

1 **Investigation of SCR Impact on Mercury Speciation under Simulated NO<sub>x</sub> Emission**  
2 **Control Conditions**

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14 **ABSTRACT**

15 Selective catalytic reduction (SCR) technology is being increasingly applied for controlling  
16 emissions of nitrogen oxides (NO<sub>x</sub>) from coal-fired boilers. Some recent field and pilot studies  
17 suggest that the operation of SCR could affect the chemical form of mercury in the coal  
18 combustion flue gases. The speciation of mercury is an important factor that influences the  
19 control and environmental fate of mercury emissions from coal combustion. The vanadium and  
20 titanium oxides (V<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>), used commonly in the vanadia-titania SCR catalyst for catalytic  
21 NO<sub>x</sub> reduction, promote the formation of oxidized mercury (Hg<sup>2+</sup>).

22  
23 The work reported in this paper focuses on the impact of SCR on elemental mercury (Hg<sup>0</sup>)  
24 oxidation. Bench-scale experiments were conducted to investigate Hg<sup>0</sup> oxidation in the presence  
25 of simulated coal combustion flue gases and under SCR reaction conditions. Flue gas mixtures  
26 with different concentrations of hydrogen chloride (HCl) and sulfur dioxide (SO<sub>2</sub>) for simulating  
27 the combustion of bituminous coals and sub-bituminous coals were tested in these experiments.  
28 The effects of HCl and SO<sub>2</sub> in the flue gases on Hg<sup>0</sup> oxidation under SCR reaction conditions  
29 were studied. It was observed that HCl is the most critical flue gas component that causes  
30 conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> under SCR reaction conditions. The importance of HCl for Hg<sup>0</sup>

31 oxidation found in the present study provides the scientific basis for the apparent coal-type  
32 dependence observed for Hg<sup>0</sup> oxidation occurring across the SCR reactors in the field.

33

#### 34 **IMPLICATIONS**

35 Boilers burning bituminous coals have shown significantly higher oxidized mercury species  
36 across SCR reactors, while those firing subbituminous coals showed little change in mercury  
37 speciation. The water-soluble oxidized mercury compounds may be removed in downstream wet  
38 scrubber cost effectively. Understanding the science behind mercury oxidation via SCR catalysts  
39 will broaden the applicability of SCR systems in mercury removal strategies. Our results suggest  
40 that a source of chlorine such as hydrochloric acid is needed for mercury oxidation under SCR  
41 conditions. This finding provides a scientific basis for the apparent coal-type dependence on  
42 mercury oxidation across SCR reactors observed in field studies.

43

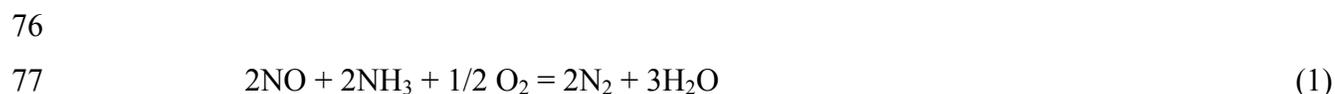
#### 44 **INTRODUCTION**

45 Coal combustion is a major source of mercury emissions that have caused environmental health  
46 concern.<sup>1</sup> Speciation (the split amongst chemical forms of mercury) is an important factor that  
47 influences the control and environmental fate of mercury emissions from coal combustion.<sup>2</sup> It is  
48 known that controlling the emissions of oxidized mercury, the water-soluble mercuric chloride  
49 (HgCl<sub>2</sub>) in particular, is much easier than controlling the insoluble elemental mercury Hg<sup>0</sup>.<sup>3</sup>  
50 Emissions of nitrogen oxides (NO<sub>x</sub>) are another major environmental concern from coal  
51 combustion; the emissions are associated with ground level ozone, acid rain formation, forest  
52 damage, degradation of visibility, and formation of fine particles in the atmosphere.<sup>4</sup> Several  
53 regulatory programs such as the Acid Rain NO<sub>x</sub> regulations, the Ozone Transport Commission's  
54 NO<sub>x</sub> Budget Program, and Ozone and Particulate Matter Transport rulemakings require  
55 significant reductions in NO<sub>x</sub> emissions from coal combustion sources. As a result of these more  
56 stringent NO<sub>x</sub> emission control requirements, selective catalytic reduction (SCR) technology is  
57 being increasingly applied for controlling NO<sub>x</sub> emissions from coal-fired boilers due to its high  
58 NO<sub>x</sub> emission control efficiency (>80%). The operation of SCR could affect the speciation of  
59 mercury in the coal combustion flue gases. Early field measurements conducted in Europe  
60 indicated that SCR reactors installed for NO<sub>x</sub> emission control promote the formation of

61 oxidized Hg species.<sup>5</sup> A recent field study conducted in the United States also found increases in  
62 Hg<sup>2+</sup> species across the SCR reactors.<sup>6</sup>

63  
64 The effect of SCR operation on mercury speciation appears to be dependent on coal type.  
65 Boilers burning bituminous coals, which typically have high chlorine (Cl) and sulfur (S) content,  
66 have been observed to have significant increases in Hg<sup>2+</sup> species across their SCR reactors.<sup>6</sup>  
67 However, a subbituminous coal from the Powder River Basin (PRB), which contains  
68 significantly lower Cl and S content and higher calcium (Ca) content compared to those of the  
69 bituminous coals, showed very little change in mercury speciation across a SCR reactor.<sup>1</sup>

70  
71 Nitrogen oxides (NO<sub>x</sub>) in coal combustion flue gas are reduced to nitrogen (N<sub>2</sub>) and water (H<sub>2</sub>O)  
72 in an SCR reactor consisting of metal oxide catalysts such as TiO<sub>2</sub>-supported V<sub>2</sub>O<sub>5</sub>. A reducing  
73 agent such as ammonia (NH<sub>3</sub>) or urea (NH<sub>2</sub>CONH<sub>2</sub>) is injected into the SCR reactor operating at  
74 temperatures of about 350 °C. The NO<sub>x</sub> reductions proceed according to the following  
75 reactions:



80  
81 Laboratory-scale experiments have indicated that metal oxides, including V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>, could  
82 promote the transformation of Hg<sup>0</sup> to Hg<sup>2+</sup> in combustion flue gases.<sup>7</sup> Recent pilot-scale tests  
83 also suggested that SCR has the potential to impact mercury speciation, and the effects appear to  
84 be dependent upon coal type.<sup>8</sup> However, the reactions that are important to transform Hg<sup>0</sup> into  
85 Hg<sup>2+</sup> in the SCR reactor are not well understood.

86  
87 The work reported here is bench-scale research that focuses on studying Hg<sup>0</sup> oxidation in the  
88 presence of simulated coal combustion flue gases and under SCR NO<sub>x</sub> emission control  
89 conditions. The effects of HCl and SO<sub>2</sub> in the flue gases on Hg<sup>0</sup> oxidation were studied. Our  
90 previous bench-scale study found that NO<sub>x</sub> and HCl promote Hg<sup>0</sup> oxidation, while SO<sub>2</sub> and H<sub>2</sub>O

91 reduce Hg<sup>0</sup> oxidation in the presence of coal combustion fly ashes.<sup>9</sup> It was hypothesized that  
92 transition metal oxides, such as iron oxide (Fe<sub>2</sub>O<sub>3</sub>), present in coal fly ash may be instrumental in  
93 catalytic oxidation of Hg<sup>0</sup>. In the present study, the effects on Hg<sup>0</sup> oxidation of the acidic flue  
94 gas components and the basic NH<sub>3</sub> gas added for NO<sub>x</sub> reduction reactions were evaluated in the  
95 presence of a SCR catalyst. The emissions of acidic flue gases generated by the combustion of  
96 different types of coals depend upon the coal type and its composition. Emission of acidic flue  
97 gases may be reduced significantly in the presence of NH<sub>3</sub>, and they may also be catalytically  
98 converted into other, more reactive, species for Hg<sup>0</sup> oxidation under the SCR emission control  
99 conditions. The objective of the study is to gain a better understanding of the complex,  
100 confounding interactions of flue gas components occurring under SCR emission control  
101 conditions and resulting in changes in mercury speciation in coal combustion flue gases.

102

## 103 **EXPERIMENTAL**

104

### **SCR Reactor System**

105 A bench-scale reactor system was designed and constructed to simulate the SCR reaction  
106 conditions for studying Hg<sup>0</sup> oxidation. A schematic of the reactor system is shown in Figure 1.  
107 The system consists of the preheating and premixing sections, the mercury generation unit, the  
108 SCR reactor, and the on-line reactor effluent measurement unit. Flue gas components, including  
109 carbon dioxide (CO<sub>2</sub>), SO<sub>2</sub>, air, and N<sub>2</sub>, were mixed and preheated to 350 °C and then mixed  
110 with another preheated stream of nitrogen oxide (NO) and HCl at the main heating section.  
111 Water was also pumped into the hot section at a calibrated rate to simulate the moisture content  
112 in flue gas and mixed with the other flue gas components. Ammonia was preheated and flowed  
113 into the static mixing section to achieve better mixing with the other flue gas components. The  
114 gas mixture then flowed into the Pyrex reactor. The alkaline NH<sub>3</sub> reacts with the acid gas  
115 components in the gas mixture to form ammonium salts at temperatures lower than the SCR  
116 reaction temperatures. Therefore, the simulated flue gas mixture was preheated by the electrical  
117 furnaces and maintained at 350 °C by temperature-controlled electrical heating tape to prevent  
118 such reactions taking place and reducing the amount of NH<sub>3</sub> available for reducing NO<sub>x</sub>. The  
119 fine-particle ammonium salts formed from the neutralization of NH<sub>3</sub> are sticky and would  
120 otherwise tend to deposit on the reactor walls and potentially adsorb mercury species in the flue

121 gas mixture. If not avoided through the use of such precautions, the deposition of ammonium  
122 salt particles on the reactor walls would make the measurement of trace mercury species in the  
123 reactor very difficult. Proper preheating and mixing of the gas mixture are very important for  
124 simulating the SCR reaction conditions and for measuring mercury speciation. All the heating  
125 and mixing sections upstream of the Pyrex reactor are made of stainless steel to minimize the  
126 corrosive effect of the acidic gases. Gas cylinders of nitrogen-diluted gaseous species were used  
127 instead of pure gases for some components (i.e.,  $\text{SO}_2/\text{N}_2$ ,  $\text{NO}/\text{N}_2$ ,  $\text{O}_2/\text{N}_2$ , and  $\text{NH}_3/\text{N}_2$ ).

128  
129 A mercury generation unit consisting of a mercury permeation tube surrounded by a  
130 temperature-controlled water bath was used to generate  $\text{Hg}^0$  vapor for the oxidation experiments.  
131 Details of the generation system are described elsewhere.<sup>3</sup> The  $\text{Hg}^0$  vapor was carried by a  
132 nitrogen stream into the top of the SCR reactor (4 cm in inner diameter and 35 cm in length).  
133 The simulated flue gas stream was introduced at the top of the SCR reactor in opposite flow  
134 direction relative to the mixed  $\text{Hg}^0/\text{N}_2$  vapor stream to create a mixing zone where mixing of  
135  $\text{Hg}^0$  with the flue gas is expected to occur. The flue gas mixture containing  $\text{Hg}^0$  and  $\text{NH}_3$  passed  
136 through a honeycomb flow straightener to obtain a good velocity distribution before passing  
137 through the honeycomb SCR catalyst. Mixing of Hg was promoted by the  $\text{N}_2$  carrier velocity,  
138 residence time, and static mixing effect of the flow straightener. A thermocouple was positioned  
139 near the inlet of the catalyst for controlling and monitoring the SCR catalyst temperature. A  
140 sampling tube was also positioned near the inlet of the flow straightener for taking gas samples  
141 close to the inlet of the SCR catalyst. The gaseous effluent stream exiting the SCR reactor  
142 passed through a drying tube to remove moisture in the flue gas. The dried gas then passed to an  
143 online ultraviolet dry  $\text{SO}_2$  analyzer (Bovar Engineering, Inc., model 721AT2; accuracy of about  
144  $\pm 5\%$ ) for measuring  $\text{SO}_2$ . An online chemiluminescent  $\text{NO}_x$  analyzer (Advanced Pollution  
145 Instrumentation, Inc., model 200AH; accuracy of about  $\pm 5\%$ ) downstream of the  $\text{SO}_2$  analyzer  
146 was used for measuring  $\text{NO}_x$ .

147

148

### Test Procedures

149 A commercial SCR catalyst with a vanadia/titania formulation and a honeycomb configuration,  
150 designated as Catalyst A, was used in the study. A small piece (2.2 cm for both sides and 1.9 cm

151 in length) of the catalyst sample was placed into the catalyst compartment of the SCR reactor.  
152 The reactor system was heated overnight at 425 °C under an N<sub>2</sub> atmosphere. This cleanup  
153 procedure was employed prior to each test for removing any adsorbed species in the catalyst in  
154 order to minimize the residue effect caused by the previous test. The temperature of the reactor  
155 was then lowered to below 350 °C, and SO<sub>2</sub> and HCl gases were added to precondition the  
156 catalyst at the same levels as the next day's experiment. The temperature of the reactor was  
157 raised to 350 °C and maintained overnight. This catalyst preconditioning procedure was applied  
158 prior to each test. The next morning, the remaining components of the simulated flue gas  
159 mixture, CO<sub>2</sub>, NO, H<sub>2</sub>O, and NH<sub>3</sub>, plus Hg<sup>0</sup> were added into the reactor. The flows of the flue  
160 gas components were maintained at the levels designed for the test by using the mass flow  
161 controllers. The variability of the gas concentrations is about ±2.5%. A constant total flow rate  
162 of 400 cm<sup>3</sup>/min [at a standard temperature of 25 °C and pressure of 101.4 kPa (STP)] was used  
163 for all tests. The concentrations of SO<sub>2</sub> and NO<sub>x</sub> at the outlet of the reactor were monitored  
164 continuously for four hours by using the SO<sub>2</sub> and NO<sub>x</sub> analyzers, respectively, to ensure that the  
165 NO<sub>x</sub> reduction reached a steady state. Then the two gas analyzers were disconnected from the  
166 outlet of the reactor and the reactor outlet was connected to a sampling train. Sampling for  
167 mercury (under positive pressure) was then started with a sampling time for each test of 2 hr.  
168 The outlet flow rate was measured by using a Gilibrator electronic flow meter (model 2) every  
169 10 minutes during the sampling period.

170

### 171 **Mercury Sampling Method**

172 The mercury speciation method<sup>10</sup> developed by Ontario Hydro (OH) was used for measuring  
173 Hg<sup>0</sup> and Hg<sup>2+</sup> in this study. The method was modified slightly for the bench-scale experiments  
174 with small volumetric gas flow, and the simulated flue gases sampled in the present study were  
175 free of particulates. No particulate filter was used, and smaller impingers (25 cm<sup>3</sup>) were installed  
176 instead of the 100 cm<sup>3</sup> impingers specified by the OH method. These smaller impingers were  
177 used for the much smaller gas volume (0.05 m<sup>3</sup>) sampled in this study than those (1 – 2.5 m<sup>3</sup>)  
178 targeted by the OH method. The smaller impingers were also equipped with screw caps  
179 designed for positive pressure sampling. In summary, the sampling train consists of a series of  
180 eight impingers immersed in an ice water bath. The first three impingers contain a 1 N

181 potassium chloride (KCl) aqueous solution for capturing  $\text{Hg}^{2+}$ .  $\text{Hg}^0$  is insoluble in the KCl  
182 solution and passed through the first three impingers. The next impinger contains a solution of 5  
183 % nitric acid and 10 % hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) followed by three impingers containing a  
184 solution of 10 % sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and 4 % potassium permanganate ( $\text{KMnO}_4$ ), for capturing  
185  $\text{Hg}^0$ . The last impinger was empty to condense and remove any moisture remaining in the flue  
186 gas. The sample fractions captured by the different impingers were prepared and analyzed as  
187 specified in the OH method.<sup>10</sup> Each prepared fraction was analyzed for total mercury by cold  
188 vapor atomic absorption. Sampling by the modified OH method was done at the SCR outlet by  
189 removing the drying tube and the two gas analyzers shown in Figure 1 and connecting to the OH  
190 sampling train. The concentrations of mercury in the impingers after a sampling period of two  
191 hours reached 3-7  $\mu\text{g/L}$ , which are well within the range (1-10  $\mu\text{g/L}$ ) of the instrument  
192 (FIMS100) calibrated according to the OH method. The low gas sampling volume (0.05  $\text{m}^3$ )  
193 employed in this study was still able to collect enough mercury required by the OH method for  
194 analysis.

195

196

### Experimental Approach and Test Conditions

197 The approach employed in this study was to pass a simulated coal combustion flue gas mixture  
198 containing  $\text{NH}_3$  and trace  $\text{Hg}^0$  through a bench-scale SCR reactor under  $\text{NO}_x$  reduction  
199 conditions and measure mercury speciation at the outlet of the reactor. The HCl and  $\text{SO}_2$  levels  
200 in the simulated flue gases were varied for simulating the combustion of PRB coals and  
201 bituminous coals with different sulfur and chlorine contents. Mercury speciation samplings near  
202 the inlet of the SCR reactor with the catalyst removed were conducted at the beginning and in the  
203 middle of the test program. It was found that the inlet concentration obtained from the two  
204 samplings was 19.3 ppb ( $\pm 1$ ppb) with very little  $\text{Hg}^{2+}$  (~2%). The small volumetric flow of the  
205 bench-scale reactor makes the simultaneous samplings of inlet and outlet of the SCR reactor  
206 impractical. The simulated flue gas mixtures preheated to 350 °C in order to avoid the formation  
207 of ammonium salts also makes the construction a by-pass of the SCR reactor for sampling  
208 reactor inlet mercury speciation impractical. Inert Teflon valves are not available for allowing  
209 by-pass operations at these temperatures.

210

211 It has been suggested in the previous field<sup>5,6</sup> and pilot<sup>8</sup> studies that coal type seems to be the  
212 major factor in determining the impact of SCR on mercury speciation. A series of four bench-  
213 scale tests were conducted in the present study to simulate the combustion of PRB and  
214 bituminous coals with different Cl and S contents. The compositions of the simulated flue gas  
215 mixtures used for these tests are shown in Table 1. A base flue gas mixture consisting of 350  
216 ppm NO<sub>x</sub>, 315 ppm of NH<sub>3</sub>, 15% CO<sub>2</sub>, 3.5% O<sub>2</sub>, 5.3% H<sub>2</sub>O, 19 ppb Hg<sup>0</sup>, and balance in N<sub>2</sub> was  
217 used for all the tests. A sub-stoichiometric NH<sub>3</sub>/NO<sub>x</sub> ratio was used in all tests in order to  
218 simulate the low NH<sub>3</sub> slip commonly practiced in the field. The concentrations of HCl and SO<sub>2</sub>  
219 gases added to the base gas mixture were varied for simulating the combustion of different types  
220 of coals. Test P1 simulated the combustion of a PRB coal that has low S and Cl contents such  
221 that most of the Cl in the coal would be converted into HCl in the combustion flue gas. Test P2  
222 also simulated combustion of a PRB coal, but no HCl was added to the flue gas mixture in order  
223 to simulate a PRB coal in which a high calcium (Ca) content would result in all Cl released from  
224 the combustion of this coal being reacted with Ca such that no HCl would exist in the flue gas.  
225 Test B1 simulated the combustion of a low-sulfur and high-chlorine bituminous coal, and the  
226 combustion of a high-sulfur and low-chlorine coal was simulated by the B2 test. All the tests  
227 were conducted at 350 °C and at a constant total flue gas flow rate of 400 cm<sup>3</sup>/min (at STP).  
228 The calculated space velocity for the tests was 2609 hr<sup>-1</sup>, similar to those used in the field.  
229 Sampling for mercury speciation using the OH method was started after the simulated flue gas  
230 mixture passed through the SCR reactor for four hours and the NO<sub>x</sub> concentration measured at  
231 the outlet of the reactor showed that the concentration reached a steady state value.

232

## 233 **RESULTS AND DISCUSSION**

234

### **NO<sub>x</sub> Reduction Results**

235 Results of the NO<sub>x</sub> reduction for the tests are summarized in Table 2. NO<sub>x</sub> reductions of 85 to  
236 88% were observed for the tests. Figure 2 shows the NO<sub>x</sub> concentration profile at the outlet of  
237 the SCR reactor for Test B1. Similar NO<sub>x</sub> concentration profiles were observed for the other  
238 three tests. During the first few minutes after the remaining components of the simulated flue  
239 gas mixture (CO<sub>2</sub>, NO, H<sub>2</sub>O, and NH<sub>3</sub>, plus Hg<sup>0</sup>) were added into the reactor, the NO<sub>x</sub>  
240 concentration remained near zero. The pre-conditioning of the SCR catalyst by SO<sub>2</sub> overnight

241 prior to the NO<sub>x</sub> reduction experiment started may make the catalyst very reactive for the initial  
242 period of reduction of NO<sub>x</sub>. Then the outlet NO<sub>x</sub> concentration increased quickly to about 120  
243 ppm and reduced slowly to reach a steady state concentration of less than 50 ppm in about 3 hr.  
244 The fresh SCR catalyst used in the tests exhibited strong NO<sub>x</sub> reduction catalytic activity under  
245 the widely different SO<sub>2</sub> concentrations (280 –2891 ppm) employed in the tests. The levels of  
246 NO<sub>x</sub> reduction (85 –87%) obtained from the bench-scale SCR reactor are similar to those  
247 observed in the field, suggesting that the reactor system used in the present study simulates  
248 closely the SCR NO<sub>x</sub> emission control conditions in the field.

249

### 250 **Effect of Flue Gas Species on Hg<sup>0</sup> Oxidation**

251 The mercury speciation results measured in the present study are summarized in Table 3. Two  
252 mercury speciation samples were taken at the inlet of the SCR catalyst by using the OH method  
253 after Tests P1 and B1. Two OH samples were also taken at the outlet of the mercury generation  
254 unit at the beginning of the test program. The total mercury concentrations (19.3 ppb) with very  
255 little Hg<sup>2+</sup> (0.5 ppb) measured near the inlet of the catalyst are the same as those (19.2 ppb total  
256 Hg with 0.5 ppb Hg<sup>2+</sup>) measured at the outlet of the mercury generation unit. The two inlet OH  
257 speciation results obtained in the presence of two different simulated flue gas mixtures (Test P1  
258 and Test B1) showed Hg<sup>0</sup> as the only mercury species. The consistent inlet results suggest that  
259 the presence of HCl and SO<sub>2</sub> at different concentrations in the simulated flue gas mixture have  
260 very little effect to change the speciation of mercury in the mixture prior to passing through the  
261 SCR catalyst. The results also suggest no gas phase, homogeneous oxidation of Hg<sup>0</sup> at the inlet.

262

263 The speciation results shown in Table 3 suggest that HCl has a significant effect on the  
264 conversion of Hg<sup>0</sup> into Hg<sup>2+</sup> under SCR NO<sub>x</sub> emission control conditions. All tests except P2  
265 showed most of the mercury sampled at the outlet of the SCR catalyst was in the Hg<sup>2+</sup> form. As  
266 shown in Table 1, the gas mixtures used for Test P1 and P2 were identical except that 8 ppm of  
267 HCl was added to the simulated flue gas mixture for the P1 Test, and no HCl was added in the  
268 P2 Test. Almost all the mercury measured in the P1 Test was Hg<sup>2+</sup>, but very little Hg<sup>2+</sup> was  
269 measured in the P2 Test. The total mercury concentration (13.1 ppb) at the outlet of the SCR  
270 catalyst measured for the P2 Test is about 60% of that (19.3 ppb) measured at the inlet. The

271 results of the two outlet replicate tests are similar to each other, indicating good precision of the  
272 tests. One possible explanation for lower mercury being measured at the outlet for the P2 Test is  
273 that the adsorption of  $\text{Hg}^0$  by the SCR catalyst may take place in the absence of HCl in the flue  
274 gas mixture. Evidence of  $\text{Hg}^0$  adsorption was observed during the initial scoping tests of the  
275 SCR reactor system. When a gas mixture with 3%  $\text{O}_2$ , 10%  $\text{CO}_2$ , 240 ppm NO, and 30 ppb  $\text{Hg}^0$   
276 (balance  $\text{N}_2$ ) was passed through the SCR catalyst at 350 °C, very little  $\text{Hg}^0$  was measured at the  
277 outlet of catalyst by using an on-line ultraviolet (UV) mercury analyzer.  $\text{Hg}^0$  was measured at  
278 detectable levels (>2 ppb) at the outlet immediately after  $\text{NH}_3$  was added to this gas mixture.  
279 The effect of flue gas species on the adsorption of  $\text{Hg}^0$  by the SCR catalyst requires further  
280 investigation.

281  
282 Two tests were conducted for simulating the combustion of bituminous coals that have S and Cl  
283 contents much different from those of the PRB coals. The B1 test simulated the combustion of a  
284 low-sulfur and high-chlorine bituminous coal, and the combustion of a high-sulfur and low-  
285 chlorine coal was simulated by the B2 test. Results presented in Table 3 show  $\text{Hg}^{2+}$  was the  
286 predominant mercury species measured at the outlet of the catalyst for both tests. It appears that  
287 the relatively high HCl concentrations present in the simulated flue gases used for these two tests  
288 provide adequate chlorine for converting  $\text{Hg}^0$  to  $\text{Hg}^{2+}$ . The total Hg concentration (16.9 ppb)  
289 measured at the outlet of the catalyst for Test B1 is comparable to that (19.3 ppb) measured at  
290 the inlet. However, much higher outlet total Hg concentration (32.7 ppb) was measured for Test  
291 B2. The reason for such high total outlet Hg concentration is not known at the present time. A  
292 sudden rapid increase in  $\text{Hg}^0$  (spike) produced by the  $\text{Hg}^0$  generation unit may be the underlying  
293 reason. The  $\text{Hg}^0$  spike had been observed by using the on-line mercury analyzer during the  
294 initial scoping tests. The high mercury concentration measured in Test B2 was unlikely due to  
295 the adsorption of mercury by the catalyst during the previous test. As discussed in the  
296 experimental section, the catalyst sample was heated overnight at 425 °C in a nitrogen  
297 atmosphere prior to each test for removing any adsorbed species including mercury for  
298 minimizing any residual effect caused by the previous test. The high mercury concentration  
299 measured in Test B2 may also represent analytical error but was not studied further.

300

### Importance of Chlorine Source on Hg<sup>0</sup> Oxidation

301  
302 It appears that HCl is the most critical flue gas component for converting Hg<sup>0</sup> to Hg<sup>2+</sup> under SCR  
303 emission control conditions. Hg<sup>2+</sup> was measured as the predominant species at the outlet of the  
304 SCR catalyst for the three tests (P1, B1, and B2) that had widely different HCl and SO<sub>2</sub>  
305 concentrations. The HCl concentration (8 ppm) used for test P1 was much lower than those used  
306 for the other two simulated bituminous coal combustion tests. However, it is still much higher  
307 than that (19 ppb) of the Hg<sup>0</sup> in the flue gas and appears to be adequate for converting most of  
308 the Hg<sup>0</sup> to Hg<sup>2+</sup>. Hg<sup>0</sup> was found to be the predominant species for the only test (P2) that had no  
309 HCl present in the flue gas. The observation of no Hg<sup>0</sup> oxidation for this test may be due to the  
310 lack of a chloride source in this test. The importance of HCl in the flue gas for oxidation of Hg<sup>0</sup>  
311 under SCR emission control conditions observed in the present study seems to be consistent with  
312 a recent field study. Significant increases in Hg<sup>2+</sup> across the SCR reactor were observed for  
313 boilers burning bituminous coals with total chloride concentration measured in the flue gases  
314 ranging from 108 to 19 ppm.<sup>6</sup> However, a boiler burning a PRB coal with 1.5 ppm total chloride  
315 measured in the flue gas showed very little change in mercury speciation across the SCR  
316 reactor.<sup>6</sup> The PRB coal tested has a Cl content below the detection limit (< 60 µg/g), and high  
317 Ca content (25%) was found in the fly ash. The lack of HCl available for Hg<sup>0</sup> oxidation for this  
318 coal with low Cl content and high Ca content may be the main reason for very little Hg<sup>0</sup>  
319 oxidation observed across the SCR reactor.

320  
321 The importance of a chlorine source in low temperature, heterogeneous oxidation of Hg<sup>0</sup>  
322 catalyzed by metal oxides present in fly ash has been suggested in a recent modeling study.<sup>11</sup>  
323 The study suggested that Hg<sup>0</sup> oxidation may be promoted by a Deacon-type process for  
324 producing Cl<sub>2</sub> from HCl which further reacts with Hg<sup>0</sup> leading to Hg<sup>0</sup> oxidation. The SCR  
325 catalyst used in the present study contains V<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>, which may be reactive for promoting  
326 the Deacon-type process. Such oxides have been shown to promote the transformation of Hg<sup>0</sup> to  
327 Hg<sup>2+</sup> in combustion flue gas.<sup>7</sup> Another recent modeling study suggested that low-temperature  
328 oxidation of Hg<sup>0</sup> by a reactive source of chlorine is significant for coals with appreciable  
329 chlorine content.<sup>12</sup> The large Cl storage capacity of unburned carbon in coal fly ash is believed  
330 to provide a source of reactive Cl for Hg<sup>0</sup> oxidation over a broad temperature range below that

331 for the homogeneous reaction.<sup>12</sup> The SCR catalysts also have significant surface areas as well as  
332 active sites, which could retain the reactive Cl generated at the catalyst surfaces and serve as a  
333 reactive Cl source for reactions with Hg<sup>0</sup> to oxidize the Hg<sup>0</sup>.

334

## 335 **CONCLUSIONS**

336 A bench-scale reactor system has been constructed in the present study for closely simulating the  
337 SCR emission control conditions in the field. The system was tested using different gas mixtures  
338 simulating the combustion of bituminous and subbituminous coals with different Cl and S  
339 contents. NO<sub>x</sub> reduction levels (~85%) similar to those observed in field units were achieved by  
340 the system under the different simulated coal combustion conditions tested in this study. Almost  
341 complete oxidation of Hg<sup>0</sup> to Hg<sup>2+</sup> was observed in all but one of the four simulated coal  
342 combustion tests. In the fourth test, no Hg oxidation was observed when HCl was absent from  
343 the simulated flue gas. This result strongly suggests that HCl is important for providing the  
344 source of Cl for Hg<sup>0</sup> oxidation under SCR emission control conditions. The importance of HCl  
345 for Hg<sup>0</sup> oxidation found in the present study provides a scientific base for the apparent coal-type  
346 dependence observed for Hg<sup>0</sup> oxidation reported across SCR reactors in prior field studies.

347

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351

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**Table 1.** Summary of simulated flue gas composition.

Flue Gas Component	Unit	Test			
		P1	P2	B1	B2
HCl	ppm	8	0	204	134
SO <sub>2</sub>	ppm	280	280	934	2891
NO <sub>x</sub>	ppm	350	350	350	350
NH <sub>3</sub>	ppm	315	315	315	315
CO <sub>2</sub>	%	15	15	15	15
O <sub>2</sub>	%	3.5	3.5	3.5	3.5
H <sub>2</sub> O	%	5.3	5.3	5.3	5.3
Hg <sup>0</sup>	ppb	19	19	19	19

**Table 2.** Summary of NO<sub>x</sub> reduction results.

NO <sub>x</sub>	Unit	Test			
		P1	P2	B1	B2
Outlet NO <sub>x</sub> Concentration	ppm	44	52	44	43
NO <sub>x</sub> Reduction	%	87	85	87	88

**Table 3.** Summary of mercury speciation results

Mercury Speciation	Unit	Test				
		Inlet	P1	P2	B1	B2
Hg <sup>0</sup> Concentration	ppb	18.8	0.7	12.6	0.7	3.3
Hg <sup>2+</sup> Concentration	ppb	0.5	17.8	0.5	16.2	29.4
Total Mercury Concentration	ppb	19.3	18.5	13.1	16.9	32.7
Hg <sup>2+</sup>	%	2.6	96.2	3.8	95.9	89.9

## List of Figures

**Figure 1.** Schematic of SCR reactor system.

**Figure 2.** NO<sub>x</sub> concentration vs. time (hours:minutes) measured at SCR reactor outlet for Test B1.

