Effect of oxy-combustion flue gas on mercury oxidation

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Abstract.

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

Keywords: mercury, speciation, oxy-fuel combustion

Introduction.

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

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

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

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

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

($<0.74\%$) whereas a large amount may have the opposite effect.²⁰ This could be due in part to the interactions with other gases such as SO_2 and NO , which in some cases favour oxidation.^{19,21-23}

On the basis of knowledge acquired so far, the present work evaluates the effect of the components of a typical oxy-coal combustion atmosphere on mercury speciation and compares this behaviour with that of a typical air coal combustion atmosphere, focusing on the impact of different proportions of CO_2 combined with O_2 , NO_x , SO_2 , H_2O and HCl upon mercury speciation. The results provide a basis for the development of systems for controlling mercury in oxy-combustion processes.

2. Experimental.

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

- i) a system to generate a stable concentration of Hg^0 in the gas phase. A Hg^0 concentration of $100 \mu\text{g}\cdot\text{m}^{-3}$ was produced by means of a VICI Metronic calibrated permeation tube placed inside a glass “U” tube which was immersed in a water bath at 40°C .
- ii) a gas blending station where different gas compositions were prepared to evaluate the effect of the gas components and their concentrations. Bronkhorst mass flow controllers were used to control the gas flow into the system. Atmospheres consisting of blends of two or more gases, $-\text{O}_2$, CO_2 and H_2O vapour in major concentrations and N_2 , SO_2 , HCl and NO_x in minor and trace concentrations-, were incorporated to the Hg^0 gas stream to assess the influence of each gas upon mercury speciation. The transfer lines for mercury are made of PTFE (polytetrafluoroethylene) and for the rest of the gases of 316 stainless steel

with a diameter of $\frac{1}{4}$ in. The temperature of the gases was maintained at 150°C.
The residence time was 3.2 s^{-1} .

iii) a system for analyzing the mercury species. A continuous Hg gas analyzer (VM 3000) was used to monitor the Hg^0 . The Hg^{2+} was determined by capturing it in an ion exchanger resin (Dowex® 1x8), suitable for the selective extraction of Hg^{2+} species.²⁴ The resin was conditioned with a solution of HCl:H₂O (1:1) at 90°C for 30 minutes and then filtered and dried. The resin was placed prior to the Hg^0 continuous analyzer ((1) in Figure 1) in such a way that the total mercury concentration was balanced. The Hg^{2+} in the resin at the end of the experiments was determined by means of an automatic mercury analyzer (AMA 254). The Hg^{2+} results obtained with the resin were compared with those obtained by the standard Ontario Hydro (OH) method and a commercial speciation sorbent trap (Ohio Lumex). The OH procedure is described in the standard ASTM D6784 test method. In accordance with this method, Hg^{2+} is collected in impingers containing a chilled aqueous KCl solution. Hg^0 is collected in subsequent impingers: one impinger containing a chilled aqueous solution of HNO₃/H₂O₂ and the other three containing chilled aqueous acidic solutions of KMnO₄ ((2) in Figure 1). The solutions are then analyzed by AMA 254. The Ohio Lumex sorbent trap allows Hg^{2+} and Hg^0 to be captured separately. Moisture resistance and acid gas scrubbers come standard with these traps in order to prevent interference with Hg^{2+} ((3) in Figure 1).

In order to identify possible reactions between gases other than mercury, the contents of O₂, CO₂, SO₂, NO and NO₂ in the gases were determined using a TESTO 350 Gas Analyzer. Different gas compositions at different temperatures were evaluated.

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

3. Results and discussion.

3.1 Mercury speciation in gas phase.

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

3.2. Effect of SO₂.

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

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

3.3. Effect of NO_x

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

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

Although in a combustion flue gas NO_2 is usually present in lower concentrations than NO, the NO_2 content could increase via reaction III in which case reactions IV and V would occur. To explore this possibility, the Hg^{2+} content was determined in an 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)

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

3.4. Effect of HCl.

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

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

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

According to these reactions, the absence of HCl could be favouring reaction IX, and hence, an increase in mercury oxidation through the formation of NO. On the other hand the presence of HCl could give rise to reaction X which would consume NO in detriment to the production of Hg^{2+} . In both cases the absence of HCl would benefit mercury oxidation in the presence of NO_x , SO_2 , O_2 , CO_2 and N_2 .

3.6. Effect of H_2O .

As already mentioned, one of the most important differences between the composition of a flue gas from coal combustion in air and from oxy-combustion is that in the latter the concentration of H_2O is much higher. The effect of different H_2O vapor concentrations (7, 12 and 20%) in the atmosphere formed by 1000 ppm SO_2 , 1000 ppm NO, 100 ppm NO_2 , 25 ppm HCl, 4% O_2 , 56-70% CO_2 and N_2 (simulated flue gas, SFG) was evaluated. The Hg^{2+} percentages are shown in Figure 10. Mercury oxidation was found to be higher (25 to 45%) in the atmospheres containing H_2O vapor than in the dry atmosphere (9%). In an atmosphere with smaller CO_2 and H_2O concentrations (1000 ppm SO_2 , 1000 ppm NO, 100 ppm NO_2 , 25 ppm HCl, 4% O_2 , 16% CO_2 , 6% H_2O and N_2) as in the case of coal combustion in air, the Hg^{2+} obtained was $30 \pm 9\%$. Therefore, in all cases mercury oxidation is favored by the presence of H_2O .

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

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

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Figure captions

Figure 1. Schematic diagram of the experimental device.

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

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

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

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

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

Figure 7. Conversion of NO_2 to NO at different temperatures

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

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

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

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Figure 2

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Figure 3

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Figure 10