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Effect of oxy-combustion flue gas on mercury oxidation

Nuria Fernández-Miranda, M. Antonia Lopez-Anton*, Mercedes Díaz-Somoano, M. Rosa Martínez-Tarazona

Instituto Nacional del Carbón (CSIC), Francisco Pintado Fe, 26, 33011, Oviedo, Spain

*Corresponding author:

Phone: +34 985 119090

Fax: +34 985 297662

Email: marian@incar.csic.es

41 **Abstract.**

42 This study evaluates the effect of the gases present in a typical oxy-coal combustion
43 atmosphere on mercury speciation and compares it with the mercury speciation
44 produced in conventional air combustion atmospheres. The work was performed at
45 laboratory scale at 150°C. It was found that the minor constituents (SO₂, NO_x and HCl)
46 significantly modify the percentages of Hg²⁺ in the gas. The influence of these species
47 on mercury oxidation was demonstrated when they were tested individually and also
48 when they were blended in different gas compositions, although the effect was different
49 to the sum of their individual effects. Of the minor constituents, NO_x were the main
50 species involved in oxidation of mercury. Moreover, it was found that a large
51 concentration of H₂O vapor also plays an important role in mercury oxidation. Around
52 50% of the total mercury was oxidized in atmospheres with H₂O vapor concentrations
53 typical of oxy-combustion conditions. When the atmospheres have similar
54 concentrations of SO₂, NO, NO₂, HCl and H₂O, the proportion of Hg⁰/Hg²⁺ is similar
55 regardless of whether CO₂ (oxy-fuel combustion) or N₂ (air combustion) are the main
56 components of the gas.

57

58 **Keywords:** mercury, speciation, oxy-fuel combustion

59 **Introduction.**

60

61

62 Over the past three decades ever since the incident of Minamata Bay the effect of
63 mercury on human health and ecosystems has continued to attract great interest.
64 Mercury is a toxic element and, although mercury species are found in coal in trace
65 concentrations, coal-fired power plants for energy production is one of the greatest
66 anthropogenic sources of mercury emissions to the environment.^{1,2} It is therefore
67 imperative to take measures to ensure its control.³⁻⁶

68 Nevertheless, the main cause of alarm in coal fired power plants are the emissions of
69 CO₂, and several technologies are being developed for its capture and sequestration.
70 Among these, oxy-combustion is the most promising but, as with any relatively new
71 technology, many problems still remain unsolved. This is the case of the effects of
72 mercury species, whose presence in the oxy-combustion flue gases is not only an
73 environmental problem, but also a technological problem. The elemental mercury (Hg⁰)
74 present in the flue gas can accumulate in the CO₂ compression units and damage the
75 aluminium heat exchangers.^{7,8} For these reasons, special attention needs to be paid to
76 mercury oxidation in oxy-combustion processes, and new control measures need to be
77 investigated.

78 Because mercury behavior is influenced by its mode of occurrence, the efficiency of
79 mercury control systems will depend on mercury speciation. The main mercury species
80 present in the flue gas steam are in gas and particulate phases. The particulate mercury
81 is mainly retained in the particulate control devices, whereas the capture of species in
82 gas phase will depend on their reaction and adsorption behavior. Therefore, as a first
83 step towards solving the problem it is necessary to determine in what way the
84 composition of the flue gases produced in the oxy-fuel process affect mercury

85 speciation and the differences that can be expected compared to air combustion
86 systems.⁹

87 It has been demonstrated that NO_x, SO_x and halogens play an important role in
88 mercury reactions in flue gases from coal combustion in air.¹⁰⁻¹³ Therefore they can be
89 expected to influence mercury behavior in oxy-fuel facilities. Although the amount of
90 SO_x is probably of the same order both in air combustion and in oxy-combustion,¹⁴
91 there is a wide variation in the SO₃/SO₂ conversion rates.^{15,16} Moreover, in oxy-
92 combustion, as the flue gas is recycled, the concentration of SO₂ will be higher than in
93 conventional air-coal combustion.^{17,18} This could lead to a higher SO₃ concentrations in
94 the system which might inhibit mercury oxidation.⁹ Consequently, a higher proportion
95 of Hg⁰ can be expected under oxy-combustion than under air combustion. A higher
96 proportion of Hg⁰ would then entail a lower retention in the Flue Gas Desulfuration
97 Systems (FGD) (if any) and increase the probability of amalgamation with aluminum
98 which might cause damage to the CO₂ compression unit. The concentration of NO_x
99 may also vary in different combustibles and plants. However, in oxy-fuel combustion,
100 the levels of NO_x will be lower than in air because the low N₂ content in the boiler will
101 lead to the formation of less thermal NO_x.¹⁶ Several studies^{9,19} have established that
102 mercury oxidation depends on the concentration of NO. For instance, it was found that
103 mercury oxidation increased when the NO concentration rose from 80 to 260 ppm,
104 remaining constant above 550 ppm.⁹ In addition, the H₂O vapor concentration is
105 significantly higher in flue gas from oxy-combustion. In fact, the concentration of H₂O
106 through recycling flue gases to the boiler can, in some cases, reach values of 30%. The
107 role of water in the behavior of mercury has so far received little attention.⁸ However, it
108 has been observed that the effect of H₂O on mercury oxidation depends on its
109 concentration. It was found that a small amount of moisture can enhance oxidation

110 (<0.74%) whereas a large amount may have the opposite effect.²⁰ This could be due in
111 part to the interactions with other gases such as SO₂ and NO, which in some cases
112 favour oxidation.^{19,21-23}

113 On the basis of knowledge acquired so far, the present work evaluates the effect of
114 the components of a typical oxy-coal combustion atmosphere on mercury speciation and
115 compares this behaviour with that of a typical air coal combustion atmosphere, focusing
116 on the impact of different proportions of CO₂ combined with O₂, NO_x, SO₂, H₂O and
117 HCl upon mercury speciation. The results provide a basis for the development of
118 systems for controlling mercury in oxy-combustion processes.

119

120 **2. Experimental.**

121 A schematic diagram of the experimental laboratory scale device employed in this
122 study is shown in Figure 1. The experimental device consists of

123 i) a system to generate a stable concentration of Hg⁰ in the gas phase. A Hg⁰
124 concentration of 100 μg·m⁻³ was produced by means of a VICI Metronic
125 calibrated permeation tube placed inside a glass “U” tube which was immersed
126 in a water bath at 40°C.

127 ii) a gas blending station where different gas compositions were prepared to
128 evaluate the effect of the gas components and their concentrations. Bronkhorst
129 mass flow controllers were used to control the gas flow into the system.
130 Atmospheres consisting of blends of two or more gases, -O₂, CO₂ and H₂O
131 vapour in major concentrations and N₂, SO₂, HCl and NO_x in minor and trace
132 concentrations-, were incorporated to the Hg⁰ gas stream to assess the influence
133 of each gas upon mercury speciation. The transfer lines for mercury are made of
134 PTFE (polytetrafluoroethylene) and for the rest of the gases of 316 stainless steel

135 with a diameter of $\frac{1}{4}$ in. The temperature of the gases was maintained at 150°C .
136 The residence time was 3.2 s^{-1} .
137 iii) a system for analyzing the mercury species. A continuous Hg gas analyzer (VM
138 3000) was used to monitor the Hg^0 . The Hg^{2+} was determined by capturing it in
139 an ion exchanger resin (Dowex® 1x8), suitable for the selective extraction of
140 Hg^{2+} species.²⁴ The resin was conditioned with a solution of HCl:H₂O (1:1) at
141 90°C for 30 minutes and then filtered and dried. The resin was placed prior to the
142 Hg^0 continuous analyzer ((1) in Figure 1) in such a way that the total mercury
143 concentration was balanced. The Hg^{2+} in the resin at the end of the experiments
144 was determined by means of an automatic mercury analyzer (AMA 254). The
145 Hg^{2+} results obtained with the resin were compared with those obtained by the
146 standard Ontario Hydro (OH) method and a commercial speciation sorbent trap
147 (Ohio Lumex). The OH procedure is described in the standard ASTM D6784
148 test method. In accordance with this method, Hg^{2+} is collected in impingers
149 containing a chilled aqueous KCl solution. Hg^0 is collected in subsequent
150 impingers: one impinger containing a chilled aqueous solution of $\text{HNO}_3/\text{H}_2\text{O}_2$
151 and the other three containing chilled aqueous acidic solutions of KMnO_4 ((2) in
152 Figure 1). The solutions are then analyzed by AMA 254. The Ohio Lumex
153 sorbent trap allows Hg^{2+} and Hg^0 to be captured separately. Moisture resistance
154 and acid gas scrubbers come standard with these traps in order to prevent
155 interference with Hg^{2+} ((3) in Figure 1).

156 In order to identify possible reactions between gases other than mercury, the contents
157 of O_2 , CO_2 , SO_2 , NO and NO_2 in the gases were determined using a TESTO 350 Gas
158 Analyzer. Different gas compositions at different temperatures were evaluated.

159 The water vapour in the outlet of the experimental device was condensed and
160 collected in two flasks prior to the VM analyzer. The sulphate, nitrite, nitrate and
161 chloride retained in the condensate were determined by ionic chromatography.

162

163 **3. Results and discussion.**

164 3.1 Mercury speciation in gas phase.

165 A comparative study of the three methods employed to determine the mercury
166 speciation was carried out. The atmosphere was prepared using all the gases that might
167 be produced during oxy-combustion in the following concentrations: 1000 ppm of SO₂,
168 1000 ppm of NO, 100 ppm of NO₂, 25 ppm of HCl, 4% of O₂, 64% of CO₂, 12% of
169 H₂O and balanced with N₂. Figure 2 compares the percentage of Hg²⁺ determined with
170 the resin, OH and trap methods. Similar results were obtained with the resin and OH
171 method. However, the result was slightly lower in the case of the trap sorbent. This may
172 be due to the fact that the experimental conditions of this work differ from the optimal
173 conditions for which the traps were designed. They were manufactured to be kept at
174 100°C and in atmospheres with low H₂O vapor content. On the other hand, the flow rate
175 through these traps must be between 200-300 ml/min to avoid breakthrough on the KCl
176 bed whereas the flow rate used in this study was 500 ml/min. Moreover, the OH method
177 is tedious and employs solutions that can become unstable with time. Since resin is
178 easily conditioned, economically viable and produces accurate results in samples with a
179 large amount of moisture,²⁵⁻²⁷ the resin method was employed in this study to evaluate
180 mercury oxidation.

181 3.2. Effect of SO₂.

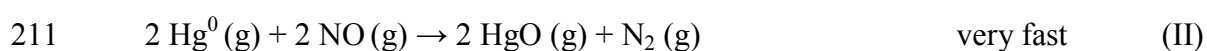
182 The main difference between a typical coal combustion atmosphere and an oxy-
183 combustion atmosphere is the higher CO₂ and lower N₂ concentration in the oxy-fuel
184 flue gas. In this study, the CO₂ content was 16% in the air combustion atmosphere and
185 approximately 70% in oxy-combustion. The atmospheres were balanced with the
186 reactive gases and N₂. When the influence of SO₂ on mercury speciation was evaluated
187 in the two atmospheres: a) 1000 ppm SO₂, 70% CO₂, 4% O₂ and 26% N₂ and b) 1000
188 ppm SO₂, 16% CO₂, 4% O₂ and 80% N₂, it was found that approximately 3% of Hg²⁺
189 was formed in both atmospheres. This percentage increased slightly to 4-5% when the
190 SO₂ concentration was increased to 2000 ppm. As postulated in previous works^{13,21,23} in
191 these simple atmospheres, mercury oxidation may have occurred as a consequence of
192 reaction (I).



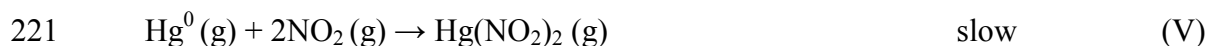
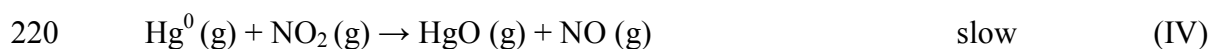
194 Because it is not possible to identify of HgO(g) to prove that this reaction occurs, the
195 change in the SO₂/SO₃ ratio was evaluated. To this end, the N₂, CO₂, O₂ and SO₂
196 contents in the outlet gases were compared with the composition in the inlet gas, and it
197 was found that the SO₂ content decreased. Figure 3 shows the concentration of SO₂ in
198 the outlet stream when the inlet gas had 1000 ppm (Figure 3a) and 2000 ppm (Figure
199 3b) of SO₂ blended with O₂ and CO₂. This decrease can be attributed to the oxidation of
200 SO₂ to SO₃ according to reaction I. The mercury oxidation was around 3% Hg²⁺ in both
201 atmospheres (16 and 70% CO₂). In both cases the concentration of SO₂ was sufficient to
202 produce the oxidation of mercury through Reaction I.

203 3.3. Effect of NO_x

204 Figure 4 shows the percentage of Hg^0 and Hg^{2+} produced in an atmosphere with
205 1000 ppm of NO in different simple gas compositions containing N_2 , CO_2 and O_2 in
206 different proportions. As can be observed, Hg^0 was oxidized by NO in an atmosphere of
207 N_2 in a proportion of ~15% which can be explained by reaction II. The same
208 percentage of Hg^{2+} was produced in the atmospheres having 4% $\text{O}_2 + \text{N}_2$ and 16% CO_2
209 + N_2 . However, the oxidation was higher (~32%) when both CO_2 and O_2 were present
210 in the gas blend, independently of CO_2 concentration.

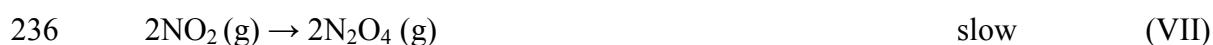


212 The analysis of the outlet gas composition (Figure 5) revealed that some of NO was
213 converted into NO_2 (Reaction III) and this transformation was higher in the presence of
214 CO_2 (Figure 5b). For example, 1000 ppm of NO resulted in 50 ppm of NO_2 in an
215 atmosphere with 70% CO_2 whereas only 5 ppm of NO_2 was formed in an atmosphere
216 free of CO_2 . Therefore, the higher oxidation of mercury observed in the presence of NO,
217 CO_2 and O_2 could have been due to the formation of a high proportion of NO_2 which
218 would react with Hg^0 according to reactions IV and/or V.



222 Although in a combustion flue gas NO_2 is usually present in lower concentrations
223 than NO, the NO_2 content could increase via reaction III in which case reactions IV and
224 V would occur. To explore this possibility, the Hg^{2+} content was determined in an
225 atmosphere with 100 ppm of NO_2 blended with CO_2 , O_2 and N_2 . The results (Figure 6)

226 demonstrated the presence of Hg^{2+} in all cases. It is worth noting that i) oxidation was
227 higher than that produced by NO in an atmosphere with only N_2 (Figure 4) and that ii)
228 the oxidation decreased when CO_2 was present. The lower oxidation of mercury
229 produced in the presence of CO_2 could have been due to the conversion of NO_2 to NO
230 or N_2O_4 through reactions VI and/or VII^{28,29}. Analysis of the gases at different
231 temperatures and concentrations showed that the decomposition of NO_2 to NO through
232 Reaction VI hardly occurred (Figure 7) whereas reaction VII may have produced. As
233 can be observed in Figure 8, the NO_2 signal decreased when CO_2 was present in the
234 atmosphere.



237 According to the data described above, NO and NO_2 individually are able to oxidize
238 mercury in different proportions (13-52%) depending on whether CO_2 is present
239 (Figures 4 and 6). However, when both gases were present in an atmosphere composed
240 of 1000 ppm NO, 100 ppm NO_2 , 4% O_2 , 70% CO_2 and 26% N_2 , mercury oxidation
241 decreased to $6 \pm 1\%$. This could have been due to:

242 i) a new reaction (Reaction VIII)^{15,29} yielding N_2O_3 which is not able to oxidize
243 mercury. This would explain why the analysis of the total NO_x content was lower
244 than the sum of NO and NO_2 (Figure 9)



246 ii) a higher concentration of NO (1000 ppm) than NO₂ (100 ppm) which would tend
247 to drive reaction IV to the left making mercury oxidation less likely.

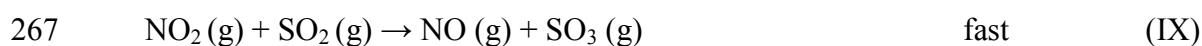
248 3.4. Effect of HCl.

249 Mercury oxidation does not take place in atmospheres with 25 ppm of HCl + 4% O₂
250 in different proportions of CO₂. Although theoretical models based on thermodynamic
251 equilibrium data (HSC Chemistry) predict the formation of HgCl₂(g) and HgCl(g), these
252 reactions did not occur in the experimental conditions of this work due to kinetic
253 limitations. These results agree with previous results obtained by the authors^{13,21,23} and
254 confirm that HCl does not influence homogeneous mercury oxidation.

255

256 3.5. Effect of the mixture of SO₂, NO_x and HCl.

257 In an atmosphere composed of 1000 ppm SO₂, 1000 ppm NO, 100 ppm NO₂, 25 ppm
258 HCl, 4%O₂, 70%CO₂ and 26%N₂, the percentage of Hg²⁺ was 9±1%. Similar
259 percentages of oxidation were obtained when CO₂ was substitute for N₂. From a
260 quantitative point of view, the results suggest that NO_x and SO₂ have an additive effect
261 on mercury oxidation. It must be remembered that the oxidation of mercury by SO₂ and
262 NO_x was approximately 3 and 6%, respectively, as a consequence of reactions I, II, IV
263 and V. It is remarkable that when HCl was removed from the atmosphere, the
264 percentage of Hg²⁺ increased to 13±1% in both the atmosphere rich in N₂ (air
265 combustion) and the atmosphere rich in CO₂ (oxy-combustion). Two reactions may
266 explain this behavior:

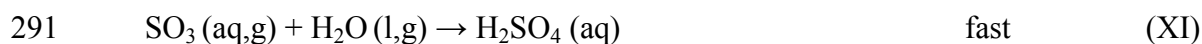


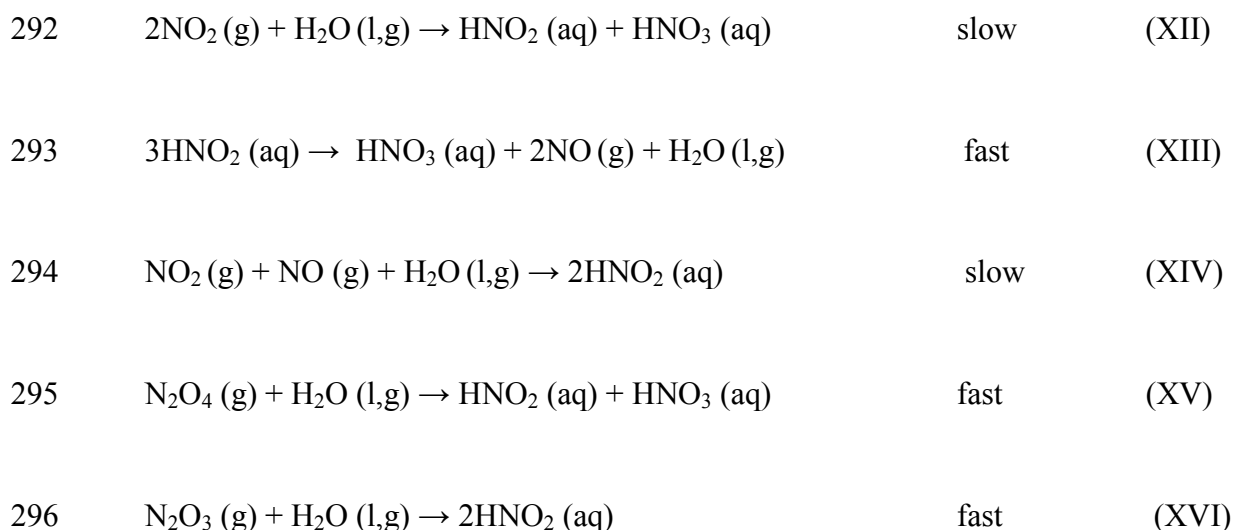
269 According to these reactions, the absence of HCl could be favouring reaction IX, and
270 hence, an increase in mercury oxidation through the formation of NO. On the other hand
271 the presence of HCl could give rise to reaction X which would consume NO in
272 detriment to the production of Hg²⁺. In both cases the absence of HCl would benefit
273 mercury oxidation in the presence of NO_x, SO₂, O₂, CO₂ and N₂.

274 3.6. Effect of H₂O.

275 As already mentioned, one of the most important differences between the
276 composition of a flue gas from coal combustion in air and from oxy-combustion is that
277 in the latter the concentration of H₂O is much higher. The effect of different H₂O vapor
278 concentrations (7, 12 and 20%) in the atmosphere formed by 1000 ppm SO₂, 1000 ppm
279 NO, 100 ppm NO₂, 25 ppm HCl, 4%O₂, 56-70%CO₂ and N₂ (simulated flue gas, SFG)
280 was evaluated. The Hg²⁺ percentages are shown in Figure 10. Mercury oxidation was
281 found to be higher (25 to 45%) in the atmospheres containing H₂O vapor than in the dry
282 atmosphere (9%). In an atmosphere with smaller CO₂ and H₂O concentrations (1000
283 ppm SO₂, 1000 ppm NO, 100 ppm NO₂, 25 ppm HCl, 4%O₂, 16%CO₂, 6%H₂O and N₂)
284 as in the case of coal combustion in air, the Hg²⁺ obtained was 30±9%. Therefore, in all
285 cases mercury oxidation is favored by the presence of H₂O.

286 Apart from homogeneous oxidation, which is the subject of this study, reactions in
287 aqueous phase can also take place giving rise to the formation of acid gases.³⁰ These
288 reactions may occur in any condensate produced at the cold points during the
289 combustion process and also need to be taken into consideration. The most important
290 reactions of this type are as follows:





297 To identify these possible reactions, the condensates obtained by cooling the gases
 298 collected prior to the VM 3000 in a flask (Figure 1) were analyzed by ion
 299 chromatography. These analysis corroborated the presence of sulphates, nitrites and
 300 nitrates. The higher oxidation of Hg^0 in the presence of H_2O could have been a
 301 consequence of the above mentioned reactions in which, in addition to the formation of
 302 sulphates, nitrites and nitrates, NO may have produced (Reaction XIII) favouring the
 303 formation of HgO through reaction II.

304 As mentioned in section 3.5, in an atmosphere without HCl (1000 ppm SO_2 , 1000
 305 ppm NO, 100 ppm NO_2 , 4% O_2 , 12% H_2O , 64% CO_2 and N_2), the percentage of Hg^{2+} is
 306 higher (45%) than in the same atmosphere with HCl (37%) (Figure 10). This supports
 307 the view that, in addition to the reactions listed above, reactions IX and X would occur,
 308 producing a higher amount of Hg^{2+} . In summary, mercury oxidation is promoted by the
 309 presence of H_2O , NO, NO_2 and SO_2 in the gas. The extent of this oxidation depends on
 310 their relative proportions and concentrations and the presence of other gases, such as
 311 HCl and CO_2 . This suggests that it is difficult to establish the exact percentage of Hg^{2+}
 312 that might be produced in a combustion process. Nevertheless, from the results of this

313 work some generalizations can be made that will be helpful for modelling and
314 predicting the behaviour of mercury in each particular case. NO and NO₂ are involved
315 in mercury oxidation through several competing reactions which are affected by the
316 concentration of CO₂. The presence of HCl together with the other gases decreases
317 mercury oxidation. On the other hand, H₂O favors the formation of Hg²⁺ which can
318 reach values as high as 50%. In oxy-combustion where high amounts of H₂O may be
319 present, oxidation may be higher than in conventional coal combustion. Independently
320 of the problems that the presence of a large amount of H₂O originates in oxy-
321 combustion, for tackling the problem of mercury, H₂O would be an advantage. An
322 increase in mercury oxidation implies a smaller amount of Hg⁰ and therefore a lesser
323 risk of damage to the CO₂ compression units.

324

325 **Acknowledgments**

326 The financial support for this work was provided by the project CTM2011-22921. The
327 authors thank PCTI Asturias for awarding Nuria Fernandez-Miranda a pre-doctoral
328 fellowship.

329

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424 **Figure captions**

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427 **Figure 1.** Schematic diagram of the experimental device.

428 **Figure 2.** Percentages of Hg^0 and Hg^{2+} in the presence of 1000ppm SO_2 , 1000ppm NO ,
429 100 ppm NO_2 , 25 ppm HCl , 4% O_2 , 12% H_2O , 64% CO_2 and N_2 retained by the resin,
430 Ontario Hydro (OH) and trap method

431 **Figure 3.** Analysis of the SO_2 concentration in the presence of O_2 and CO_2

432 **Figure 4.** Percentages of Hg^0 and Hg^{2+} in the presence of NO , O_2 , CO_2 and N_2
433 determined by VM analyser and resin, respectively.

434 **Figure 5.** Conversion of NO to NO_2 at 150°C in the presence of a) 4% O_2 and N_2 and b)
435 4% O_2 and 70% CO_2

436 **Figure 6.** Percentages of Hg^0 and Hg^{2+} in the presence of NO_2 , O_2 , CO_2 and N_2
437 determined by VM analyser and resin, respectively.

438 **Figure 7.** Conversion of NO_2 to NO at different temperatures

439 **Figure 8.** Analysis of the NO_2 concentration in the presence of O_2 , CO_2 and N_2

440 **Figure 9.** Analysis of the NO_x concentration in the presence of O_2 , CO_2 and N_2

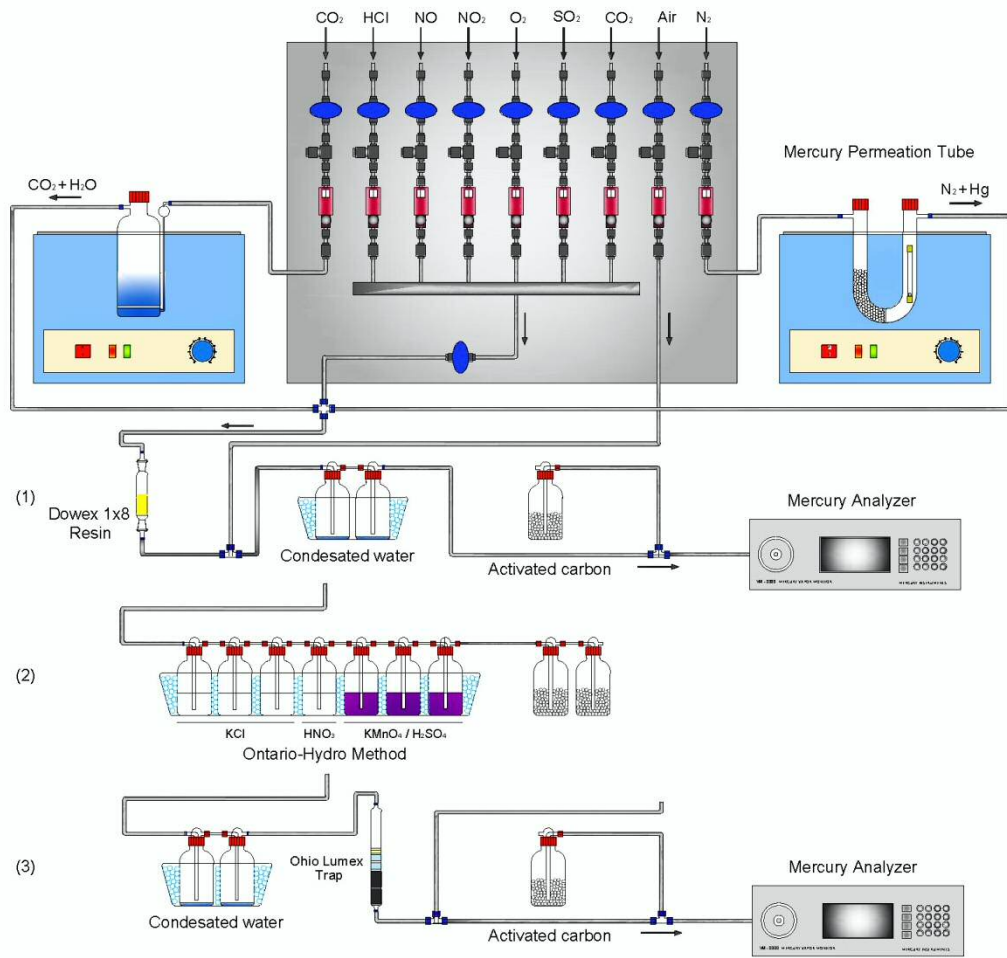
441 **Figure 10.** Percentages of Hg^0 and Hg^{2+} in the presence of 1000ppm SO_2 , 1000ppm
442 NO , 100 ppm NO_2 , 25 ppm HCl , 4% O_2 , 70% CO_2 and N_2 (SFG: simulated flue gas) with
443 different amounts of H_2O determined by VM analyser and resin, respectively.

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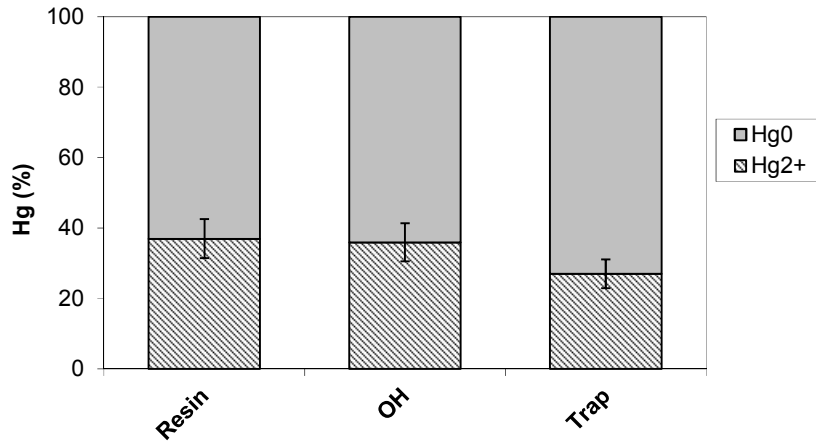


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451 Figure 1.



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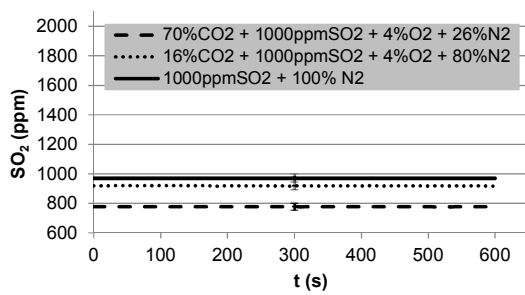
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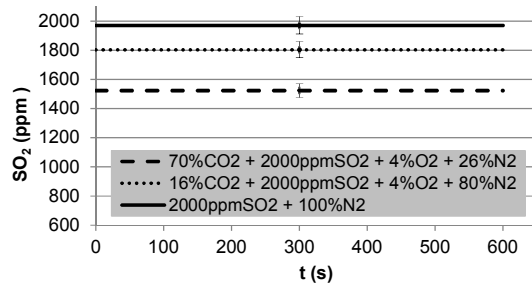
455 Figure 2

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(a)



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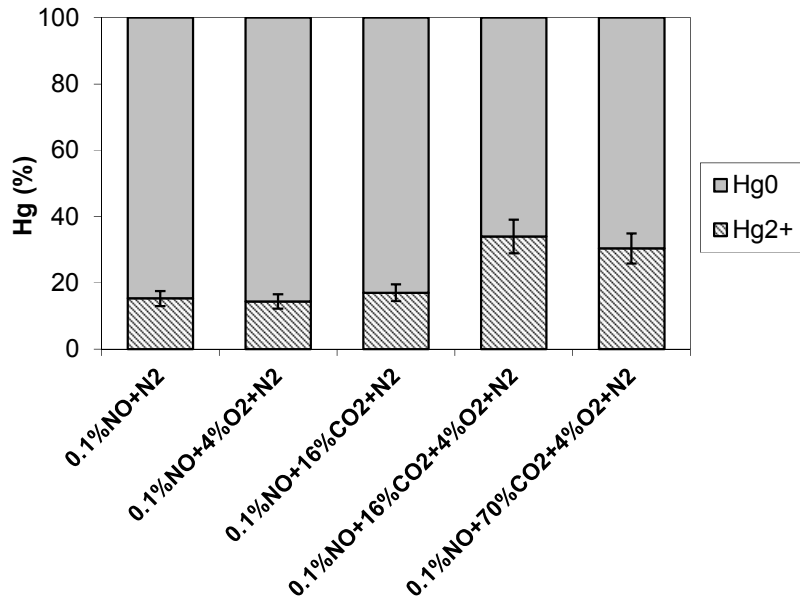
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461 Figure 3

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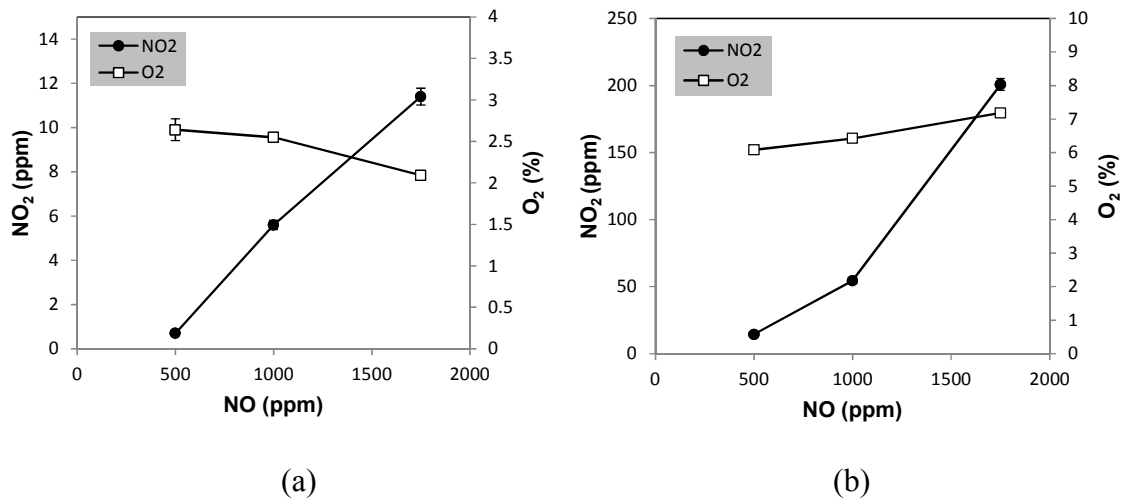


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465 Figure 4

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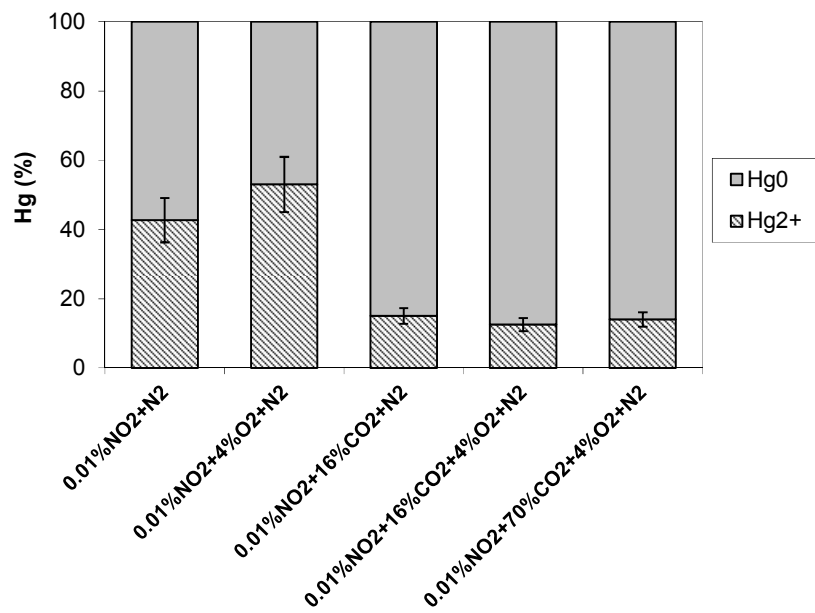
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470 Figure 5

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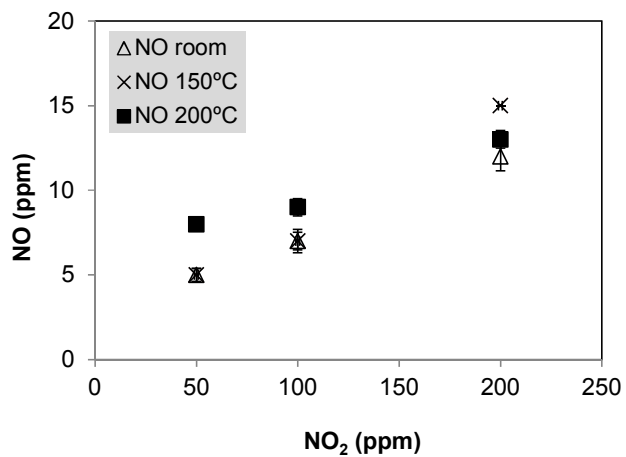


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474 Figure 6

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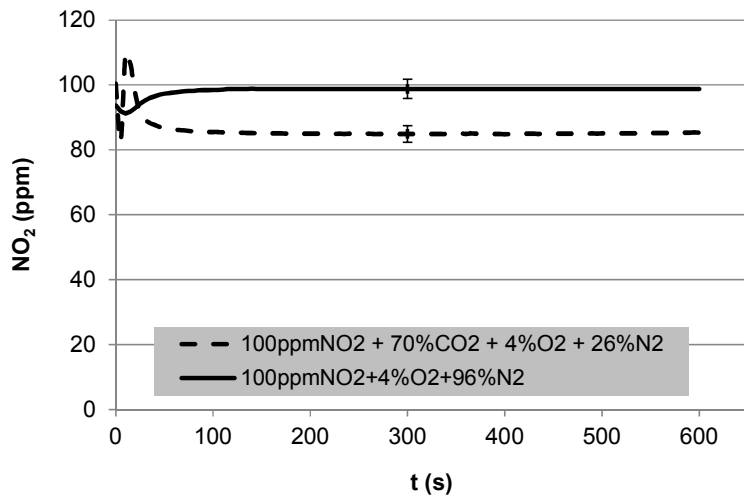
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479 Figure 7

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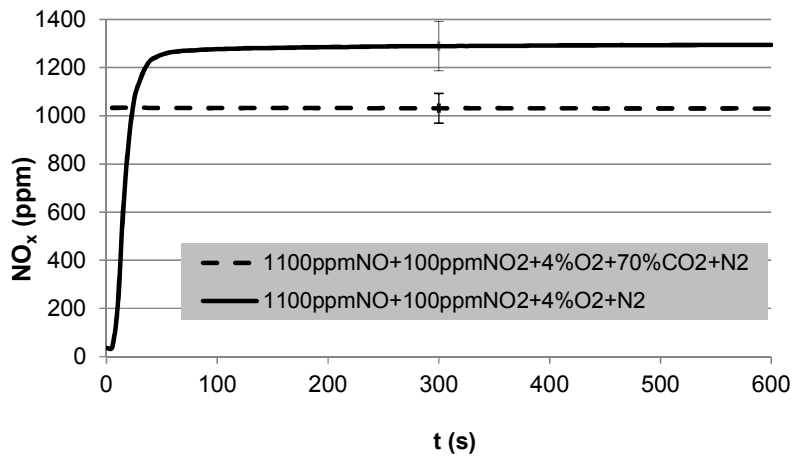


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483 Figure 8

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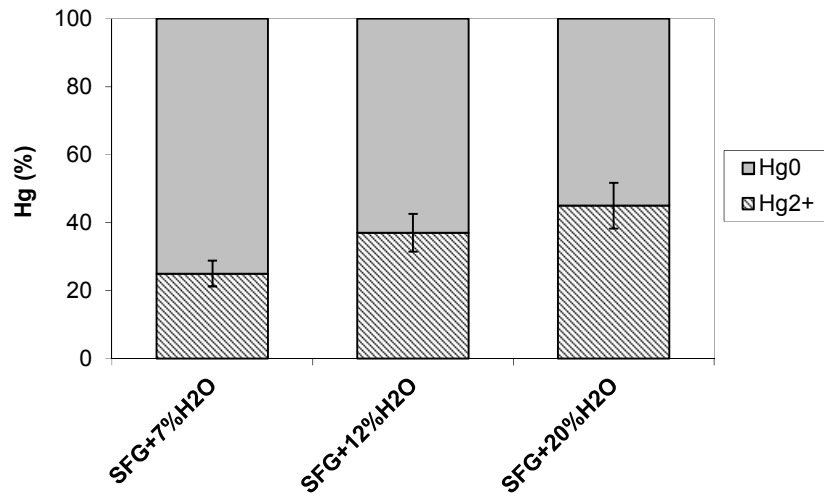
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487 Figure 9

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492 Figure 10

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