

1 **Investigation of SCR Impact on Mercury Speciation under Simulated NO_x Emission**
2 **Control Conditions**

3
4 **Chun W. Lee, Ravi K. Srivastava**

5 *U.S. Environmental Protection Agency, Office of Research and Development, National Risk*
6 *Management Research Laboratory, Research Triangle Park, North Carolina*

7
8 **S. Behrooz Ghorishi**

9 *ARCADIS Geraghty & Miller, Inc., Research Triangle Park, North Carolina*

10
11 **Thomas W. Hastings, and Frank M. Stevens**

12 *Cormetech, Inc., Durham, North Carolina*

13
14 **ABSTRACT**

15 Selective catalytic reduction (SCR) technology is being increasingly applied for controlling
16 emissions of nitrogen oxides (NO_x) 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 (V₂O₅, TiO₂), used commonly in the vanadia-titania SCR catalyst for catalytic
21 NO_x reduction, promote the formation of oxidized mercury (Hg²⁺).

22
23 The work reported in this paper focuses on the impact of SCR on elemental mercury (Hg⁰)
24 oxidation. Bench-scale experiments were conducted to investigate Hg⁰ 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 (SO₂) for simulating
27 the combustion of bituminous coals and sub-bituminous coals were tested in these experiments.
28 The effects of HCl and SO₂ in the flue gases on Hg⁰ 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 Hg⁰ to Hg²⁺ under SCR reaction conditions. The importance of HCl for Hg⁰

31 oxidation found in the present study provides the scientific basis for the apparent coal-type
32 dependence observed for Hg⁰ 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

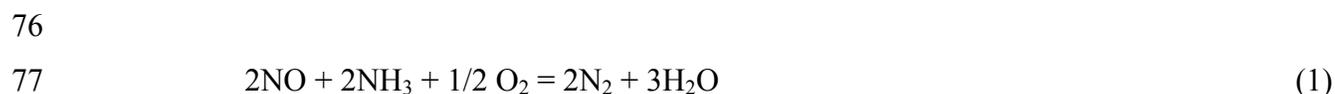
44 **INTRODUCTION**

45 Coal combustion is a major source of mercury emissions that have caused environmental health
46 concern.¹ 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.² It is
48 known that controlling the emissions of oxidized mercury, the water-soluble mercuric chloride
49 (HgCl₂) in particular, is much easier than controlling the insoluble elemental mercury Hg⁰.³
50 Emissions of nitrogen oxides (NO_x) 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.⁴ Several
53 regulatory programs such as the Acid Rain NO_x regulations, the Ozone Transport Commission's
54 NO_x Budget Program, and Ozone and Particulate Matter Transport rulemakings require
55 significant reductions in NO_x emissions from coal combustion sources. As a result of these more
56 stringent NO_x emission control requirements, selective catalytic reduction (SCR) technology is
57 being increasingly applied for controlling NO_x emissions from coal-fired boilers due to its high
58 NO_x 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_x emission control promote the formation of

61 oxidized Hg species.⁵ A recent field study conducted in the United States also found increases in
62 Hg²⁺ species across the SCR reactors.⁶

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 Hg²⁺ species across their SCR reactors.⁶
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.¹

70
71 Nitrogen oxides (NO_x) in coal combustion flue gas are reduced to nitrogen (N₂) and water (H₂O)
72 in an SCR reactor consisting of metal oxide catalysts such as TiO₂-supported V₂O₅. A reducing
73 agent such as ammonia (NH₃) or urea (NH₂CONH₂) is injected into the SCR reactor operating at
74 temperatures of about 350 °C. The NO_x reductions proceed according to the following
75 reactions:



80
81 Laboratory-scale experiments have indicated that metal oxides, including V₂O₅ and TiO₂, could
82 promote the transformation of Hg⁰ to Hg²⁺ in combustion flue gases.⁷ 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.⁸ However, the reactions that are important to transform Hg⁰ into
85 Hg²⁺ in the SCR reactor are not well understood.

86
87 The work reported here is bench-scale research that focuses on studying Hg⁰ oxidation in the
88 presence of simulated coal combustion flue gases and under SCR NO_x emission control
89 conditions. The effects of HCl and SO₂ in the flue gases on Hg⁰ oxidation were studied. Our
90 previous bench-scale study found that NO_x and HCl promote Hg⁰ oxidation, while SO₂ and H₂O

91 reduce Hg⁰ oxidation in the presence of coal combustion fly ashes.⁹ It was hypothesized that
92 transition metal oxides, such as iron oxide (Fe₂O₃), present in coal fly ash may be instrumental in
93 catalytic oxidation of Hg⁰. In the present study, the effects on Hg⁰ oxidation of the acidic flue
94 gas components and the basic NH₃ gas added for NO_x 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 NH₃, and they may also be catalytically
98 converted into other, more reactive, species for Hg⁰ 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 Hg⁰ 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 (CO₂), SO₂, air, and N₂, 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 NH₃ 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 NH₃ available for reducing NO_x. The
119 fine-particle ammonium salts formed from the neutralization of NH₃ 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., SO_2/N_2 , NO/N_2 , O_2/N_2 , and NH_3/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 Hg^0 vapor for the oxidation experiments.
131 Details of the generation system are described elsewhere.³ The 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 Hg^0/N_2 vapor stream to create a mixing zone where mixing of
135 Hg^0 with the flue gas is expected to occur. The flue gas mixture containing Hg^0 and 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 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 SO_2 analyzer (Bovar Engineering, Inc., model 721AT2; accuracy of about
144 $\pm 5\%$) for measuring SO_2 . An online chemiluminescent NO_x analyzer (Advanced Pollution
145 Instrumentation, Inc., model 200AH; accuracy of about $\pm 5\%$) downstream of the SO_2 analyzer
146 was used for measuring 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 N₂ 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 SO₂ 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, CO₂, NO, H₂O, and NH₃, plus Hg⁰ 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 cm³/min [at a standard temperature of 25 °C and pressure of 101.4 kPa (STP)] was used
163 for all tests. The concentrations of SO₂ and NO_x at the outlet of the reactor were monitored
164 continuously for four hours by using the SO₂ and NO_x analyzers, respectively, to ensure that the
165 NO_x 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 method¹⁰ developed by Ontario Hydro (OH) was used for measuring
173 Hg⁰ and Hg²⁺ 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 cm³) were installed
176 instead of the 100 cm³ impingers specified by the OH method. These smaller impingers were
177 used for the much smaller gas volume (0.05 m³) sampled in this study than those (1 – 2.5 m³)
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 Hg^{2+} . 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 (H_2O_2) followed by three impingers containing a
184 solution of 10 % sulfuric acid (H_2SO_4) and 4 % potassium permanganate (KMnO_4), for capturing
185 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.¹⁰ 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 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 NH_3 and trace Hg^0 through a bench-scale SCR reactor under NO_x reduction
199 conditions and measure mercury speciation at the outlet of the reactor. The HCl and 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 (± 1 ppb) with very little 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^{5,6} and pilot⁸ 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_x, 315 ppm of NH₃, 15% CO₂, 3.5% O₂, 5.3% H₂O, 19 ppb Hg⁰, and balance in N₂ was
217 used for all the tests. A sub-stoichiometric NH₃/NO_x ratio was used in all tests in order to
218 simulate the low NH₃ slip commonly practiced in the field. The concentrations of HCl and SO₂
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 cm³/min (at STP).
228 The calculated space velocity for the tests was 2609 hr⁻¹, 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_x 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_x Reduction Results

235 Results of the NO_x reduction for the tests are summarized in Table 2. NO_x reductions of 85 to
236 88% were observed for the tests. Figure 2 shows the NO_x concentration profile at the outlet of
237 the SCR reactor for Test B1. Similar NO_x 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 (CO₂, NO, H₂O, and NH₃, plus Hg⁰) were added into the reactor, the NO_x
240 concentration remained near zero. The pre-conditioning of the SCR catalyst by SO₂ overnight

241 prior to the NO_x reduction experiment started may make the catalyst very reactive for the initial
242 period of reduction of NO_x. Then the outlet NO_x 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_x reduction catalytic activity under
245 the widely different SO₂ concentrations (280 –2891 ppm) employed in the tests. The levels of
246 NO_x 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_x emission control conditions in the field.

249

250 **Effect of Flue Gas Species on Hg⁰ 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 Hg²⁺ (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 Hg²⁺) 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 Hg⁰ as the only mercury species. The consistent inlet results suggest that
259 the presence of HCl and SO₂ 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 Hg⁰ at the inlet.

262

263 The speciation results shown in Table 3 suggest that HCl has a significant effect on the
264 conversion of Hg⁰ into Hg²⁺ under SCR NO_x emission control conditions. All tests except P2
265 showed most of the mercury sampled at the outlet of the SCR catalyst was in the Hg²⁺ 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 Hg²⁺, but very little Hg²⁺ 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 Hg^0 by the SCR catalyst may take place in the absence of HCl in the flue
274 gas mixture. Evidence of Hg^0 adsorption was observed during the initial scoping tests of the
275 SCR reactor system. When a gas mixture with 3% O_2 , 10% CO_2 , 240 ppm NO, and 30 ppb Hg^0
276 (balance N_2) was passed through the SCR catalyst at 350 °C, very little Hg^0 was measured at the
277 outlet of catalyst by using an on-line ultraviolet (UV) mercury analyzer. Hg^0 was measured at
278 detectable levels (>2 ppb) at the outlet immediately after NH_3 was added to this gas mixture.
279 The effect of flue gas species on the adsorption of 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 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 Hg^0 to 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 Hg^0 (spike) produced by the Hg^0 generation unit may be the underlying
293 reason. The 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 Hg⁰ Oxidation

301
302 It appears that HCl is the most critical flue gas component for converting Hg⁰ to Hg²⁺ under SCR
303 emission control conditions. Hg²⁺ 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 SO₂
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 Hg⁰ in the flue gas and appears to be adequate for converting most of
308 the Hg⁰ to Hg²⁺. Hg⁰ 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 Hg⁰ 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 Hg⁰
311 under SCR emission control conditions observed in the present study seems to be consistent with
312 a recent field study. Significant increases in Hg²⁺ 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.⁶ 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.⁶ 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 Hg⁰ oxidation for this
318 coal with low Cl content and high Ca content may be the main reason for very little Hg⁰
319 oxidation observed across the SCR reactor.

320
321 The importance of a chlorine source in low temperature, heterogeneous oxidation of Hg⁰
322 catalyzed by metal oxides present in fly ash has been suggested in a recent modeling study.¹¹
323 The study suggested that Hg⁰ oxidation may be promoted by a Deacon-type process for
324 producing Cl₂ from HCl which further reacts with Hg⁰ leading to Hg⁰ oxidation. The SCR
325 catalyst used in the present study contains V₂O₅ and TiO₂, which may be reactive for promoting
326 the Deacon-type process. Such oxides have been shown to promote the transformation of Hg⁰ to
327 Hg²⁺ in combustion flue gas.⁷ Another recent modeling study suggested that low-temperature
328 oxidation of Hg⁰ by a reactive source of chlorine is significant for coals with appreciable
329 chlorine content.¹² The large Cl storage capacity of unburned carbon in coal fly ash is believed
330 to provide a source of reactive Cl for Hg⁰ oxidation over a broad temperature range below that

331 for the homogeneous reaction.¹² 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 Hg⁰ to oxidize the Hg⁰.

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_x 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 Hg⁰ to Hg²⁺ 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 Hg⁰ oxidation under SCR emission control conditions. The importance of HCl
345 for Hg⁰ oxidation found in the present study provides a scientific base for the apparent coal-type
346 dependence observed for Hg⁰ oxidation reported across SCR reactors in prior field studies.

347

348 **ACKNOWLEDGEMENTS**

349 The extensive technical assistance provided by Jarek Karwowski of Aracadis Geraghty & Miller,
350 Inc. is greatly appreciated.

351

352 **REFERENCES**

353 1. Keating, M.H.; Mahaffey, K.R.; Schoeny, R.; Rice, G.E.; Bullock, O.R.; Ambrose, R.B., Jr.;
354 Swartout, J.; Nichols, J.W. *Mercury Study Report to Congress*, volumes I-VIII; U.S.

355 Environmental Protection Agency, Office of Air Quality Planning and Standards and Office of
356 Research and Development, Research Triangle Park, NC, December 1997; EPA-452/R-97-003
357 through 010.

358

359 2. Brown, T.D.; Smith, D.N.; Hargis, R.A., Jr.; O'Dowd, W.J. *J. Air & Waste Manage. Assoc.*
360 1999, 49, 628-640.

- 361 3. Ghorishi, S.B.; Gullett, B.K.; Jozewicz, W. *Waste Management Research*. 1998, 16:6, 582-
362 593.
- 363
- 364 4. Price, D.; Birnbaum, R.; Batiuk, R.; McCullough, M.; Smith, R. *Nitrogen Oxides: Impacts on*
365 *Public Health and the Environment*; U.S. Environmental Protection Agency, Office of Air and
366 Radiation, Washington, DC, August 1997; EPA-452/R-97-002 (NTIS PB 98-104631).
- 367
- 368 5. Gutberlet, H.; Schluten, A; Lienta, A. "SCR Impacts on Mercury Emissions on Coal-fired
369 Boilers," presented at EPRI's SCR Workshop, Memphis, TN, April, 2000.
- 370
- 371 6. Laudal, D.L.; Thompson, J.S.; Pavlish, J.H.; Brickett, L; Chu, P.; Srivastava, R.K.; Lee,
372 C.W.; Kilgroe, J.D. Evaluation of Mercury Speciation at Power Plants Using SCR and SCR
373 NOx Control Technologies. 3rd International Air Quality Conference, Arlington, Virginia,
374 September 9 –12, 2002.
- 375
- 376 7. Galbreath, K.C.; Zygarlicke, C.L.; Oslon, E.S.; Pavlish, J.H.; Toman, D.L. "Evaluating
377 Mercury Transformation Mechanisms in a Laboratory-Scale Combustion System," *The Science*
378 *of the Total Environment*, 2000, 261:1-3, 149-155.
- 379
- 380 8. Laudal, D.L.; Pavlish, J.H.; Galbreath, K.C.; Thompson, J.S.; Weber, G.F.; Sondreal, E.A.
381 Pilot-Scale Screening Evaluation of the Impact of Selective Catalytic Reduction for NOx on
382 Mercury Speciation. Electric Power Research Institute Report No. 1000755. Palo Alto, CA,
383 2000.
- 384
- 385 9. Lee, C.W.; Kilgroe, J.D.; Ghorishi, S.B. "Speciation of Mercury in the Presence of Coal and
386 Waste Combustion Fly Ashes," 93rd Air & Waste Management Association Annual Meeting &
387 Exhibition, Salt Lake City, UT, June 18-22, 2000.
- 388

389 10. Method D 6782-02. “Standard Test Method for Elemental, Oxidized, Particle-bound and
390 Total Mercury in Flue Gas Generated from Coal-fired Stationary Sources (Ontario Hydro
391 Method).” American Society for Testing and Materials, 2002.

392

393 11. Edwards, J.R.; Srivastava, R.K.; Lee, C.W.; Kilgroe, J.D.; Ghorishi, S.B. paper presented at
394 the EPRI-DOE-EPA Combined Air Pollution Control Symposium: The Mega Symposium,
395 August 21 –23, 2001, Chicago, IL.

396

397 12. Niksa, S.; Fujiwara, N.; Fujita, Y.; Tomura, K.; Moritomi, H.; Tuji, T.; Takasu, S. Journal of
398 Air & Waste Management Association, 2002, 52, 894-901.

399

400 **About the Authors**

401 Chun W. Lee is a senior research scientist and Ravis K. Srivastava is a senior research engineer

402 with the U.S. Environmental Protection Agency, Office of Research and Development at the

403 National Risk Management Research Laboratory in Research Triangle Park, NC. S. Behrooz

404 Ghorishi, formerly with ARCADIS Geraghty & Miller, Inc., is a principal engineer with

405 Babcock & Wilcox in Alliance, OH. Thomas W. Hastings is a new business development

406 manager with Cormetech, Inc., in Durham, NC. Frank M. Stevens is a former employee of

407 Cormetech, Inc. Address correspondence to: Chun W. Lee, Air Pollution Prevention and Control

408 Division, E305-01, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711;

409 email: lee.chun-wai@epa.gov.

Table 1. Summary of simulated flue gas composition.

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

Table 2. Summary of NO_x reduction results.

NO _x	Unit	Test			
		P1	P2	B1	B2
Outlet NO _x Concentration	ppm	44	52	44	43
NO _x Reduction	%	87	85	87	88

Table 3. Summary of mercury speciation results

Mercury Speciation	Unit	Test				
		Inlet	P1	P2	B1	B2
Hg ⁰ Concentration	ppb	18.8	0.7	12.6	0.7	3.3
Hg ²⁺ 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 ²⁺	%	2.6	96.2	3.8	95.9	89.9

List of Figures

Figure 1. Schematic of SCR reactor system.

Figure 2. NO_x concentration vs. time (hours:minutes) measured at SCR reactor outlet for Test B1.

