1 **Differential Partitioning and Speciation of Hg in Wet FGD**

2 **Facilities of two Spanish PCC Power Plants**

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18

19   **Abstract**

20   This paper evaluates the speciation and partitioning of mercury in two Spanish

21   pulverized coal combustion power plants (PP1 and PP2), equipped with wet limestone-

22   based flue gas desulphurization facilities (FGD) operating with forced oxidation and re-

23   circulation of FGD water streams. These plants are fed with coal (PP1) and coal/pet-

24   coke blends (PP2) with different mercury contents. The behaviour, partitioning and

25   speciation of Hg were found to be similar during the combustion processes but different

26   in the FGD systems of the two power plants. A high proportion (86-88%) of Hg escaped

27   the electrostatic precipitator in gaseous form, $Hg^{2+}$ being the predominant mercury

28   species (68-86%) to enter the FGD. At this point, a relatively high total Hg retention (72

29   and 65%) was achieved in the PP1 and PP2 (2007) FGD facilities respectively.

30   However, during the second sampling campaign for PP2 (2008), the mercury removal

31   achieved by the FGD was much lower (26%). Lab-scale tests point to liquid/gas ratio as

32   the main parameter affecting oxidised mercury capture in the scrubber. The partitioning

33   of the gaseous mercury reaching the FGD system in the wastes and by-products

34   differed. In the low mercury input power plant (PP1) most of the mercury (67%) was

35   associated with the FGD gypsum. Moreover in PP2 a significant proportion of the

36   gaseous mercury reaching the FGD system remained in the aqueous phase (45%) in the

37   2007 sampling campaign while most of it escaped in 2008 (74%). This may be

38   attributed to the scrubber operating conditions and the different composition and

39   chemistry of the scrubber solution probably due to the use of an additive.

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41   **Keywords:** Mercury partitioning, speciation, wet FGD

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43   **1. Introduction**

44        Mercury is an element of special environmental concern because of its toxicity,

45    persistence and bioaccumulation in the environment (US EPA, 2011). Today about 66%

46    of total worldwide mercury emissions come from coal-fired power plants and future

47    predictions point to an increase in this contribution due to the important role of coal

48    combustion in electricity generation in developing countries (Pacyna et al., 2010). The

49    major pathways for mercury release from coal combustion are via air and wastes.

50    Unlike most other heavy metals, the majority of the mercury in the exhaust gas from

51    combustion remains in gas phase (Meij, 1991; Clarke and Sloss., 1992; Sloss, 1995;

52    Miller et al., 2002; Park et al., 2008). During combustion, most of the Hg bound in the

53    coal is released as gaseous elemental mercury. Subsequent cooling of the combustion

54    gas and interactions between the gaseous $Hg^0$ and other combustion products convert

55    $Hg^0$ to gaseous oxidized mercury ($Hg^{2+}$) and particle-bound mercury ($Hg_p$) (Sloss, 1995;

56    Park et al., 2008;). The extent of this transformation depends on the characteristics of

57    the coal and combustion conditions (Park et al. 2008). Particle-bound mercury can be

58    retained in particle control devices such as electrostatic precipitators (ESPs). However,

59    gaseous elemental and oxidized mercury are emitted to the environment in different

60    proportions.

61        The 1990 Clean Air Act Amendments listed mercury compounds as hazardous

62    air pollutants and required the Environmental Protection Agency (EPA) to establish

63    technology-based standards for certain sources that emit these air toxics. In line with

64    this requirement, EPA is developing air toxics emissions standards for power plants and

65    intends to propose air toxics standards for coal- and oil-fired electric generating units by

66    March 10, 2011 and finalize a rule by November 16, 2011 (US EPA, 2011). In Europe,

67    the European Commission launched the EU Mercury strategy in 2005 (EC, 2005). In

68    this document coal burning is identified as one of the largest sources of mercury release.

69  Coal burning in plants above 50 MWth is covered by the Integrated Pollution

70  Prevention and Control and 2001/80/EC Directives.

71     Among the different systems proposed for the reduction of mercury emissions in

72  power stations, multi-pollutant gas cleaning systems are considered a valuable option in

73  terms of efficiency and low investment (Niksa and Fujiwara, 2005; Álvarez-Ayuso et

74  al., 2006; Meij and Te Winkel, 2006; Díaz-Somoano et al., 2007; Meij and Te Winkel,

75  2007; Senior, 2007; Cao et al, 2008; Hutson et al., 2008; Stergarsek et al., 2008; Tao et

76  al., 2009). In this approach, the wet flue gas desulfurization (wet FGD) units installed in

77  power plants for $SO_2$ capture could be optimized for the co-capture of pollutants other

78  than sulphur, including some mercury species. Unlike elemental mercury, which is not

79  water-soluble, oxidized mercury compounds such as $HgCl_2$ dissolve in water.

80  Therefore, wet FGD technologies could be used for the co-removal of highly-soluble

81  oxidized mercury (8-72%) (Niksa and Fujiwara, 2005; Meij and Te Winkel, 2006; Díaz-

82  Somoano et al., 2007; Senior, 2007; Hutson et al., 2008; Stergarsek et al., 2008; Tao et

83  al., 2009), a portion of which could be retained in the FGD slurry and FGD gypsum

84  end-product. Accordingly, FGD facilities should be regarded as potential systems for

85  mercury reduction emissions. However, this fact makes that high amount of toxic

86  species could be present in the produced gypsum. For these reasons, it is important to

87  have a clear understanding of the speciation and partitioning of mercury in wet FGD

88  facilities and to determine which parameters influence mercury behaviour in these

89  facilities. It is known that the efficiency of FGD plants for mercury emission reductions

90  may vary considerably even among similar units due to the wide range of operational

91  parameters and to the different pollution control devices employed (ESP and De-$NO_X$).

92     The objective of this study was to evaluate the speciation and partitioning of

93  mercury in two Spanish Pulverised Coal Combustion (PCC) power plants equipped with

94    wet limestone-based FGD facilities operating with forced oxidation and re-circulation of

95    FGD water streams. These plants are fed with coal and coal/pet-coke blends that have

96    different mercury contents. The results were obtained from the simultaneous sampling

97    of solid, liquid and gaseous streams and their subsequent analysis in two separate

98    laboratories to ensure the accuracy of the quantitative analysis. On the basis of the

99    results mercury retention efficiency in wet FGD facilities operating with recirculation of

100   FGD water streams was evaluated.

101

102   **2. Materials and methods**

103   *2.1. Power stations and sampling procedures*

104        Three sampling campaigns were undertaken in two large (1050 and 1200 MW)

105   Spanish PCC power stations (labelled PP1 and PP2, respectively) equipped with wet

106   limestone-based with forced oxidation FGD systems (Ochoa et al., 2009). The PP1

107   power plant was fed with a 100% coal blend (60:40 local sub-bituminous coal:

108   bituminous coal), containing a relatively low mercury input (16 g h$^{-1}$ per unit). The PP2

109   power plant was fed with 82:18 and 84:16 coal:petroleum coke blends for the 2007 and

110   2008 samplings respectively. These combustible blends provided a relatively high

111   mercury input (30-31 g h$^{-1}$).

112        Both FGD systems use limestone as reagent and operate in forced oxidation

113   mode in order to ensure the conversion of the captured $SO_2$ to $CaSO_4 \cdot 2H_2O$. The

114   gypsum slurry was discharged over filters, previous separation of the liquid fraction by

115   hydro-cyclones which was re-used in the scrubber. In PP1 the limestone slurry was

116   prepared by mixing the pulverised limestone with the process water (taken from a

117   nearby reservoir and subsequently treated to reduce the content of salts) and a fraction

118   of the re-circulated water in the reagent tank. The remaining filtered water (45%) was

119 sent directly to the spray nozzles of the scrubber. In PP2 the filtered water was sent

120 directly to the spray-nozzles and was not used in the preparation of the limestone slurry.

121 In this plant the limestone slurry is prepared with process water also arising from a

122 nearby reservoir. Furthermore, an aluminium additive was injected into the scrubber of

123 PP2 plant in order to improve the sorption of $SO_x$ by Ca and to favour the reaction of F

124 with the Al preventing the presence of F in the gypsum (Álvarez-Ayuso et al., 2008;

125 Font et al., 2008). It should be pointed out that the amount of additive dosed to the

126 scrubber was in 2007 twice the amount added in 2008.

127    The sampling campaigns were carried out at 100% maximum capacity and 100%

128 desulphurisation over two consecutive days. Solid, liquid and gaseous streams were

129 collected simultaneously from each power plant in order to calculate the mass balance

130 of mercury. The solid samples were mixed, crushed, milled and rafted and

131 representative samples of each sampling day were analysed. The water streams and gas

132 trapping solution samples were filtered in situ. $K_2Cr_2O_7$ was employed to stabilize the

133 mercury in the solutions. All the samples were divided into two groups for analysis in

134 two separate laboratories [a] and [b].

135    The concentration of mercury in the gas was measured at two different sampling

136 points, upstream, (IN)-FGD, and downstream, (OUT)-FGD, in the FGD unit. The

137 speciation of mercury emissions were determined according Ontario-Hydro method

138 (ASTM D6784-02, 2008). In such a method a sample of 1 $m^3$ (or higher) was

139 withdrawn from the flue gas stream through a filter system. Due to the high solubility in

140 water of oxidised mercury, it was trapped in bottles containing a chilled aqueous

141 solution of KCl. Elemental Hg is collected in the subsequent bottles containing chilled

142 solutions of 5% $HNO_3$ in 10% $H_2O_2$ and 4% $KMnO_4$ in 10% $H_2SO_4$.

143 *2.2. Mercury analysis*

144     The mercury content of the solid, liquid, gaseous and particulate matter (PM)

145     samples was measured by means of an Automatic Mercury Analyser (AMA-254) in two

146     separate laboratories, [a] and [b], following the ASTM Standard D 6722-01 method

147     (ASTM, 2006). The solid samples were previously acid digested following the method

148     devised by Querol et al. (1995) whereas the particulate Hg contents were determined

149     directly from the quartz filter samples.

150     *2.3. Lab-scale tests*

151     In order to investigate the different mercury behaviour observed during the two

152     sampling campaigns carried out in PP2, a lab-scale device was built (Fig. 1). The

153     apparatus consists of a closed glass vessel in a thermostat system to ensure a constant

154     temperature. A calibration gas generator system (HOVACAL, IAS GmbH) coupled

155     with an evaporator was used to generate oxidised mercury in gas phase.

156     Limestone slurry was prepared using sulphuric acid and the limestone collected

157     during the sampling campaign in PP2. A simulated flue gas containing nitrogen, oxygen

158     and a known amount of mercury was passed through the slurry solution. When sulfite

159     ions were added to the reaction vessel flue gas only contained mercury and nitrogen in

160     order to favour $Hg^0$ formation. A continuous mercury emission monitors (VM3000) was

161     used to follow elemental mercury concentration in gas phase. The continuous mercury

162     analyser was replaced by Ontario-Hydro sampling train when mercury speciation at the

163     gas outlet was necessary.

164

165     **3. Results and discussion**

166     *3.1. Mercury analysis*

167     The results of the mercury analysis obtained by the two laboratories [a] and [b]

168     were in good agreement. The differences between the mercury concentrations obtained

169    in the two laboratories are calculated, as well as the reproducibility value (R) both in

170    accordance with the ASTM, D-6722-01 standard method (ASTM, 2006). The

171    differences between results obtained for mercury concentrations in both laboratories

172    were lower than 0.01 ppm except for gypsum samples in which the values ranged

173    between 0.02 and 0.04 ppm. The R value provides an indication of the deviations

174    between the results from the two laboratories but it is based only on the mercury content

175    range between 0.017 and 0.586 $\mu g\ g^{-1}$ in accordance with ASTM rules. Due to the high

176    correlation between the results obtained in both laboratories the results of all the

177    mercury analyses are reported as mean values.

178    *3.2. Mercury mass balances*

179        In order to validate the design of the sampling campaign and to assure the

180    reliability of the results, the following mass balance calculations were performed: i)

181    through the entire installation (total) ii) around the Boiler + ESP and iii) around the

182    FGD system. The different stream flows are based on information provided by the

183    power plant.

184        Table 1 shows all the inputs an outputs considered for the mass balance

185    calculations therefore the achieved mass balance closure. In general good mass balance

186    closures were achieved, with Out/In ratios ranging from 0.8 to 1.0 (Table 1). Mercury

187    flows of the different sampled streams are shown in Fig. 2. As expected, the feed fuel

188    blend is the main source of mercury in the combustion process. In PP1 this input was 16

189    g $h^{-1}$ of mercury and it was higher in PP2, close to 30 g $h^{-1}$ (Table 1). An additional

190    contribution to mercury input in PP2 came from the re-circulated water (45 to 50 g $h^{-1}$),

191    but this was compensated for by the mercury output from the scrubber, the gypsum

192    slurry (water + solid gypsum), 60 and 53 g $h^{-1}$ in PP2 (2007) and PP2 (2008),

193    respectively (Table 1). The high concentration of mercury in the water is a consequence

194   of its accumulation as it dissolves over consecutive cycles. If all the inputs are added up,

195   the total mercury input to FGD amounted to 16 and almost 80 g h$^{-1}$ in the PP1 and PP2

196   plants respectively though it should be remembered that in PP2 a 45% of the water is

197   returned to the plant.

198   Mercury behaviour during combustion was similar in the two power plants. A

199   very low proportion of the incoming mercury was retained in the slag (< 0.1%), whereas

200   in the pulverised fly ash only 10% was captured. Due to the high volatility of mercury,

201   most of this element (86 at PP1 and 78-89% at PP2) escapes the ESP in gas phase. As a

202   result 11 and 25-27 g h$^{-1}$ of mercury reached the FGD system in gas phase in PP1 and

203   PP2, respectively (Table 2).

204   *3.3. Mercury removal in FGD systems*

205   Significant differences were observed for mercury behaviour in the FGD plants

206   and as a consequence, after passing through the FGD system (OUT-FGD) different

207   mercury concentrations were emitted in gas phase, 3.6, 9.3 and 21 g h$^{-1}$ in PP1, PP2-

208   2007 and PP2-2008, respectively (Table 2). The concentrations of Hg in the gaseous

209   streams IN and OUT-FGD in the three samplings are summarised in Table 2. As

210   previously mentioned most of the mercury escapes the ESP in gas phase, 7.8 and

211   approximately 20 μg m$^{-3}$ of mercury input in the gas phase to the FGD system in PP1

212   and PP2, respectively (Table 2). These concentrations represent a flow of 11 and

213   approximately 25-27 g h$^{-1}$ of gaseous mercury input to the FGD in PP1 and PP2,

214   respectively. Most of this gaseous mercury was found to be in oxidised form. In PP1,

215   74% of the incoming mercury was Hg$^{2+}$ whereas in PP2 it was 85 and 88% for each

216   sampling campaign. These results agree with the generally held view that HgCl$_2$ can be

217   expected to be the predominant species under the typical operating conditions of ESP

218   prior to entry into the FGD plant (Meij and Te Winkel, 2006).

219        A relatively high total mercury removal was achieved in the scrubber of PP1

220    (72%) and PP2 (2007) (65%). However a lower total mercury abatement was attained

221    during the second sampling campaign in PP2 (26%) (Table 3). As was expected, due to

222    the different solubility of Hg species, elemental mercury passed through the FGD

223    systems being emitted in gaseous form. The emission of elemental mercury represents

224    3-5% of the total mercury input. The fact that the quantity of elemental mercury at the

225    FGD outlet and inlet was found to be similar implies that oxidised mercury reduction

226    and re-emission as elemental mercury that take place in some FGD plants (Meij and Te

227    Winkel, 2006; Díaz-Somoano et al., 2007; Senior, 2007; Hutson et al., 2008; Stergasek

228    et al., 2008) did not occur in the plants evaluated in this study. The main mercury

229    species retained in the FGD was oxidised mercury with retention efficiencies ranging

230    from 67 to 62% in PP1 and PP2 (2007) respectively, although it was found to be notably

231    lower (23%) in PP2 (2008). These different mercury abatements could be due to the

232    different mercury concentrations in the scrubber. The highest oxidised mercury

233    abatement occurred in PP1 where the mercury concentration input in gas phase was low.

234    However, this variation in mercury concentration cannot explain the different mercury

235    behaviour in the FGD plant in the two sampling campaigns of PP2. In order to explain

236    this fact, a thorough investigation on mercury behaviour in FGD systems has been

237    carried out using a lab-scale device (Fig. 1). As a first approach it was considered that in

238    these Spanish power plants an important flow of water coming from the scrubber is re-

239    circulated. As a consequence, a high concentration of mercury can be reached in the

240    FGD water stream, representing a serious drawback because equilibrium between the

241    aqueous and gas phases would lead to the formation of the gaseous form of mercury

242    according to the Henry´s Law. So a sequence of tests has been carried using different

243    mercury concentration in the scrubber solution. The results (Fig. 3a) show that in the

244    experimental conditions an increase in mercury concentration in flue gas favours

245    mercury reduction and re-emission. However no correlation with the amount of $Hg^{2+}$ in

246    gas phase was observed. Consequently the variation in mercury concentration cannot

247    explain the different mercury behaviour in the FGD plant in the two sampling

248    campaigns of PP2.

249        In addition to mercury content, variations in the concentration of other

250    components in the gas and aqueous phases may play an important role. The content of

251    halogen in both the gases and water is also known to modify mercury behaviour and

252    mercury oxidation (Senior, 2007). Although the proportion of mercury species and

253    chloro input in the FGD were similar in the 2 samplings at PP2, the fluorine content

254    differed (Table 2). In PP2 2008 sampling the amount of gaseous fluorine that reached

255    the scrubber was 28.6 mg m$^{-3}$, while in PP2 2007 it amounted to 14.4 mg m$^{-3}$, as a

256    consequence of the different F contents in the fuel blend (378 and 182 ppm,

257    respectively). However, lab-tests show that no effect on oxidised mercury removal

258    should be expected due to fluorine concentration in the scrubbing liquor. Experiments

259    with fluorine concentrations of 0-4000 ppm have been carried out. However, no

260    differences between oxidised mercury in the gas coming from the scrubber were

261    detected.

262        Finally the influence of the liquid/gas ratio (L/G) has been tested. For the lab-

263    scale tests the amount of liquid remained constant while the amount of gas passing

264    through the system was increased. This parameter is directly related to residence time of

265    the gases in the scrubber. Results show that oxidised mercury capture decreases when

266    gas flow through the FGD increases (Fig. 3b). Most of the oxidised mercury is captured

267    in the scrubber until a gas flow value in which the oxidised mercury capture decreased

268    notably, probably due to the low residence time of the gas in the scrubber. This fact

269    reveals that the low oxidised mercury removal in PP2 (2008) is probably due to L/G

270    ratio. Although the flow of the limestone slurry was quite similar in both sampling

271    campaigns in PP2, the gas flow through the scrubber was a 16% higher in 2008 than in

272    2007 producing a decrease in the residence time of the gases in the scrubber and a lower

273    oxidised mercury removal. The oxidised mercury that is not dissolve in the aqueous

274    phase goes out to the FGD.

275    *3.4. Mercury partitioning in the FGD by-products*

276        Mercury partitioning in the FGD by-products was also observed to differ during

277    the three sampling campaigns (Fig. 4). In PP1 most of the outgoing mercury was

278    associated with the FGD gypsum (67%) while a low proportion was trapped by the

279    gypsum slurry water (5%). The rest of the gaseous mercury input remained in gas phase

280    (28%). The high retention of Hg in the gypsum by wet FGD plant in PP1 suggests that

281    an insoluble Hg species, such as Hg-sulphate (Cao et al., 2008), may have been present

282    in the scrubber. In the wet FGD plant of PP2 the partitioning was different from that of

283    PP1 as most of the mercury was retained in the FGD water streams. In 2007 sampling

284    45% of the gaseous mercury that reached the FGD system was collected with the

285    gypsum slurry water, while 20% was associated with the gypsum. A relatively high

286    proportion of mercury remained in gas phase (35%). In the PP2 2008 sampling

287    campaign, the mercury in the aqueous solution amounted to 16% against 10% for

288    gypsum.

289        The difference observed between PP1 and PP2 is probably related with the use

290    of Al-sulphate in PP2. This compound could favour the formation of soluble mercury

291    species (HgO) instead of $HgSO_4$ which is commonly associated with calcium sulphate

292    particles. Although more research is necessary, the different partitioning of mercury in

293    PP1 and PP2 is probably related to the use of Al-sulphate.

294

**4. Conclusions**

296       The amount of mercury removed in a FGD unit is highly influenced by the

297       mercury concentration entering the scrubber. This parameter is clearly related to the

298       amount of mercury fed to the boiler and to the efficiency of the particle control device.

299       However, it should be remarked that a high amount of mercury and other species such

300       as halogens, are being introduced to the scrubber due to the recirculation of the water.

301       Moreover, the results discussed in this work underline the importance of carrying out a

302       thorough control of the working conditions in the scrubber, being the L/G ratio an

303       important parameter related to the oxidised mercury removal due to mass transfer and

304       the gas residence time in the scrubber.

305       The use of an additive in PP2 favours the presence of mercury in the aqueous

306       phase avoiding its association with the resulting gypsum. However some precaution

307       should be taken because this water can be partially re-circulated to the scrubber.

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385       Asia-Pac. J. Chem. 5, 756-762.

386   US Environmental Protection Agency (EPA), 2011. Reducing Toxic Emissions From

387       Power Plants. Proposed Rule To Control Mercury And Other Toxic Air

388       Emissions From Powerplants, www.epa.gov/airquality/powerplanttoxics/actions.

389    **Table 1.** Mass balances around the boiler and ESP (PCC system); FGD (FGD) and the

390    whole installation (Total); Hg (g h$^{-1}$).

| Stream | | PP1 | PP2 (2007) | PP2 (2008) |
|---|---|---|---|---|
| | | **TOTAL** | | |
| Fuel Blend | | 15.5 | 30.0 | 30.8 |
| Limestone | IN | 0.09 | 0.00 | 0.02 |
| Process Water | | 0.17 | 0.00 | 0.00 |
| Recirculated water | | 0.14 | 49.3 | 44.8 |
| Fly ash | | 1.58 | 3.11 | 3.07 |
| Slag | | 0.02 | 0.04 | 0.01 |
| Slag Water | | 0.00 | 0.05 | 0.05 |
| Gypsum | OUT | 6.90 | 3.95 | 3.62 |
| Gypsum slurry Water | | 0.60 | 56.0 | 49.3 |
| PM-OUT | | 0.01 | 0.01 | 0.00 |
| Gas-OUT | | 3.57 | 9.31 | 21.1 |
| ∑OUT/∑IN | | 0.8 | 0.9 | 1.0 |
| | | **PCC** | | |
| Fuel Blend | IN | 15.5 | 30.0 | 30.8 |
| Fly ash | | 1.58 | 3.11 | 3.07 |
| Slag | | 0.02 | 0.04 | 0.01 |
| Slag Water | OUT | 0.00 | 0.05 | 0.05 |
| PM-IN | | 0.00 | 0.00 | 0.01 |
| Gas-IN | | 10.9 | 24.9 | 26.6 |
| ∑OUT/∑IN | | 0.8 | 1.0 | 1.0 |
| | | **FGD** | | |
| Limestone | | 0.09 | 0.00 | 0.02 |
| Process Water | | 0.17 | 0.00 | 0.00 |
| Recirculated water | IN | 0.14 | 49.3 | 44.8 |
| PM-IN | | 0.00 | 0.00 | 0.01 |
| Gas-IN | | 10.9 | 24.9 | 26.6 |
| Gypsum | | 6.90 | 3.95 | 3.62 |
| Gypsum slurry Water | OUT | 0.60 | 56.0 | 49.3 |
| PM-OUT | | 0.01 | 0.01 | 0.00 |
| Gas-OUT | | 3.57 | 9.31 | 21.1 |
| ∑OUT/∑IN | | 1.0 | 0.9 | 1.0 |

391

392    **Table 2.** Concentrations of main gaseous pollutants and mercury in the gas stream

393    flowing IN and OUT of the FGD.

| μg m$^{-3}$ (g h$^{-1}$) | IN-FGD | | | OUT-FGD | | |
|---|---|---|---|---|---|---|
| | PP1 | PP2 2007 | PP2 2008 | PP1 | PP2 2007 | PP2 2008 |
| Hg$_{total}$ | 7.8 (11) | 20.5 (25) | 19.0 (27) | 2.2 (3.6) | 7.1 (9.3) | 14.0 (21) |
| Hg$^{2+}$ | 5.8 (8.1) | 17.5 (21) | 16.8 (24) | 0.6 (1.0) | 4.7 (6.2) | 12.3 (18) |
| Hg$^{0}$ | 2.0 (2.8) | 3.0 (3.6) | 2.2 (3.1) | 1.6 (2.6) | 2.4 (3.1) | 1.7 (2.6) |
| Hg$_{PM}$[1] | 1.3 | 7.3 | 0.7 | 8.8 | 9.4 | 1.8 |
| F$^{-}$ | 23.0[2] | 14.4[2] | 28.6[2] | 370 | 78 | 147 |
| Cl$^{-}$ | 6188 | 7191 | 6148 | 233 | 51 | 93 |
| SO$_2$[2] | 14.6[2] | 4319 | 4746 | 988 | 779 | 555 |

394    [1]ng m$^{-3}$; [2] mg m$^{-3}$

395

396    **Table 3.** Mercury retention in the FGD systems of the PP1 and PP2 power stations.

| Hg removal (%) | Total Hg (%) | Hg$^{2+}$ (%) | Hg$^0$ (%) |
|---|---|---|---|
| PP1 | 72 | 67 | 5 |
| PP2 (2007) | 65 | 62 | 3 |
| PP2 (2008) | 26 | 23 | 3 |

397

| Hg removal (%) | Total Hg (%) | Hg$^{2+}$ (%) | Hg$^0$ (%) |
|---|---|---|---|

398 **Figure captions**

399

400 **Figure 1.** Schematic diagram of lab-scale scrubber used for the experimental tests.
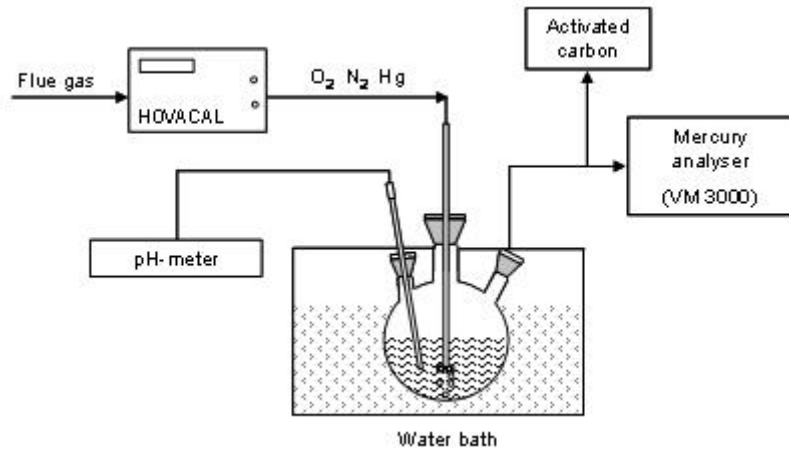
401

402 **Figure 2.** Schematic diagrams of the mercury flows in the sampled power plants in (a)

403 PP1; (b) PP2 (2007) and (c) PP2 (2008) sampling campaigns.

404

405 **Figure 3.** Lab-scale test results. (a) Influence of mercury concentration in elemental

406 mercury emission and (b) influence of gas flow through the scrubber solution on
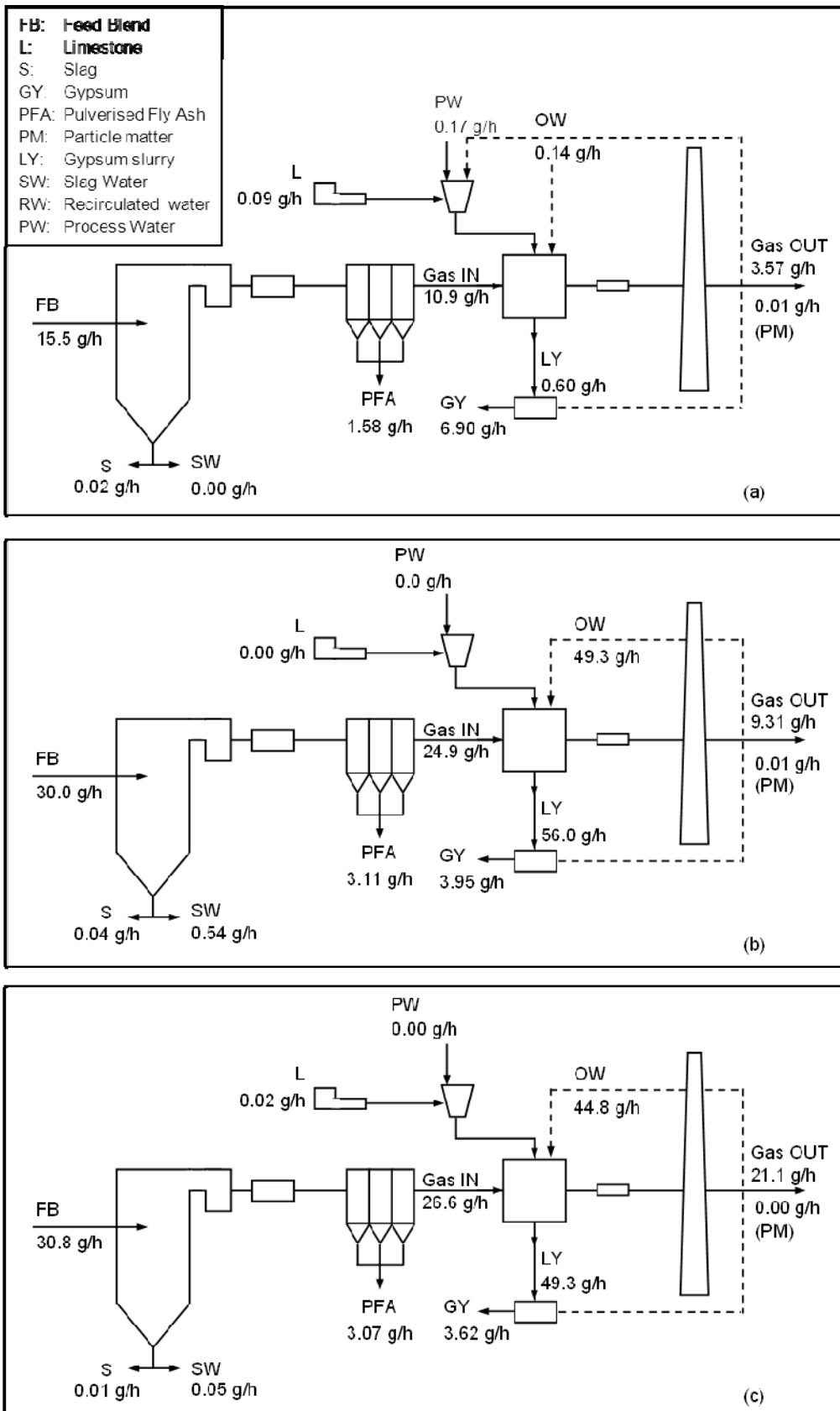
407 oxidised mercury emission.

408

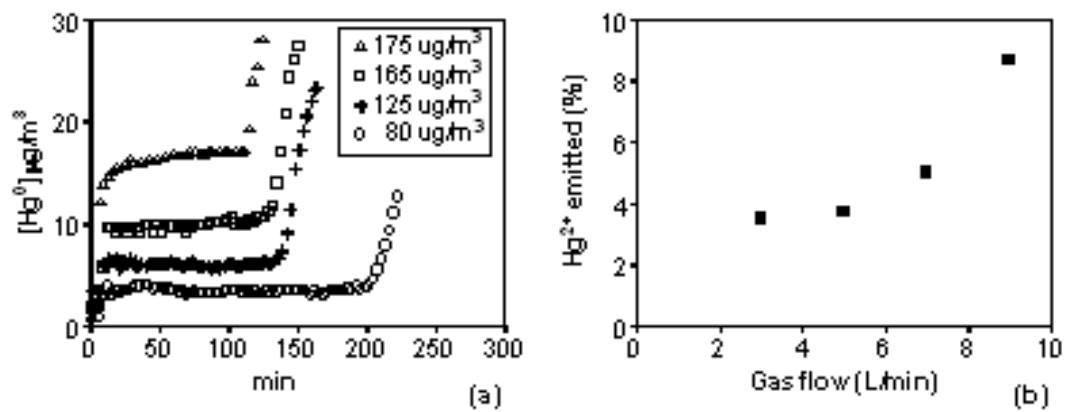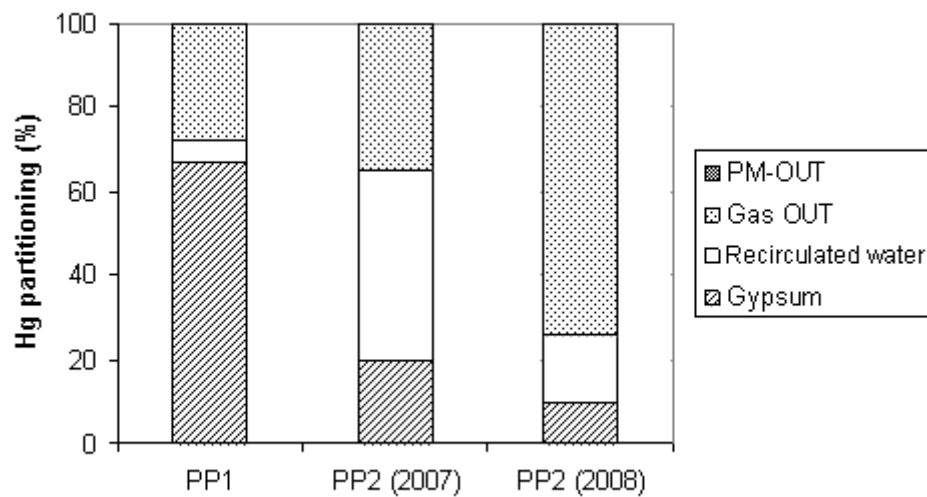409 **Figure 4.** Mercury distribution in the FGD by-products.

410

411    Fig. 1

412

Fig. 2

Legend:

FB: Feed Blend
L: Limestone
S: Slag
GY: Gypsum
PFA: Pulverised Fly Ash
PM: Particle matter
LY: Gypsum slurry
SW: Slag Water
RW: Recirculated water
PW: Process Water

**(a)**
- PW: 0.17 g/h
- OW: 0.14 g/h
- L: 0.09 g/h
- FB: 15.5 g/h
- Gas IN: 10.9 g/h
- Gas OUT: 3.57 g/h, 0.01 g/h (PM)
- LY: 0.60 g/h
- GY: 6.90 g/h
- PFA: 1.58 g/h
- S: 0.02 g/h
- SW: 0.00 g/h

**(b)**
- PW: 0.0 g/h
- OW: 49.3 g/h
- L: 0.00 g/h
- FB: 30.0 g/h
- Gas IN: 24.9 g/h
- Gas OUT: 9.31 g/h, 0.01 g/h (PM)
- LY: 56.0 g/h
- GY: 3.95 g/h
- PFA: 3.11 g/h
- S: 0.04 g/h
- SW: 0.54 g/h

**(c)**
- PW: 0.00 g/h
- OW: 44.8 g/h
- L: 0.02 g/h
- FB: 30.8 g/h
- Gas IN: 26.6 g/h
- Gas OUT: 21.1 g/h, 0.00 g/h (PM)
- LY: 49.3 g/h
- GY: 3.62 g/h
- PFA: 3.07 g/h
- S: 0.01 g/h
- SW: 0.05 g/h

413

414    Fig. 2

22

(a)

(b)

415

416    Fig. 3

417



418

419    Fig. 4