mercury content ranging from 2 to 35 lb/TBtu.[26, 85] The chloride content of bituminous coal ranges from 80 to 3,000 ppm by weight on a dry basis.[26-27, 93] Bromine content ranges from 0 to 100 ppm by weight on a dry basis.[93, 94] Flue gas mercury speciation, i.e., proportion of oxidized and elemental mercury forms, is correlated with the halogen content of the coal; higher halogen concentrations lead to higher oxidized mercury percentages.[24] Bituminous coals then yield flue gas containing from 30 to 95% of the total mercury as oxidized mercury.[28, 86] It is the concentration of flue gas elemental mercury remaining that largely sets the attainable lower limit of mercury emissions for EGUs that rely on their WFGD for mercury capture.[16]

The impact of flue gas mercury speciation relative to total mercury emission limitations is illustrated in Table I. Assuming a power plant fueled with bituminous coal containing 10 lb mercury/TBtu of heat input, theoretical mercury capture cases are constructed. For illustration purposes, the assumptions are that there is no removal of mercury from the flue gas between the boiler exit and the inlet of the WFGD and that the flue gas total mercury content at the WFGD inlet is equal to the coal mercury content. Often, this is not the case, as capture of particulate mercury in upstream particulate control devices can occur.

**Table I:** Illustrative Unit Mercury Emission Scenarios.

| Mercury (lb/TBtu) | Coal | Case 1 | | Case 2 | | Case 3 | |
|---|---|---|---|---|---|---|---|
| | | Inlet | Stack | Inlet | Stack | Inlet | Stack |
| Total Hg | 10.0 | 10.0 | 3.0 | 10.0 | 2.4 | 10.0 | 0.5 |
| Elemental Hg | 3.0 | 3.0 | 3.0 | 0.5 | 2.4 | 0.5 | 0.5 |
| Oxidized Hg | 7.0 | 7.0 | 0 | 9.5 | 0 | 9.5 | 0 |
| *EGU Mercury Performance Indicators (%)* | | | | | | | |
| Hg Oxidation[a] | | 70% | | 95% | | 95% | |
| Hg Capture[b] | | | 70% | | 76% | | 95% |

[a]Oxidation is the percent of total mercury concentration in the flue gas that is oxidized (see Appendix A for calculation).
[b]Hg Capture is the percent of total mercury captured by unit based on coal concentration (see Appendix A for calculation).

In Table I, Case 1 represents a "typical" EGU burning bituminous coal that contains 10 lb mercury /TBtu and with natural mercury speciation of 70% oxidation. The WFGD captures 100% of oxidized mercury and the EGU stack mercury emissions are 3 lb/TBtu. This EGU <u>fails to meet</u> mercury emission limitations due to the excessive elemental mercury content of the flue gas entering the scrubber (i.e., 3 lb/TBtu). This case illustrates the importance of **mercury oxidation** in flue gas entering the WFGD in relation to mercury emissions compliance. Case 1 also demonstrates the **criticality of accurate speciation measurements** of flue gas mercury at the WFGD inlet as it pertains to implementing mercury emission control strategies.

In Case 2 of Table I above, an EGU burns the identical bituminous coal but the resulting flue gas has a higher oxidized mercury fraction, i.e., 95% oxidized mercury. **Note:** *The stack mercury measurements alone do not accurately represent the inlet flue gas mercury speciation.* For example, based on stack measurements, the WFGD inlet flue gas mercury oxidation could be assumed as 76%. This would incorrectly suggest the need for higher oxidation of flue gas mercury as a course of action to bring this unit into compliance. The critical nature of accurate flue gas mercury speciation at several points within an EGU is thus demonstrated here. Returning to Case 2, the EGU also <u>does not meet</u> mercury emission limitations, i.e., stack total mercury is 2.4 lb/TBtu despite mercury oxidation of 95% at the WFGD inlet. With the WFGD capturing 100% of the oxidized mercury, Case 2 EGU should capture 95% of the total mercury in the coal. The inability of this unit to reach 95% capture is due to the presence of mercury reemission as will be discussed below.

Finally, in Case 3 of Table I an EGU burning the same coal is also achieving high flue gas oxidation of mercury, i.e., 95% oxidation entering the WFGD which captures 100% of the oxidized mercury. In this case, the stack total mercury emission is 0.5 lb/TBtu. This unit <u>is compliant</u> with mercury emission limitations. Yet, the industry and EGU operators are left wondering why the unit of Case 2 is not performing at the same desired level as the unit of Case 3. The importance of this observation is discussed in detail below in Section II.2.

Flue gas mercury oxidation is enhanced by either or both catalysts and additives. Selective catalytic reduction (SCR) catalysts produce higher oxidized mercury flue gas percentages as a co-benefit.[17, 29, 30] Additives such as halide-containing inorganic salts applied to the fuel or additives injected into the flue gas also yield higher oxidation of flue gas mercury.[31-33] A more detailed discussion is available through several sources.[11-17, 22-25, 29-33]

The remainder of this paper assumes that mercury oxidation is sufficient so that the flue gas elemental mercury concentration entering the EGU WFGD is equal to or below mercury emission limitations and

that the failure of the unit to meet mercury emission limitations is due to the phenomenon termed **mercury reemission**.

## II.    DISCUSSION

### II.1 Flue Gas Mercury Transition into WFGD Slurry

In the WFGD process, constituents in the boiler combustion gas are transferred from the gas phase to the liquid phase through absorption.  The process is illustrated in Figure 1.  In general, the solubility of a gas in water can be described using Henry's law constant as defined:

$$k_H = c_a / p_g$$                         Equation 1

where:  $k_H$ = Henry's law constant
        $c_a$ = concentration of the species in an aqueous phase
        $p_g$ = the partial pressure of the species in the gas phase

It should be noted that Henry's law constants describe equilibrium conditions at various temperatures and for pure water.  The concentration of species in water is driven by activity coefficients that are complex functions of the composition of the water phase.  Hence, it is important to understand that the following discussion is limited in scope by the variation of WFGD liquor composition and because WFGD operations are seldom at equilibrium.  For simplicity, the quench zone of the flue gas is not shown (Figure 1).  In addition, the absorption of sulfur dioxide from the flue gas to the scrubber liquor, the primary function of the WFGD, is also omitted here.
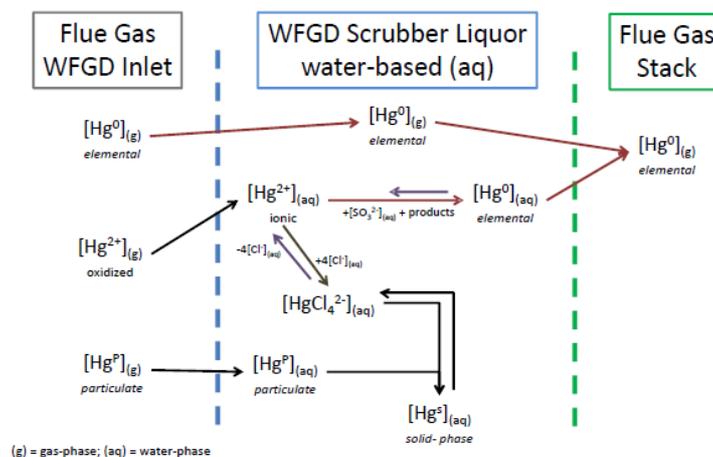


**Figure 1:**  Illustration is provided of flue gas mercury absorption/desorption across WFGD.

The particulate mercury entrained in the flue gas, $[Hg^P]_g$, that enters the WFGD is transferred from the gas phase into the scrubber liquor and subsequently removed from the WFGD.  For the purposes of the discussion here, it is assumed that particulate mercury does not contribute to any water-phase mercury species.

As shown in Figure 1, elemental mercury in the flue gas, $[Hg^0]_g$, predominantly remains in the flue gas passing through the WFGD to the stack.  Referring to Table II below, the Henry's law constant for

elemental mercury is 0.11 M atm$^{-1}$ which is $10^7$ times smaller than that of oxidized mercury. In addition, elemental mercury is by definition insoluble in water with a solubility of 2.7 X $10^{-4}$ g/L at 158 F, see Table III.[34, 35] Therefore, flue gas elemental mercury entering the WFGD passes through to the stack as shown in Figure 1.[41, 71]

**Table II:** Henry's law constants for select species.

| Species | Henry's law constant (M atm$^{-1}$) | Reference |
|---|---|---|
| Sulfur Dioxide, $SO_2$ | 1.2 | 36 |
| Hydrochloric Acid, HCl | 19 | 36 |
| Hydrobromic Acid, HBr | 25 | 36 |
| Mercuric Chloride, $HgCl_2$ | 1.4 x $10^6$ | 37, 39 |
| Elemental Mercury, $Hg^0$ | 0.11 | 38, 39 |

**Table III:** Solubility of mercury species in water.

| Species | Solubility, g/L (Temperature) | Reference |
|---|---|---|
| Elemental Mercury, $Hg^0$ | Insoluble, 2.7x$10^{-4}$ (158 F) | 34, 35 |
| Mercuric Chloride, $HgCl_2$ | 6.9 | 34 |

The third fraction of flue gas mercury entering the WFGD, i.e., oxidized mercury $[Hg^{2+}]_g$, is absorbed by the scrubber liquor to form various hydrated ionic mercury salts. In this paper <u>oxidized mercury</u> refers to flue gas speciation while <u>ionic mercury</u> refers to mercuric species in aqueous solution. As seen in Table II, the Henry's law constant for oxidized mercury is about 1,000,000 times greater than for sulfur dioxide. Additionally the solubility of ionic mercury in water is 6.9 g/L. Together these predict that the water-based scrubber liquor readily absorbs flue gas oxidized mercury entering WFGDs. Several laboratory and commercial studies confirm these conclusions as illustrated in Figure 1.[18-22, 40-43, 52-74] In Figure 1, hydrated ionic mercury, $[Hg^{2+}]_{aq}$ and other salts such as mercuric chloride, i.e. $[HgCl_4^{2-}]_{aq}$ result in the scrubber liquor. For a more detailed discussion see DeBerry and others.[18, 43, 69, 70]

Each EGU has a unique combination of water sources entering the WFGD as well as unique scrubber liquor exiting the WFGD. While these are not in "steady state" during "normal" operations, an overall balance is reached at given loads, fuel, and equipment operations with regard to mercury within the WFGD liquor circuit and mercury entering and leaving the WFGD in the flue gas. Startup of a unit after outage is a unique condition and is impacted by things like the initial scrubber liquor charge and unit startup procedures. In addition to startup, load swings also create unique conditions around the WFGD. Changes in sulfur dioxide content at the inlet resulting from fuel changes also impact WFGD scrubber chemistry. The intent of these comments is to emphasize recommendations made in the previous ICAC paper regarding the duration of mercury demonstrations: that is, short demonstrations are good to show feasibility but longer demonstrations are needed to show validity of long-term solutions.[44]

## II.2 Mercury Reemission across WFGDs

There are documented cases of EGUs with WFGDs experiencing extended periods of high mercury emission despite adequate flue gas mercury oxidation.[45-51] Such cases are examples of the phenomenon termed **mercury reemission** attributed to insufficient WFGD scrubber liquor mercury management.

The simplest definition of **mercury reemission** is a measured increase in flue gas elemental mercury concentration across the WFGD, i.e., inlet flue gas elemental mercury concentration less than stack gas elemental mercury concentration for same period. "Reemission" is defined as "again or back to an original place, condition, etc."[79] As illustrated in Figure 1 reemission appropriately defines the phenomenon. (Note: In this paper, 'mercury reemission' will be used while the spelling 'mercury re-emission' appears in the literature.)

Reemission of elemental mercury, $[Hg^0]_{gas}$, occurs when aqueous divalent ionic mercury, $[Hg^{2+}]_{aq}$ is chemically reduced to elemental mercury and released back into the gas. The ionic mercury reduction reaction that occurs involving sulfite ion is shown here:

$$[HgSO_3]_{aq} + H_2O \rightarrow [Hg^0]_{aq} + [H_2SO_4]_{aq} \qquad \text{Equation 2}$$

$$[Hg^0]_{aq} \rightarrow [Hg^0]_{gas} \qquad \text{Equation 3}$$

Knowledge of both the elemental and oxidized mercury flue gas concentrations at the WFGD inlet and the EGU's stack simultaneously are required to clearly identify mercury reemission. There are several methods available to quantify mercury in flue gas before and after a WFGD. The methods include: CMMs (continuous mercury monitors) which can be both permanent and temporary; Ontario Hydro Method (ASTM Method D6784-02); and sorbent trap method (EPA Method 30B). The susceptibility of these methods to process or operational conditions requires knowledgeable proven practitioners and often warrants application of more than one method to assure reliable results.[95-99] More information on this topic is available elsewhere.[44,95-99]

To illustrate the impact of mercury reemission on EGU mercury emission, examples are provided in Table IV. The case studies in Table IV were first presented in Table I and discussed in the Introduction. Recall the EGUs are burning bituminous coal with a "typical" coal mercury concentration of 10 lb/TBtu. In addition, the assumption is made that AQCDs ahead of the WFGD do not contribute to mercury capture.

**Table IV:** Illustrative EGU Cases of Mercury Emissions and WFGD Performance Indicators.

| Mercury (lb/TBtu) | Coal | Case 1 | | Case 2 | | Case 3 | |
|---|---|---|---|---|---|---|---|
| | | Inlet | Stack | Inlet | Stack | Inlet | Stack |
| Total Hg | 10.0 | 10.0 | 3.0 | 10.0 | 2.4 | 10.0 | 0.5 |
| Elemental Hg | 3.0 | 3.0 | 3.0 | 0.5 | 2.4 | 0.5 | 0.5 |
| Oxidized Hg | 7.0 | 7.0 | 0 | 9.5 | 0 | 9.5 | 0 |
| *EGU Mercury Performance Indicators (%)* | | | | | | | |
| Hg Oxidation[a] | | 70% | | 95% | | 95% | |
| Hg Capture[b] | | | 70% | | 76% | | 95% |
| WFGD Hg Eff[c] | | | 100% | | 80% | | 100% |
| Hg Reemission[d] | | | 0% | | 20% | | 0% |

[a]Oxidation is the percent of total mercury concentration in the flue gas that is oxidized (see Appendix A for calculation).
[b]Hg Capture is the percent of total mercury captured by unit based on coal concentration (see Appendix A for calculation).
[c]WFGD Hg EFF is the percent of oxidized mercury entering a WFGD that is captured (see Appendix A for calculation).
[d]Hg Reemission is the percent of oxidized mercury entering a WFGD converted to elemental mercury (see Appendix A for calculation).

Case 1 in Table IV is an EGU with 70% of the flue gas mercury oxidized as it enters the WFGD. Comparison of the inlet and stack flue gas elemental mercury concentrations shows that they are equivalent. By definition this unit is **not** experiencing mercury reemission. However Case 1 EGU is not compliant with mercury emission limitations. The WFGD is capturing 100% of the flue gas oxidized

mercury and hence the WFGD mercury efficiency (WFGD Hg Eff) is 100%. The root cause of noncompliance is insufficient flue gas mercury oxidation or excessive flue gas elemental mercury. The strategy to bring this unit into mercury emission compliance is to decrease the elemental mercury concentration of the inlet flue gas while maintaining 100% WFGD mercury capture efficiency.

Case 2 shows an EGU that also is **not** compliant with mercury emission limitations. In this case, flue gas mercury oxidation entering the WFGD is 95% with only 0.5 lb/TBtu elemental mercury entering the scrubber. Comparison of the inlet and stack flue gas elemental mercury concentrations reveals an increase of 1.9 lb/TBtu across the WFGD. This fits the definition of mercury reemission, i.e., stack elemental mercury concentration higher than the inlet concentration. Mercury reemission can be quantified as the amount of incoming oxidized mercury that exits the scrubber as elemental mercury and is 20%. The WFGD net mercury capture efficiency is similarly reduced to only 80%. In this case, control of mercury reemission would enable the unit to meet emission limitations.

Case 3 represents a version of Case 2 in which a strategy to control mercury reemission has been successfully implemented. Note that the inlet elemental mercury flue gas concentration equals that of the stack. The result is that this unit is now compliant with mercury emission limitations.

## II.3 Control of Mercury Reemission across WFGDs

It has been shown that the control of mercury reemission across WFGDs by active scrubber liquor mercury management is a strategy that enables EGU compliance with mercury emission limitation regulations. There are several reported means to minimize or control mercury reemission.[15, 19-22, 40-42, 45-74] This section of the paper will focus on operational variables and scrubber additives that control the magnitude of mercury reemission.

### II.3.1 Mercury reemission control via WFGD operational variables.

A number of WFGD operational variables have been shown in laboratory studies to impact the magnitude of mercury reemission.[18, 40-42, 45, 52-59, 61, 64-69] The variable range and extent of impact is different for each of the variables depending on scrubber design and required $SO_2$ removal efficiencies. Operational variables discussed in this section include: sulfite, pH, halides, and oxidation reduction potential (ORP) (see Table V).

**Table V:** Summary of WFGD Operational Impacts on Mercury Reemission

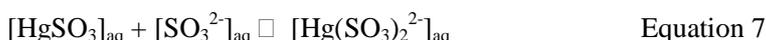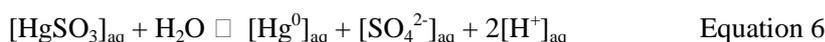| Factor | General Effects on Mercury Reemission |
|---|---|
| **Sulfur dioxide** | ☐ Low or high S(IV) as sulfite or bisulfite scrubber liquor concentrations contribute to mercury reemission<br>☐ Formation of persulfate or peroxymonosulfate contributes to mercury reemission |
| **pH** | ☐ pH< 6; bisulfite is dominant and lower mercury reemission is expected* |
| **Halides** | ☐ High halide levels (>10,000 ppm) decrease mercury reemission* |
| **ORP\*\*** | ☐ < 0 mV or swinging ORP: increased mercury reemission*<br>☐ < 250 mV: solid bound mercury increased; reduced mercury reemission<br>☐ > 250 mV: soluble mercury increased; increased mercury reemission\*\*\* |

\***Caution**: Please see comments for potential negative operational or equipment impacts.
\*\*ORP is measured relative to silver/silver chloride reference electrode.
\*\*\***Comment**: At >700 mV reemission can be eliminated but corrosion and selenium impacts may negate benefit.

Ultimately, the purpose of the WFGD is to control sulfur dioxide emissions. As such, alterations in WFGD or unit operations become a compromise between maximizing sulfur dioxide removal along with maximizing mercury capture as well as addressing other issues such as byproduct purity, corrosion and scale formation.

Sulfur dioxide absorbed into the WFGD liquor from the flue gas yields typical aqueous sulfite concentrations between <5 and 3000 mg/L.[100] In scrubber liquor the +4 oxidation state absorbed sulfur, S(IV), is exemplified by sulfite, $[SO_3^{2-}]_{aq}$ and bisulfite, $[HSO_3^-]_{aq}$. Sulfur(IV) is a main factor in the reduction of ionic mercury to elemental mercury.[18, 56, 57] The reactions are shown in Equations 6 through 9.

$$[Hg^{2+}]_{aq} + [SO_3^{2-}]_{aq} \ \square \ [HgSO_3]_{aq} \qquad\qquad \text{Equation 4}$$

$$[Hg^{2+}]_{aq} + [HSO_3^-]_{aq} + [H^+]_{aq} \ \square \ [HgSO_3]_{aq} + 2[H^+]_{aq} \qquad\qquad \text{Equation 5}$$

$$[HgSO_3]_{aq} + H_2O \ \square \ [Hg^0]_{aq} + [SO_4^{2-}]_{aq} + 2[H^+]_{aq} \qquad\qquad \text{Equation 6}$$

$$[HgSO_3]_{aq} + [SO_3^{2-}]_{aq} \ \square \ [Hg(SO_3)_2^{2-}]_{aq} \qquad\qquad \text{Equation 7}$$

Mercuric sulfite, $[HgSO_3]_{aq}$, formed in the scrubber liquor, decomposes to elemental mercury, $[Hg^0]_{aq}$, in water and sulfate ion as shown in Equation 8. At high sulfite ion concentrations the more stable disulfito-mercury complex,[18, 56, 57] $[Hg(SO_3)_2^{2-}]_{aq}$ is formed as shown in Eq. 9. Since the disulfito-mercury complex is more stable toward reductive mercury decomposition, the magnitude of mercury reemission decreases and lower total mercury stack emission is observed.[18, 56, 57] Sulfur(IV) species and complexes present in scrubber liquor can be influenced by operational pH, forced oxidation air rates, and concentration of some transition metals.

There are quite a few published investigations on the effect of scrubber pH on mercury reemission across WFGDs.[51-59, 61, 68, 69] The general conclusion is that scrubber liquor pH should be maintained below 6. This is due the shift in sulfite ion to bisulfite ion, $[HSO_3^-]_{aq}$, as shown in Figure 2. By decreasing the sulfite ion concentration less mercuric sulfite is formed thereby minimizing mercury reduction (see Eq. 8) and reemission of elemental mercury.

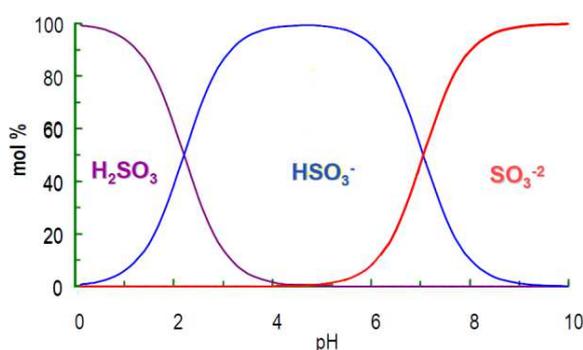**Equilibrium diagram of $H_2SO_3$, $HSO_3^-$, and $SO_3^{-2}$**



**Figure 2:** Equilibrium diagram of dissolved sulfite species is shown.[40]

However, close attention should be paid to scrubber liquor pH to avoid large swings in pH as well. Swings in liquor pH can lead to mercury reemission events and total stack mercury emission excursions. Others have reported low pH, i.e., less than 4.5, produce increased mercury reemission.[68-70] Still others report "Higher pH" promotes mercury reemission.[84] While this seems inconsistent, it is the unique

combination of these variables and impact on ORP and transition metals that yield EGU-specific mercury reemission. It is clear **Table V contains 'general' trends with specific** studies necessary to define operational limits for individual EGUs.

Forced oxidation air introduced into the scrubber slurry in the absorber reaction tank promotes oxidation of S(IV) to S(VI) which yields calcium sulfate or gypsum. The natural oxidation rate is influenced by a combination of the sulfur loading of the unit and the liquid to gas ratio (L/G; e.g., the gallons of scrubber liquor recirculated to the absorber divided by the cubic feet of flue gas scrubbed) along with other factors. These other factors include slurry depth, location of air injection and bubble fineness. Cheng et al.[68] found that mercury reemission was prevalent when the S/O ratio (defined as unit sulfur load (kg S) divided by forced oxidation air volume (scm)) was between 0.12 to 0.18 Kg S/scm oxidation air. This S/O ratio converts to 3.3 to 5 moles O divided by moles S. Presumably the exhibited higher mercury reemission is due to higher residual S(IV) liquor concentrations. Increasing the amount of forced air has been observed to suppress mercury reemission in several lab scale studies,[40, 53, 59] and in full scale tests.[66, 67] Yet other studies have concluded that increased air flow results in higher mercury reemission.[66] Here again, testing on a specific EGU is necessary along with characterization of the unit including scrubber liquor ORP and sulfite and mercury concentrations. Finally, caution is necessary as the S/O ratio or the more common O:S can impact gypsum quality in forced oxidation scrubbers and scaling in inhibited oxidation scrubbers.

WFGD liquor halide content typically is currently controlled based on scrubber metallurgy to minimize corrosion. However, liquor halides interact with ionic mercury and can stabilize it against reduction to elemental mercury. One simplified aqueous phase equilibrium involving halide ions ($X^-$; such as $Cl^-$ and/or $Br^-$) can be illustrated as:

$$[Hg^{2+}]_{aq} \ \square \ [HgX^+]_{aq} \ \square \ [HgX_2]_{aq} \ \square \ [HgX_3^-]_{aq} \ \square \ [HgX_4^{2-}]_{aq} \qquad \text{Equation 8}$$

Halides (e.g. $F^-$, $Cl^-$, $Br^-$, $I^-$) have been reported to suppress mercury reemission in laboratory[55, 59] and commercial EGU[19, 60] studies. In particular, chloride concentrations of greater than 2,000 ppm appear to be effective[61], while bromide and iodide may be effective at lower concentrations.[53, 55] Practical anecdotal results suggest that the chloride concentrations should be greater than 10,000 ppm.[100] Caution is recommended in applying this process modification as increased scrubber liquor halide concentration potentially leads to increased metallurgical corrosion as well as increased concentrations in discharge water.

The oxidation reduction potential (ORP) of the scrubber liquor is a relative measure of the propensity of the medium to be chemically oxidizing (attracting electrons) or reducing (losing electrons). It would follow that a positive ORP value would suppress the reduction of mercury and thereby suppress mercury reemission. The literature contains recommendations for the optimum operational range of scrubber ORP of greater than +200 mV and even higher than +500 mV to decrease mercury reemission.[65, 66] Additionally, ORP modification additives have been suggested to promote higher ORP.[66] On the contrary, other studies suggest lower ORP is optimum.[75] While somewhat counterintuitive, low to moderately positive ORP values are recommended to minimize mercury reemission.[51, 64] The ORP recommendations in Table V represent the collective anecdotal results from full-scale FGD systems of the authors and industry consultants despite appearing contradictive to the public literature.[100]

The control of ORP in a commercial scrubber is exercised through control of forced oxidation air or scrubber additives or both.[62-66, 75] **However, the determination of an "appropriate" operatio**nal range for ORP is dependent on parameters specific to an EGU dictating specific definition. At best then, the

recommendation of an operating ORP of between 150 to 250 mV made in this section is a guideline based on a collection of anecdotal results allowing for deviation based on specific unit operations.

In summary, WFGD and unit process changes can reduce mercury reemission and should be explored within practical operational ranges (Table V). As indicated above, understanding mercury reemission continues to be an area of study by several investigators. At present there is little universal guidance available due to unique nature of commercial unit operations and FGD chemistry. However, additional control is available through the use of scrubber additives, which are discussed in the next subsection.

## II.3.2 Mercury reemission control via WFGD additives.

Technologies discussed below control mercury reemission through active management of scrubber liquor mercury. Generally, this is accomplished through adsorption or precipitation of ionic mercury from the scrubber liquor. By decreasing the soluble mercury content of the scrubber liquor, the potential magnitude of mercury reemission is diminished, leading to lower total mercury emissions.

The management of ionic mercury species, for example $[Hg^{2+}]_{aq}$, can be achieved by transferring $[Hg^{2+}]_{aq}$ and other aqueous phase mercury-containing species to the solid phase by adsorption. There is ample evidence in the literature that points to high affinity of aqueous ionic mercury for activated carbon adsorbents. Gomez-Serrano et al.[77] demonstrated good mercury capture from aqueous solution using thermally and sulfur-impregnated activated carbons. They reported lower adsorption at lower pH (2 or lower). In an EPA report[78] various established and evolving technologies for treating aqueous mercury are described.

Injection of activated carbon into the WFGD can be accomplished at various locations but is typically added into the scrubber recirculation lines. One application technique disperses activated carbon into water prior to scrubber liquor injection. Results for a number of field trials are published.[45, 50, 76] Once inside the WFGD system activated carbon adsorbs mercury and is removed by the dewatering. If preservation of gypsum byproduct is important, different dewatering systems can provide separation of gypsum crystals from the activated carbon particles.[50, 76]

Several mercury sequestering agents have been tested in laboratories[18, 40, 80] and proven commercially.[11, 13, 19, 20-22, 47, 50, 64] Generally these scrubber additives can be grouped into five categories:[47,49,60,62,73-74, 80]

1) inorganic sulfides;
2) organic sulfides;
3) organic compounds containing nitrogen and sulfur;
4) organic compounds containing oxygen and sulfur;
5) and low molecular weight sulfur-containing polymers.

Representative additives of these five categories are shown in Figure 3 for reference. Generally, scrubber additives collect "soluble ionic mercury" by forming a complex ion utilizing sulfur as the mercury ligand. The resulting mercury-containing complex ion prevents ionic mercury reduction to elemental mercury in the scrubber liquor. Thus mercury reemission is decreased and mercury emission compliance is facilitated. Some scrubber additives provide additional benefits beyond that of mercury reemission control that include control of other pollutants such as selenium.[87, 88] Additionally, these scrubber additives have little impact on gypsum quality.[89, 90]
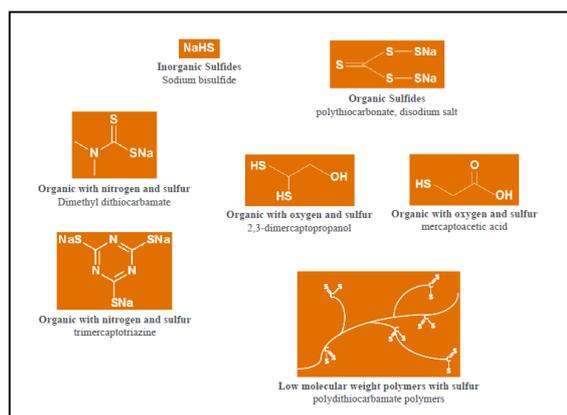
**Figure 3:** Example chemical structures of representatives of the five scrubber additive categories are shown along with the chemical name.

### II.3.3 Summary of Mercury reemission control.

Mercury reemission across WFGDs contributes elemental mercury to the exiting cleaned flue gas and can cause EGUs to exceed regulatory mercury emission limitations. The mercury reemission magnitude dictates the extent of control necessary to reliably meet the established regulatory limitations. Combined or alone, process operations variables or scrubber additives provide means to reliably reduce and control mercury reemission. The application of these strategies depends on the individual EGU. Scrubber additives provide a low capital cost solution for minimizing periodic or consistent mercury reemission from a given unit.

Absorbed flue gas mercury exits a WFGD via three pathways. These pathways are: remitting into the flue gas, the liquid phase and the solid phase of the scrubber liquor. Controlling mercury reemission restricts mercury departure via the flue gas as elemental mercury. Depending on the scrubber additive, the captured mercury exits the scrubber either in the liquid or solid phases. Chemical composition and mechanical processing of scrubber blowdown can be manipulated to manage the distribution of mercury across the two pathways. A discussion of the ultimate fate of captured mercury is beyond the scope of this paper.[81-83]

## III.  FINAL COMMENTS

Improving mercury capture across existing AQCDs can facilitate EGU compliance with mercury emission limitations. This paper has described a phenomenon that impedes mercury emissions compliance for EGUs that have WFGDs as part of their AQCDs. The phenomenon, termed "mercury reemission," is typified by an observed increase in elemental mercury concentration in flue gas across the WFGD (i.e. inlet to stack flue gas concentrations) attributed to poor scrubber liquor mercury management. EGUs can experience consistent or intermittent mercury reemission. Methods to control mercury reemission discussed include both operational variables as well as scrubber additives to actively manage soluble mercury. Operational variables include sulfite and halide concentration as well as scrubber pH and ORP. Scrubber additives were described which actively control liquor mercury content and prevent mercury reemission. Mercury reemission control can be designed around existing

mechanical and process practices of a specific EGU.  The information provided here is meant as a starting point.

## IV.    Acronyms and Symbols

| | |
|---|---|
| AQCD | Air quality control device (examples: Fabric Filter, WFGD, etc.) |
| $c_a$ | Concentration of the species in the aqueous phase |
| CMMs | Continuous mercury monitoring system measures gas phase mercury concentration. |
| EGU | Electricity generating unit |
| EPA | U.S. Environmental Protection Agency |
| $k_H$ | Henry's law constant |
| L/G ratio | The ratio of liquid to gas flow rate of a WFGD |
| MATS | Mercury and Air Toxic Standards |
| MMBtu | Millions of British Thermal Units (of heat input) |
| ORP | Oxidation-Reduction Potential.  It is an indication of a solution's propensity to contribute or accept electrons. |
| $p_g$ | Partial pressure of the species in the gas phase |
| SCR | Selective Catalytic Reduction |
| TBtu | Trillions of British Thermal Units (of heat input) |
| WFGD | Wet flue gas desulfurization (system) |

## V.    Appendix A

EGU and WFGD Performance Indicators

Flue gas mercury speciation is indicated by the fraction of the total mercury that is in the oxidized state. This is represented by percent mercury oxidation which is calculated in the following way:

$$\% \, \text{Hg Oxidation} = \left( \frac{Hg^T - Hg^0}{Hg^T} \right) \times 100$$

Equation A.1

Flue gas speciation may be calculated at any point along the unit through stack. It is for this reason no subscripts are added to Eq. 1.

A key performance indicator for an EGU relative to mercury emission limitations is the percent mercury capture. Overall, this value is based on coal mercury content. With regard to WFGD performance, this indicator is calculated based on inlet flue gas total mercury in the following way:

$$\% \, \text{Hg Capture} = \left( \frac{Hg^T_{inlet} - Hg^T_{stack}}{Hg^T_{inlet}} \right) \times 100$$

Equation A.2

The WFGD performance relative to mercury capture is indicated by the extent of oxidized mercury that is removed from the flue gas. This performance indicator is calculated as follows:

$$\% \, \text{WFGD Efficiency} = \left( \frac{Hg^T_{inlet} - Hg^T_{stack}}{Hg^T_{inlet} - Hg^0_{inlet}} \right) \times 100$$

Equation A.3

Mercury reemission (i.e. higher stack elemental mercury concentration in the flue gas relative to the WFGD inlet flue gas concentration) is calculated in the following way as a way to monitor WFGD performance in mercury capture:

$$\% \, \text{Hg Reemission} = \left( \frac{Hg^0_{stack} - Hg^0_{inlet}}{Hg^T_{inlet} - Hg^0_{inlet}} \right) \times 100$$

Equation A.4

Where in the above terms are defined as:

$Hg^T_{inlet}$    Total flue gas mercury concentration at the WFGD inlet

$Hg^0_{inlet}$    Flue gas elemental mercury concentration at the WFGD inlet

$Hg^T_{stack}$    Flue gas total mercury concentration at the unit stack

$Hg^0_{stack}$    Flue gas elemental mercury concentration at the WFGD outlet or stack

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