CleanAir

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Increasing Collection Efficiency

Mercury Control Additive and Condensables

How are the following words related?

- OILRIG;
- Speciated Mercury; and
- Condensable Particulate Matter.

The Setup

Diverse mercury control options are continually being developed in order to meet unique challenges for various plants. One of these options is a coal additive that can enhance oxidation of mercury.

Mercury is a highly toxic element commonly found in coal and municipal waste. Wet scrubbers are only effective for removal of soluble mercury species, such as oxidized mercury (e.g. $HgCl_2$). Mercury vapor in its elemental form, Hg^0, is insoluble in the scrubber slurry and not removed. Therefore, Hg^0 conversion is required to complete mercury capture.

Usually an addition of halogens to the flue gas is used for this purpose. The type of coal being used as well as the presence of an SCR can affect the ratio of elemental to oxidized mercury in the flue gas and thus the degree to which mercury is removed.

In the flame, all Hg forms Hg(0) and Cl and Br present from the coal form HCl and HBr.

On cooling, starting around 1,000ºF, the hydro-halogens can form straight halogens:

$$4HCl + O_2 \rightarrow 2H_2O + Cl_2$$

$$4HBr + O_2 \rightarrow 2H_2O + Br_2$$

Preferentially, Cl_2 (but not Br_2) is consumed by SO_2, forming sulfur trioxide:

$$SO_2 + Cl_2 + H_2O \rightarrow SO_3 + 2HCl$$

The result is that although total Cl >> total Br, $Br_2 > Cl_2$. Or:

- Chlorides end up as HCl; and
- Bromides will end up as Br_2, in the presence of sulfur dioxide.

And that $2Hg + Br_2 \rightarrow Hg_2Br_2$ dominates the oxidation of mercury when SO_2 is present (because the chlorides preferentially oxidize sulfur dioxide into sulfur trioxide).

Therefore: especially in low chlorine coals (e.g. PRB), bromine is the critical factor for Hg oxidation.

This is why various vendors have an inexpensive additive (a calcium bromide solution) that can be sprayed on the coal on the conveyor belt during silo charging. This additive adds bromide to the coal. The introduction mechanism (spraying onto the coal) is very inexpensive. In general, it also delivers a uniform distribution of additive within the boiler

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flue gas in order to provide uniform Hg oxidation. It also does not require much additive for the relatively small amounts of Hg present (e.g. on the order of gallon(s) per hour of a mixed solution in water).

OILRIG

This is an acronym commonly used to explain the above-mentioned chemistry. Most think of oxidation as burning. A carbonaceous fuel is mixed with air (oxygen) producing heat along with carbon dioxide and water as products of combustion.

In a broader sense, oxidation and reduction (redox) reactions occur all over chemistry. It has to do with an exchange of electrons. The acronym used is as follows:

- Oxidation Is Loss of electrons (OIL); and
- Reduction Is Gain of electrons (RIG).

In chemistry, an oxidizing agent oxidizes something else. In the above example, bromine is an oxidizing agent for mercury in a flue gas. This also means that the oxidizing agent must be reduced (OILRIG). Thus, an oxidizing agent must gain electrons.

This can potentially be confusing you're trying to learn both what oxidation and reduction mean in terms of electron transfer. Especially if you're trying to learn definitions or oxidizing and reducing agents in the same terms.

Reporting Speciated Mercury Results

A full understanding of the REDOX chemistry is not required. But, the above explanation may lead us to where some reporting options might be needed.

When a fuel additive (e.g. calcium bromide is being used), just reporting the overall mercury removal efficiency is not enough information. The customer might be interested in the efficacy of the additive.

- How much of the mercury was oxidized between different additive conditions?
- How much of any oxidized mercury was collected between different additive conditions?

Are We Done?

Not by a long shot! How might this additive affect Particulate Matter Emissions? Especially the Condensable Particulate Matter (CPM)?

For this type of project, the customer may wish to characterize their emissions of particulate matter. This should actually be another selling/reporting opportunity for Clean Air.

Any bromide ions that make it into the CPM fraction of the sampling train (impinger catch) will affect the CPM. But, most probably not how one might expect.

Bromide ions (in a liquid solution) are strong enough reducing agents to reduce concentrated sulfuric acid to sulfur dioxide gas. This is a decrease of oxidation state of sulfur from +6 in the acid to +4 in the gaseous phase.

$$H_2SO_4 + 2H^+ + 2Br^- \rightarrow Br_2 + SO_2 + 2H_2O$$

At this point, any hydrogen bromide is caught in solution and dissociates into hydrogen ions ($^+$) and bromide ions ($^-$). The bromide ions combine as bromine and are off-gassed out of solution (Br_2). The free electrons combine with sulfuric acid and the free hydrogen ions forming sulfur

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dioxide and water. The sulfur dioxide will also off-gas out of solution.

The exact opposite of what might be expected. An additive that forms a water-soluble condensable particulate….could actually reduce the measured condensable particulate matter.

This leaves an analytical and reporting opportunity for Clean Air Engineering. These catches should be analyzed for bromides and sulfates (post-gravimetric analyses) at a minimum.

This effect has actually been measured in samples acquired by Clean Air!

How Can Bromine Be Both An Oxidizing Agent and A Reducing Agent?

The bigger the halide ion, the further the outer electrons are from the atomic nucleus, and the more they are screened from it by inner electrons. It therefore gets easier for the halide ions to lose electrons as one progresses down the periodic group. Bromine's outer electron shell can readily receive or yield electrons. It depends on the matrix and other available reactants.

Other Reporting Opportunities

REDOX reactions may also affect other soluble compounds, which can be measured. These compounds include:

- Nitrates;
- Nitrites;
- Sulfites; and
- Ammonium.

All of the above should be correlated in our final report with:

- The additive injection condition;
- Mercury oxidation efficacy; and
- Mercury removal.

Note 1: This is a simplification of the chemistry that occurs.

Note 2: Ammonium is added to M202 samples during acidic component neutralization.