Transformation of mercury speciation through the SCR system in power plants

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Abstract

Coal-fired utility boilers are now identified as the largest source of mercury in the United States. There is speculation that the installation of selective catalytic reduction (SCR) system for reduction of NO_x can also prompt the oxidation and removal of mercury. In this paper, tests at six full-scale power plants with similar type of the SCR systems are conducted to investigate the effect of the SCR on the transformation of mercury speciation. The results show that the SCR system can achieve more than 70%–80% oxidation of elemental mercury and enhance the mercury removal ability in these units. The oxidation of elemental mercury in the SCR system strongly depends on the coal properties and the operation conditions of the SCR systems. The content of chloride in the coal is the key factor for the oxidization process and the maximum oxidation of elemental mercury is found when chloride content changes from 400 to 600 ppm. The sulfur content is no significant impact on oxidation of elemental mercury.

Key words: electric utility boiler; selective catalytic reduction; mercury speciation; oxidation

Introduction

Mercury is a leading concern among the air toxic metals because of its volatility, persistence, and bioaccumulation in the environment and its neurological health impacts. In USA, two mercury reports are issued to Congress: Mercury Study Report to Congress (USEPA, 1997) and Utility Air Toxics Report to Congress (USEPA, 1998). From these two reports, EPA concluded that mercury from coal-fired utilities is a potential threat to human health. In addition to mercury, NO_x emissions are an environmental concern primarily because they are associated with increased acidic precipitation. The selective catalytic reduction (SCR) technology, which can reduce NO_x emissions by 90%, is, therefore, becoming more attractive.

Mercury speciation in flue gases can be classified into three main forms (Tan *et al*., 2004): Gaseous elemental mercury (Hg(0)), Gaseous oxidized mercury (Hg(2+)) and particle bound mercury (Hg(P)). The sum of these mercury speciations is indicated as total mecury (Hg(T)). Oxidized mercury is soluble and has a tendency to adsorb by the particulate matter. On the other hand, elemental mercury is hard to be captured by flue gas desulfurization (FGD) and other kind of pollution control device systems.

Laboratory-scale testing indicates that metal oxides, including V_2O_5 and TiO_2, promote the conversion of Hg(0) to Hg(2+) (Galbreath *et al*., 2000; Eswaran and Stenger, 2005; Benson *et al*., 2005). Therefore, it has been hypothesized that the use of a SCR may improve the mercury control efficiency of existing air pollution control devices by promoting Hg(2+) formation. Based on the aforementioned evidence, there is speculation that the installation of the SCR for reduction of NO_x could significantly increase oxidation and improve removal of mercury in coal-fired plants. Some investigators (Lee *et al*., 2004) have reported complete oxidation of Hg(0) to $HgCl_2$ on the surface of the SCR catalyst in the presence of HCl in laboratory tests, where the effect of the SCR catalyst is believed to be influenced by reducing gases and fly ash. Pilot-scale tests performed by the EERC on the effect of the SCR (Laudal *et al*., 2001) showed a substantial increase in the fraction of particulate-bound mercury across the SCR, but essentially no effect on speciation when a subbituminous coal is burned.

In this paper, field tests at six full-scale power plants with the SCR system are conducted and the effect of the SCR system on the transformation of mercury speciation in flue gas is investigated. Six types of coal with different mercury, chloride, sulfur content are studied to evaluate the effect of coal property on the mercury speciation. An understanding of mercury reaction behavior through the SCR system has the potential to optimize the mercury control levels through the combination of multipollution control devices. Changes in mercury speciation are related to the chloride, sulfur, and calcium content of the coal, as well as operating temperature.

Table 1 Descriptions of six full-scale tested units

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Capacity (MWt)	525	650	650	650	508	650
Coal type	Low sulfur bituminous	Medium sulfur bituminous	Medium sulfur bituminous	High sulfur bituminous	High sulfur bituminous	High sulfur bituminous
Boiler type	Tangential fired	Opposite wall fired	Opposite wall fired	Opposite wall fired	Wall fired	Opposite wall fired
SCR temperature (°F)	684	690	701	698	689	704
SO_2 concentration at SCR inlet (ppm)	420	620	690	1020	1190	980
NH_3 slip (ppm)	5	<5	4	<5	<6	<7

1 Experiments

The mercury field samplings were performed in six full-scale power plants in USA. The electric capacities of these units are similar which range from 508 to 650 MWt. Table 1 summarizes the descriptions for these tested units. All of these six units equipped the SCR, electrostatic precipitators (ESP) and wet flue gas desulfurization. The mercury samplings of Ontario hydro method (OHM) are conducted at the SCR inlet and outlet during two different SCR operating stages–SCR bypass and SCR in service. Every sampling and analyzing are performed triply. In order to monitor the overall mercury removal effect in power plant, the OHM sampling is also performed at the stack.

The OHM is the standard method of measuring and speciating mercury in flue gas. A sample is withdrawn from the flue gas stream isokinetically. Hg(2+) is collected in impingers containing 1% potassium chloride solution; and elemental mercury 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 and 4% potassium permanganate. The samples are analyzed using Leeman Labs Hydra AA. The Hydra AA is a cold vapor atomic absorption (CVAA) instrument dedicated to mercury analysis.

Coal and ash samples is analyzed by the Leco Advanced Mercury Analyzer 254 (AMA 254) The AMA 254 is CVAA instrument. The AMA 254 has a detection limit of 0.01 ng and a detection range of 0.05–600 ng.

2 Results and discussion

2.1 Coal analysis

The average composition of the coals fired in tested power plants is shown in Table 2. The coal used in Case 1 contains low sulfur (0.75%) and high chloride (1003 ppm). The two coals used in Cases 2 and 3 are similar and contain the medium sulfur (1.49%, 1.56%) and high chloride (1703 ppm, 1101 ppm) respectively. In Cases 4 and 6, the coals contain the high sulfur (3.02%, 2.99%) and medium chloride (462 ppm, 629 ppm). The coal used in case 5 contains extremely low chloride (<100 ppm) and high sulfur (3.45%). The mercury contents of these coals are in the range of 0.06 to 0.13 ppm.

The mineral composition of these tested ashes from XRF analysis is presented in Table 3, as is fairly typical for bituminous coals, the coal ash is about 90% alumina,

silica and iron oxides and less than 5% alkali constituents. The ash of Cases 2 and 3 contain higher calcium and magnesium content. The highest Fe_2O_3 and Al_2O_3 are found in Case 4 and Case 1 which are 28.04% and 28.31%, respectively.

2.2 Transformation of mercury speciation through the SCR system

The comparison of average mercury speciation at the SCR inlet and outlet by OHM method are shown in Fig.1. The results show that the elemental mercury is the predominant mercury species present at the inlet of the SCR. On the contrary, the mercury species is dominated by the oxidized mercury at the SCR outlet for most of tested cases. For example, in Case 3, the proportion of the elemental mercury in total mercury is decreased from 86.2% to 24.6% and the oxidized mercury is increased from 13.8% to 75.4% across the SCR system. Very little particulate bound mercury is found in the fly ash at inlet and outlet of the SCR since the temperature at the SCR system (>700 °F) is too high for the absorption of the mercury in ash particles.

Table 2 Ultimate analysis results for coals

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Carbon (%)	71.1	71.5	70.62	69.86	81.7	68.66
Hydrogen (%)	5.01	5.3	5.45	5.36	6.86	5.04
Nitrogen (%)	1.29	1.53	1.53	1.61	1.65	1.28
Oxygen (%)	8.39	11.81	12.87	11.35	18.55	9.52
Sulfur (%)	0.75	1.49	1.56	3.02	3.45	2.99
Ash (%)	9.47	9.36	7.97	8.82	8.86	10.53
Chlorine (ppm)	1003	1703	1101	462	<100	629
Mercury (ppm)	0.06	0.12	0.07	0.13	0.09	0.13
Coal LHV (Btu/lb)	12589	12413	12435	12483	14464	12269

Table 3 The primary composition in the tested ashes

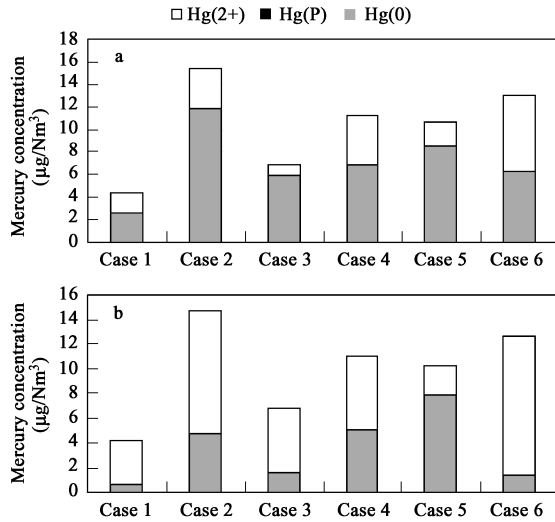|	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
CaO (%)	0.71	2.71	2.39	1.1	1.12	1.67
Fe_2O_3 (%)	5.03	13.92	16.61	28.04	23.17	21.45
MgO (%)	0.31	0.43	0.33	0.17	0.25	0.12
SiO_2 (%)	58.31	53.16	51.56	43.25	49.66	47.65
Al_2O_3 (%)	28.31	20.97	21.52	20.16	15.56	21.51

Fig. 1 Comparison of average mercury speciation at SCR inlet (a) and outlet (b).

Fig. 2 Oxidation efficiency of elemental mercury across the SCR system.

Fig. 3 Removal efficiency for mercury speciations across the SCR.

The oxidation efficiency of elemental mercury (ω) which is defined as the fraction of the elemental mercury that is converted to the oxidized mercury can be calculated from the ratio of the increase in oxidized mercury Hg(2+) to the decrease in elemental mercury Hg(0) across the SCR system:

$$\omega = \frac{Hg(2+)_{outlet} - Hg(2+)_{inlet}}{Hg(0)_{inlet} - Hg(0)_{outlet}} \times 100\% \qquad (1)$$

In order to evaluate the effect of the SCR on mercury removal process, the removal efficiency (η) of mercury species across the SCR system can be described as follows:

$$\eta = \frac{Hg(species)_{inlet} - Hg(species)_{outlet}}{Hg(species)_{inlet}} \times 100\%$$

$$Hg(species) \longrightarrow Hg(0), Hg(2+), Hg(VT) \qquad (2)$$

The overall mercury removal efficiency (η_T) through air pollution control devices (SCR + cold ESP + FGD) is formulate with the mercury data at the SCR inlet and stack, which is described as follows:

$$\eta_T = \frac{Hg(species)_{SCRinlet} - Hg(species)_{Stack}}{Hg(species)_{SCRinlet}} \times 100\%$$

$$Hg(species) \longrightarrow Hg(0), Hg(2+), Hg(VT) \qquad (3)$$

The oxidation efficiency of elemental mercury across the SCR system is shown in Fig.2. Except the Cases 4 and 5, majority of the elemental mercury are converted to oxidized mercury. The oxidation efficiency can be achieved above 90% in other four cases. This result indicated that the SCR catalyst has a strong ability to promote the oxidation of elemental mercury and decrease elemental mercury to an insignificant level at the outlet of the SCR for most tested cases. Such high levels of the oxidation of elemental mercury are consistent with the observation in the previous bench-scale test (Laudal *et al.*, 2001).

The removal efficiency of mercury speciation across the SCR system is shown in Fig.3. Although a great portion of
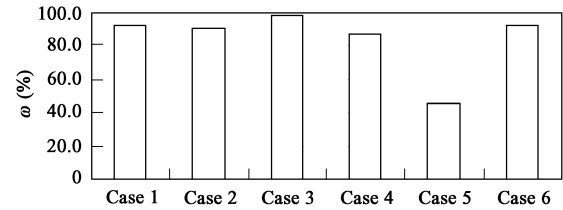
elemental mercury is transformed by the SCR, the removal efficiency of the total mercury is less than 10%. The overall mercury removal efficiency (η_T) through APCD is also tested in Case 4 during two SCR operation phases including the SCR bypass and SCR in service. The results of these tests are presented in Fig.4. The overall mercury removal efficiency shows a great impact on the SCR catalyst. The overall mercury removal efficiency jumped from 48% under SCR by-pass to over 88% with SCR in service. This result indicates that the SCR itself can only oxidize elemental mercury with high efficiency, the ability to remove mercury is very poor. In order to achieve higher removal effect, the SCR system has to cooperate with other air pollution control devices, such as FGD and ESP, the oxidized mercury will be removed in downstream of the SCR. It is impractical to pursue a high removal efficiency (η) by SCR itself, optimization of the configuration of APCD in power plant will help to achieve higher overall mercury removal efficiency (η_T).

2.3 Effect of coal and ash property on mercury transformation

Fig.5 shows the tendency of mercury oxidation according to the chloride content in the coal. For the coal with extremely low chloride content, the amount of Hg(0) oxidation is very low. The coal chloride content of Case 5
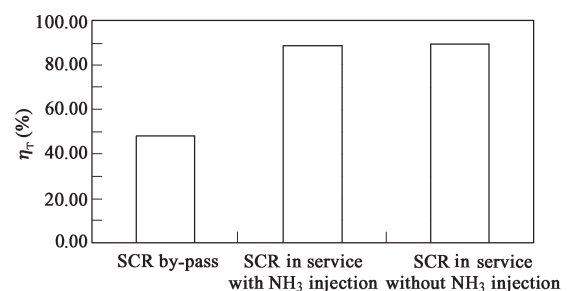

Fig. 4 Overall removal efficiency for mercury speciations at the different SCR operation phases in Case 4.
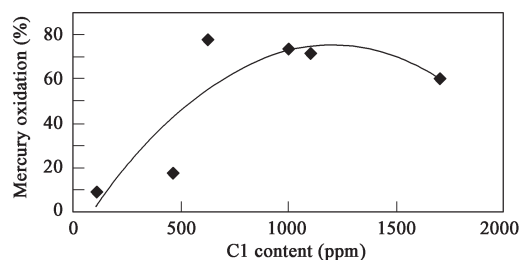
Fig. 5 Mercury oxidation efficiency vs. chlorine content.

is less than 100 ppm, the oxidation efficiency of Hg(0) is as low as 8.2%.

In the Cases 4, 5 and 6, the sulfur content of the coals are close to each other, but with the increasing of chloride content, the efficiency of elemental mercury oxidation increases from 8.2%, 25.2% and 77.6%. Especially, when the chloride content increase from 462 to 629 ppm, there is a sharp increasing for Hg(0) oxidation. It is suggested that the concentration of chloride around 500 ppm is the critical condition for the effective action to transform elemental mercury to oxidized mercury.

Compared with Cases 1, 2 and 3, no obvious effect of chloride on mercury oxidization is found when the chloride content in the coal is higher than 800 ppm. The efficiency of the Hg(0) oxidation keeps at high level (above 60%–70%) stably. In both Cases of 1 and 3, the chloride content are very close as 1003 and 1101 ppm, the sulfur content changes from 0.75% to 1.56%, very little variation is found in oxidation efficiency of Hg(0) which are 73.8% and 71.8%, respectively (Table 2). The sulfur content and the concentration of SO_2 have very little impact on Hg(0) oxidation.

For the mineral composition of these tested ashes, the higher calcium and magnesium content are suspected to be a competitor for mercury oxidation to consume the hydrogen chloride (HCl) and then impact the mercury speciation. Compared with Cases 1, 2 and 3, the chloride contents of these coals keep at high level (all of them are above 1000 ppm and the highest chloride content is found in Case 2 which is 1703 ppm), but the oxidation of mercury across the SCR in Case 2 is only 59.7% which is much lower than that of Cases 1 and 3 (73.8% and 71.8% respectively). This fact indicates that ash with high CaO and MgO contents tends to inhibit the oxidation of mercury associated with high chloride content.

3 Conclusions

The results of field testing show the SCR catalyst has a strong ability to promote Hg(0) oxidation, the effect of the SCR on promoting Hg(0) oxidation appears to be coal-type dependent. Chloride content is the most important composition in the coal. With the increasing of the chloride in the coal, the oxidation of Hg(0) through the SCR system increases obviously. When the chloride content increase from 462 to 629 ppm, there seems to be a sharp increasing for Hg(0) oxidation. It is suggested that the concentration of chloride around 500 ppm is the critical condition for the effective oxidation. When chloride content is more than 1000 ppm, no obvious increasing tendency of mercury oxidation is found with the increasing of chloride content.

The sulfur content and the concentration of SO_2 seem to have very little impact on Hg(0) oxidation. The mineral analysis of XRF for ashes shows that ashes with high CaO and MgO contents tends to inhibit the oxidation of mercury associated with a high chloride content.

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