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Mercury capture by boiler modifications with sub-bituminous coals

Harun Bilirgen *, Carlos Romero

Energy Research Center, Lehigh University, Bethlehem, PA 18015, United States

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ABSTRACT

The extent of mercury (Hg) emissions at a particular coal-fired boiler is unit-specific and determined by factors that include the type of coal fired, boiler operating conditions, and the amount of Hg removed at the boiler back-end by the pollution control devices. Mercury speciation, adsorption and removal in the boiler are affected by parameters such as the flue gas and fly ash characteristics, and back-end boiler configuration/operation. Various studies have reported that boiler operating conditions can be optimized to enhance the "naturally" occurring Hg capture in coal-fired boilers.

A study was carried out to investigate the impact of boiler operating conditions on Hg emissions at a full-scale coal-fired power plant. Testing was performed at a 810 MW coal-fired power plant firing a Northern Powder River Basin (PRB) coal, and equipped with a low-NO_x system and a wet flue gas desulfurization (FGD) system for particulate and sulfur dioxide (SO_2) control. Speciated (total and elemental, Hg^0) Hg measurements and analytical procedures were performed according to the Ontario Hydro Method (OHM)/ASTM D6784-02 Method. OHM measurements were conducted at the air preheater (APH) inlet and the stack. Mercury emissions were also continuously monitored using single-point, non-isokinetic sampling with semi-continuous emissions monitors (SCEM). Readings from these analyzers were used for guidance during boiler control setting manipulations. Individual semi-continuous sampling modules were installed at four single-point locations along the convective pass: APH inlet, FGD inlet, FGD outlet and the stack.

The test results obtained in this study showed the benefit of boiler modifications for Hg control and the extent to which the "natural" Hg control could be influenced. Parametric testing indicated a modest, but inconsistent improvement in the stack Hg (Hg^T) emissions at reduced excess oxygen. This was probably due to the fact that the fly ash unburned carbon levels were very low (less than 1.0%). Modifications to the low-NO_x system over-fire registers, burner tilt and FGD liquid-to-gas (L/G) ratio resulted in stack Hg^T reductions in excess of 25%. The FGD L/G ratio manipulations also resulted in an improvement in oxidized mercury removal across the FGD. However, none of the test data suggested any reduction in Hg^0 across the FGD. The combination of optimal boiler control settings for reduced Hg emission operation resulted in a 34.5% reduction in Hg^T at the stack.

1. Introduction

Technologies that offer high levels of Hg control for different utility boilers, burning various types of coal, are estimated to have high costs of compliance. Activated carbon (AC) is the control technology commercially available for reducing Hg emissions from coal-fired power plants [1]. This technology has evolved in terms of cost and its Hg control effectiveness for the wide spectrum of US coals.

Power plant data have shown that the percentage of uncontrolled Hg emitted from different plants varies widely, from approximately 10% to 90% of the Hg in the coal [2,3]. The extent of Hg emissions at a particular plant is plant-specific and is determined by factors that include the type of coal fired and the amount of Hg removed at the boiler back-end by pollution control devices. Mercury speciation, adsorption and removal in the boiler is affected by parameters such as flue gas and fly ash characteristics, back-end boiler configuration, and the type of pollution control equipment used at the plant. There is evidence that with the right combination of these parameters, it is possible in some units to achieve significant removal of Hg without installing additional control systems [4,5]. Furthermore, various studies have reported that boiler operating conditions can be optimized to enhance the naturally occurring Hg capture mechanisms in coal-fired boilers [5,8].

Boiler operating conditions influence the extent of Hg speciation and the extent to which Hg is retained in the ash or emitted with the stack gas. At combustion temperatures, Hg is present as elemental vapor (Hg^0). However, due to processes which occur

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* Corresponding author. Tel.: +1 610 758 6289.
E-mail address: hab4@lehigh.edu (H. Bilirgen).

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naturally in the boiler, by the time the flue gas reaches to the back-end of the boiler, a fraction of elemental mercury is converted into various oxidized forms (Hg^{2+}) and particulate bound mercury (Hg_p) [6,7]. Elemental mercury is insoluble and is extremely volatile at the operating temperatures of typical air pollution control devices (APCD) and, hence, is much more difficult to capture. On the other hand, oxidized mercury is water-soluble and has a tendency to associate with particulate matter, making it the preferred species. Therefore, oxidized Hg can be removed in scrubbers, and electrostatic precipitators (ESPs) and fiber filters for particle control.

In this study, the impacts and benefits of modified boiler operating conditions on Hg emissions from coal-fired power plants were investigated. Testing was performed at a 805 MW coal-fired power plant to demonstrate the benefit of boiler optimization for low-Hg operation. The unit is a tangentially-fired boiler that fires sub-bituminous Powder River Basin (PRB) coal and is equipped with a wet venturi flue gas desulfurization (FGD) system. This study indicated the importance of boiler control settings for enhancing the "natural" capture of Hg in the boiler. Additional Hg reductions were achieved by modifying the operation of the air pre-heaters (APHs), ESPs, and FGD system.

2. Unit description

The boiler is a tangentially-fired 810 MW unit, designed and manufactured by Combustion Engineering (CE). The unit has a dual balanced draft furnace and excess oxygen trim control. Typical full load average economizer excess oxygen level is about 3.5%. The firing system is composed of 8 corners, with 8 levels of conventional burners, 14 secondary air nozzle elevations and 2 levels of tiltable closed-couple overfire air (CCOFA) registers for NO_x control. Steam temperatures are controlled by a combination of burner tilt, attemperating sprays and sootblowing. Due to a high sensitivity with slagging, sootblowers are continuously activated. The coal calorific value (average of approximately 6394 kcal/kg) allows vertical fuel biasing and operation with a mill out-of-service (O/S). No on-line adjustment of the classifiers exists on the pulverizers. The unit fires a sub-bituminous Northern-PRB, with a typical Hg content in the range from 0.05 to 0.07 ppm_w and chlorine content of <100 ppm_w. Particulate and SO_2 control is accomplished by a lime-base (calcium or dolomitic), 8-vessel wet venturi FGD system. Each scrubber vessel contains a venturi spray section for most of the fly ash and some SO_2 removal. A absorption spray section is used to additional SO_2 removal. The design scrubbing efficiency for the FGD is 95% for SO_2 and 99.5% for particulate.

3. Testing

Over the 13-day testing period, a total of 32 sets of coal samples and 2 sets of pyrite samples were collected during testing. Analysis results are included in Table 1. No significant differences in Hg concentration were found between samples from different silos, which motivated that the coal samples were mixed together, as composite samples from all the mills.

The analytical results in Table 1 indicate a consistently low sulfur and chlorine content in the coal. The average sulfur and chloride contents are 0.94% (with a range from 0.43% to 1.94%) and 58 ppm_w (with a range from 16 to 120 ppm_w), respectively. The average high heating value for the test coal is 6304.44 kcal/kg with a standard deviation of 2.6%. The average Hg content in the coal for the test period is 53 ppb_w (with a range from 40 to 80 ppb_w). The Hg content in the coal is consistent, with only 4 samples exceeding one standard deviation (0.0528 ± 0.0077 ppm_w) out of the total 32 samples. It is known that the overall Hg removal efficiency over the boiler back-end train is affected by the coal Hg and Cl content, with high Cl concentrations being beneficial to obtain reduced Hg stack emissions. For the particular sub-bituminous Northern-PRB coal fired at this particular unit, it will be more difficult to achieve large increases in "natural" Hg capture, due to the low level of Cl content level of this coal.

For the two pyrite samples obtained from the test period, the average Hg contents were 1.07 and 0.93 ppm_w. The first sample was obtained from the rejection drum of the top Mill while the second sample was a composite of samples obtained from the rejection drums of all mills.

Speciated (total and elemental) Hg measurements were conducted using near-real-time Hg semi-continuous emission monitors (SCEM) and by the Ontario Hydro Method (OHM). Individual SCEM sampling modules were installed on the unit at four single-point locations along the convective pass: APH inlet, FGD inlet, FGD outlet and at the stack. Common SCEM analyzers were installed at the APH inlet and FGD inlet, and at the FGD outlet and the stack, respectively. The purpose of these measurements was to obtain as much on-line information as possible on the behavior of Hg as it interacts with the different pieces of equipment at the back-end of the boiler. OHM measurements were mainly conducted at the APH inlet and the stack and used for reporting. Selective OHM samples were also taken across the FGD unit. Sampling at the FGD took place at one of the eight scrubber vessels. The FGD inlet sampling location was located 110 ft. above the ground. The FGD outlet sampling location was located at the bottom of the scrubber recycle tank. The stack sampling location was located 380 ft. above the ground (approximately 8 stack diameters from the inlet to the stack). Flue gas at the APH inlet and stack were OHM sampled using a 2×3 sampling matrix, with 2 ports and 3 traverse points. The FGD inlet and outlet locations were OHM sampled using a 1×2 sampling matrix.

3.1. Analytical techniques

Instrumentation setup and analytical procedures for Hg measurements were performed according to the ASTM D6784-02 Method. Ontario Hydro Method (OHM) measurements were used as the standard for Hg removal performance assessment. On-line Hg emission monitors were also used for single-point sampling. Readings from these analyzers were used for guidance during boiler control settings manipulation, and for Hg monitoring.

Two PSA mercury CEMs were used. Each mercury CEM provided alternating readings at the APH inlet and FGD inlet, and the FGD outlet and the stack, respectively. One individual FGD scrubber vessel was used for sampling. Apogee inertial filtration probes were used prior to the pretreatment/conversion systems of the PSA monitors at the APH inlet and FGD inlet and outlet locations. A conventional EPA Method 5 filter probe was used at the stack, due to the very low-ash concentration associated with this location.

For the OHM, the EPA Reference Method 17 (in-stack filtration for flue gas temperatures greater than 120 °C) was performed at the APH inlet and outlet of each unit to carry out the isokinetic sampling, while the EPA Reference Method 5 was performed after the ESPs and the FGD system. Fig. 1 shows a schematic of the OHM Hg speciation sampling train [8,10]. The OHM sampling train includes a filtration system with sampling probe with glass liner, heated filter box; an impinger box; and console meter and sampling pump. The impinger box consists of KCl, HNO_3/H_2O_2, $KMnO_4/H_2SO_4$ and silica gel impingers. The particulate-bound mercury is collected in the front-side of the system and on the filter. The oxidized Hg is collected in the impingers containing 1 N potassium chloride solution. The elemental Hg is collected in one impinger containing a 5% nitric acid and 10% peroxide solution and in three impingers containing a solution of 10% sulfuric acid