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DEVELOPMENT OF AN OXIDIZED MERCURY SPIKING SYSTEM

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Project Description

Liquid chemistry conditioning/conversion systems can become sinks (cold spots, absorbing residues) and then sources (condensation, desorbing residues) of gaseous mercury that adversely affects continuous mercury monitoring (CMM) results (1). Dry reduction catalyst conversion systems can also be compromised by the chemical components of flue gas. To determine conditioning/conversion system biases, an oxidized mercury-spiking system is being developed. This system will enable CMM operators to detect and troubleshoot biases and provide researchers with an indication of CMM performance.

Goal

The goal is to design a spiking system that can be used in the field to perform relative accuracy tests of Hg CMMs. This will be accomplished by reacting Hg^0 with chlorine on a gold catalyst to form HgCl_2 .

Rationale

Mercury monitoring, when applied to coal combustion systems, is daunting. While calibrations can be performed on instruments and elemental mercury (Hg^0) added to the sample stream (or in its place), the ability for a continuous emission monitor to measure oxidized mercury is of great concern (2). Site-specific flue gas composition and other conditions can lead to performance differences in CMM installations.

Calibration gas cylinders for various oxidized mercury compounds exist but are unreliable because of low vapor pressure and reactions with stainless steel, making transport to a CMM system difficult. Permeation sources of solid mercury compounds have similar issues, with the added difficulty of containing several grams of hazardous material. Using either a calibration gas or permeation source requires a modified M101A measurement to determine the concentration being emitted.

Hg^0 permeation sources are readily available and simple to use. A Hg^0 -spiking system was constructed that allows concentrations of mercury between 0.5 and 20 $\mu\text{g}/\text{m}^3$ to be delivered to various test points in a typical CMM.

An oxidized spiking system based on gold catalysis has been demonstrated, based on reacting Hg^0 from the permeation source with a precursor gas. The amount of Hg^0 entering the oxidation reactor can be directly measured with the instrument within the CMM. This allows a known amount of gaseous oxidized mercury to be formed on demand. Similarly, during use, the precursor gas can be added and subtracted, in essence, switching the spiking gas between oxidized mercury and Hg^0 . A difference in total mercury between these two states is an indication of how well the CMM can measure oxidized mercury, i.e., allowing the quantification of captured or released oxidized mercury in the CMM system. Another advantage to this system is that the reactor is small enough to mount to the probe injecting directly to the probe inlet. This further reduces problems associated with transporting oxidized mercury to the CMM system. This system can identify and quantify biases in a CMM installation and provide a troubleshooting tool for CMM operators and a QA/QC test for researchers and plant engineers.

Approach

Literature and previous experience with gold catalysts indicate three parameters need to be considered to accomplish the goal of this project: gold thickness, temperature, and precursor concentration (3–5). The effect of these parameters on the gold reactor to transform all elemental mercury into HgCl_2 will be measured using the experimental apparatus described below.

Experimental Apparatus

The parts of the experimental apparatus are the mercury source, chlorine source, reactor, conversion/conditioning system, and CMM. Chlorine and mercury are metered, preheated, and mixed before the reactor. The reactor is composed of a filter holder, support, and gold-coated quartz filter. The product gas is diluted after the reactor and carried to a conversion/conditioning unit through heated lines. After the stream is split, it is processed and measured to find the amount of elemental and oxidized mercury present in the gas.

Permeation ovens and sources for chlorine and mercury from VICI Metronics are being used to control the precursor concentrations. Rotometer flow controllers and pressure gauges will be used in this test apparatus all traceable to NIST standards using Gilibrator calibrations.

The research plan developed based on previous results consists of testing three different thicknesses of gold electrodeposited onto quartz filters and one noncoated quartz filter as a control. The test plan for each catalyst sample will involve applying stoichiometric amounts of mercury and chlorine and measuring the amount of capture and oxidation at temperatures between 250° and 550°F at 50° increments.

When the optimized temperature for each catalyst sample is determined, a new sample, held at this temperature, will be subjected to various ratios of chlorine and mercury. At chlorine to mercury ratios above 1:1, a change in oxidization is expected due to the abundance of chlorine reaching some critical value.

Progress

The instrument being used for this experiment has arrived and is being installed in the apparatus. Permeation ovens, sources and flow controllers are expected to arrive in early January 2005. Four quartz

filters have been sputtered with gold at four thicknesses, from approximately $1 \mu\text{g}/\text{cm}^2$ to $20 \mu\text{g}/\text{cm}^2$. At $20 \mu\text{g}/\text{cm}^2$, the gold is thick enough to exhibit the properties of bulk gold.

The instrument (Nippon DM-6B) has a detection limit of $0.1 \mu\text{g}/\text{m}^3$ and can determine both elemental and oxidized mercury simultaneously, printing averages every 10 seconds. The instrument's dry conversion system is being replaced with a simplified wet-chemistry system. Testing of different wet-chemistry solutions has taken place. While the need for sodium hydroxide is less because of the absence of SO_2 , we found it necessary to block chlorine from reaching the fluorescence instruments in the initial proof-of-concept research. So far, concentrations of 2% SnCl_2 and 5% NaOH for the Hg_{total} side and 1 mol KCl and 5% NaOH for the Hg^0 side yielded results in agreement with traditional wet conversion/conditioning systems.

Quality Assurance/Quality Control

QA/QC design for this project recognizes that the ability to measure the ratios of elemental, oxidized mercury, and trapped mercury are more critical than the measurement of absolute mercury concentrations. Nevertheless, permeation sources will be certified using EPA M101A to quantify the permeation rates for elemental mercury sources. VICI has been instructed to certify the chlorine permeation device at two separate temperatures in order to allow the ability to adjust this source's output. Rotometer flow controllers will be used for flow regulation throughout, and all flows will be calibrated using the NIST traceable Gilibrator primary flow standard.

Status

This project is waiting for several pieces of minor equipment before proceeding.

Potential Users/Technology Transfer

CMM manufacturers, researchers, and power plants can benefit from such a QA/QC tool.

References

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