1   **Mercury removal from MSW incineration flue gas by mineral-based sorbents**

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Abstract

Three samples of commercially available mineral-based sorbents (zeolite, bentonite and diatomaceous earth) were selected and evaluated for Hg capture under conditions of simulated dry flue gas atmosphere typical in Municipal Solid Waste Incineration (MSWI). The experiments were carried out in a lab-scale fixed-bed device at temperatures between 120-200 ºC. Two samples of activated carbons (AC) (raw-AC and sulphur impregnated AC) were tested under the same conditions. The mineral-based sorbents were chemically promoted by sulphur, $FeCl_3$ and $CaBr_2$, achieving an improvement in the overall reduction percentage of Hg^0out (g) up to 85%, which was comparable to that obtained using a commercial activated carbon for Hg capture (sulphur impregnated AC). The study demonstrates that sorbents with a matrix relatively richer in TiO_2, Fe_2O_3 and Al_2O_3, as bentonite, favour Hg heterogeneous oxidation. The best Hg capture capacity was achieved with a zeolite sorbent sample characterized by high specific surface (132 m^2/g) and impregnated with elemental sulphur. The final form of mercury retained in this sorbent was HgS with proved long-term stability in disposal and landfilling. The higher the temperature, the lower the efficiency of Hg capture being the optimum temperature for Hg-capture in the range of 120-150ºC. This study provides a basis for the development of new efficient non-carbon sorbents for mercury removal in the air pollution control lines of MSWI facilities considering the non-hazardous final form of mercury and its long-term landfilling/sequestration.

1. Introduction

Increasing attention is being paid on mercury pollution abatement owing to its long-range atmospheric transport, its persistence in the environment, its ability to bioaccumulate in ecosystems and its harmful effects on human health and the environment (UNEP, 2013; Rice *et al.*, 2014). In 2013, Minamata Convention declared combustion and incineration processes (coal combustion, waste incineration) as one of the major anthropogenic sources of Hg emissions together with mining, smelting, production of metals, and cement clinker production (UNEP, 2013). Waste incineration facilities are sources of mercury emissions due to the presence of Hg-containing products (e.g. batteries, paint residues, thermometers, thermostats, light switches, etc.) in the input mixed-waste fuel. Fortunately, in highly developed countries, the average content of mercury in municipal solid waste decreases, but still with some significant temporary fluctuations of the mercury content in the waste (Horowitz et al., 2014; Veizen *et al.*, 2002). When waste materials containing mercury are incinerated, elemental mercury (Hg^0) is released from the incinerator (850-1200 ºC) into the flue gas and, as the temperature goes down, Hg undergoes a large number of homogeneous and heterogeneous oxidation processes. Hg^0 is converted either to oxidized mercury (Hg^{2+}) compounds (mainly $HgCl_2$) and/or Hg adsorbed compounds (Hg_p) onto particles. The efficiency of mercury removal from the flue gas is substantially affected by its speciation, the flue gas composition and the process conditions in air pollution control (APC) lines (e.g. nature of gas cleaning processes, temperature, sequence of the cleaning processes, etc.). Hg_p (related with solid particles) is easily removed by dust removal control devices such as electrostatic precipitators (ESP), bag filters, etc. The oxidized part of mercury (Hg^{+2} species), such as $HgCl_2$, is water soluble and easily removable by wet type of APC devices, e.g. in wet flue-gas desulfurization/de-HCl. In contrast with those forms of mercury mentioned above, Hg^0 vapour is difficult to control because of its high volatility and insolubility in water

(Pavlish *et al.*, 2003). Dry flue gas cleaning methods based on solid reactive sorbents are often used in MSWI, but their efficiency in mercury removal, interferences and side effects need to be further studied (Svoboda *et al.*, 2016). Injection of activated carbon is a potentially applicable method for capturing mercury, which is removed downstream by a particulate matter control device (Svoboda *et al.*, 2016). However, some flue gas components are also adsorbed by activated carbon, competing with mercury and therefore the efficiency of Hg-sorption is compromised. A chemical impregnation is usually needed to improved mercury removal by single, virgin (un-modified) ACs (Lee *et al.*, 2004). Further advances are still necessary in AC technology to reduce costs and to limit the balance-of-plant impacts associated with its use (Sjostrom *et al.*, 2010). Many researchers have been focused on searching other low-cost and versatile alternatives to ACs (Pflughoeft-Hassett *et al.*, 2009). A wide kind of mineral sorbents, such as sepiolite (Mendioroz *et al.*, 1999), mordenite (Eswaran *et al.*, 2007), zeolite (Morency *et al.*, 2002; Jurng *et al.*, 2002; Qi *et al.*, 2015), bentonite and other similar kind of sorbents (Ding *et al.*, 2012; U.S. EPA, 2003), displayed results comparable with activated carbons. Mineral-based sorbents are potential and economically viable sorbent from the point of view of capturing of various organic micro-pollutants from incineration flue gases (e.g. dioxins/furans (PCDD/PCDF), PAH and PCB (Lhoist group, 2016; Svoboda *et al.,* 2016). Various chemical-promoters such as elemental sulphur, alkali polysulfides, transition metal oxides, $FeCl_3$ and various salts of halides have demonstrated that they can enhance the Hg adsorption on sorbents such as activated carbons and zeolites (Wilcox *et al.*, 2011; Lee *et al.*, 2008; Liu *et al.*, 2007). In this study, three mineral-based sorbents were selected to evaluate Hg removal efficiencies under simulated conditions of dry flue gas from MSWI. For this purpose, three chemical impregnation methods were used with the aim of improving the sorbents efficiencies for the reduction of Hg^0 (g) in the outlet flue gas

95 stream. The results obtained were compared with those results obtained using two

96 activated carbons (either without or with impregnation).

2. Materials and methods

98 *2.1. Samples*

99 Three samples of commercial mineral-based sorbents were selected to study mercury

100 retention and oxidation under a synthetic dry-MSW incineration atmosphere. These

101 sorbents consist on a sample of Minsorb Dx. (zeolite), Ekobent B. (bentonite) and Eco-

102 dry (diatomaceous earth) supplied by Lhoist Group, Keramost a.s. and Reo Amos, Ltd.

103 respectively. Minsorb Dx, Ekobent B and Eco-dry were labelled as (M), (Eb) and (Ec).

104 Only the M sorbent is specifically designed for flue gas treatment (removal of organic

105 compounds from flue and waste gases). Furthermore, one sample of raw activated carbon

106 (labelled as raw-AC) and another sample of a commercially-available activated carbon

107 (Activated Carbon IPK from CarboTech AC GmbH)) impregnated with sulphur (labelled

108 as sulphur-AC), were used for comparing the removal efficiencies of the mineral-based

109 sorbents with those efficiencies obtained with AC-based sorbents. Raw-AC was prepared

110 from a fluid coke (steam activated) by crushing and sieving, with a particle diameter of

111 300 μm. Sulphur-AC (Activated Carbon IPK) is manufactured from various grades of

112 coal under stringently controlled conditions by steam activation, to produce a porous

113 adsorbent with a highly developed internal surface area, which is impregnated with

114 sulphuric acid (H_2SO_4). These five sorbents samples were analysed to determine their

115 properties. The chemical composition was determined by XRF (X-ray fluorescence)

116 method (spectrometer ARL 9400 XP byTHERMO ARL) and ion chromatography after

117 microwave enhanced digestion by HNO_3 + H_2O_2 (DIONEX ICS 1000 by Thermo

118 Scientific). The Brunauer−Emmett−Teller (BET) surface area was determined by

119 volumetric adsorption of nitrogen (ASAP 2020-2050 by Micromeritics, USA). The

120   textural characteristics have been determined by mercury porosimetry (AutoPore IV 9520

121   analyser by Micromeritics, USA).

122   *2.2. Chemical impregnation methods*

123   The three sorbents, M, Eb and Ec were impregnated by sulphur, FeCl3*6H2O and CaBr2,

124   respectively, obtaining their corresponding impregnated sorbents called (M+S), (Eb+Cl)

125   and (Ec+Br).

126   6 g of fine sulphur powder were dissolved in 100 mL toluene (high purity) and then,

127   stirred intensively during three hours at 35 ℃. The sulphur particles were separated and

128   30 g of Minsorb Dx (size fraction 100 – 250 μm) were added into the resulting solution

129   at 35 ℃. After 3 hours of stirring at 35 ℃, the suspension was filtrated. The separated

130   particles were dried at 90 ℃ in nitrogen atmosphere during 5-6 hours. The selected Fe-

131   salt used for impregnation of Ekobent B was Iron (III) chloride hexahydrate

132   (FeCl$_3$*6H$_2$O) in ethanol 96%. 40 g of Iron (III) chloride hexahydrate were dissolved in

133   400 mL of ethanol at 25 ℃ and the solution was acidified by two small drops of 30%

134   hydrochloric acid (HCl). 30 g of dried sorbent Ekobent B (size fraction 0.5 – 1.5 mm)

135   were added into the solution under stirring. After 2 hours, the sorbent particles were

136   filtrated and separated. The wet particles were dried at temperature 110 ℃. Eco-dry (size

137   fraction 1 – 2 mm) was impregnated by aqueous solution of CaBr$_2$. 20 g of dried sorbent

138   Eco-dry were added into 150 mL of CaBr$_2$ 7% m/m under stirring. After 2 hours of

139   stirring, the particles were filtrated and then dried at 140 ℃ (until the constant mass).

140   *2.3. Experimental apparatus for mercury capture*

141   A lab-scale device was specifically designed and built to carry out the Hg oxidation and

142   capture experiments. All the pipes used were composed of polytetrafluoroethylene

143   (diameter 6 mm) to prevent possible mercury attacks and memory effects. Those pipes

144 where gaseous mercury is present were heated by controlled heating tapes and kept at

145 120-140 ºC to avoid condensation of Hg. The experimental device (Figure 1) consists of:

146 (i) a battery of four Bronkhorst mass flow controllers and two rotameters (OMEGA)

147 which served for simulation of the MSW-incineration flue gas atmosphere (10% CO_2,

148 74% N_2, 5% O_2, 300 ppm SO_2, 200 ppm NO and 600 ppm HCl), (ii) a certified VICI

149 Metronic Hg^0-permeation tube and a Dynacalibrator 150 unit that were used to generate

150 a constant feed of Hg^0 of 100 µg·m^{-3} in the flue gas at the entrance of the reactor, (iii) a

151 quartz reactor (diameter, 25 mm) heated by a furnace (Carbolite Gero) at temperature of

152 150ºC. The sorbent bed (0.100 g of sorbent in 4 g of sand) was placed on a frit in the

153 middle part of the quartz tube, and (iv) a system for determining the mercury species (Hg^0

154 and Hg^{2+}). This system consists of an on-line elemental mercury analyser (VM3000)

155 serving for continuous measurement of Hg^0 vapour concentration downstream the fixed-

156 bed reactor (sorbent) and downstream the unit with the selective sorption/removal of

157 gaseous oxidized mercury (Hg^{2+}). The Hg^{2+} was captured by means of a conditioned-ion

158 exchanger resin (Dowex® 1×8), suitable for the selective extraction of Hg^{2+} species

159 (Fuente-Cuesta *et al.*, 2014) at the flue gas temperature (120-140 ºC. Prior to application,

160 the resin was conditioned with a solution of HCl:H_2O (1:1) at 90 °C for 30 min and then

161 filtered and dried. 1.5 g of the resin was situated upstream the Hg^0 vapour analyser (Figure

162 1) in a fixed bed reactor. Both the Hg^{2+} in the resin and the total mercury content captured

163 by the sorbent was determined by means of an automatic mercury analyser (AMA 254

164 LECO) (Sysalová *et al.*, 2013). The percentage of Hg^{2+}out (outlet stream) is derived from

165 both homogeneous oxidation (gas-gas interaction) and heterogeneous oxidation (gas-

166 sorbent interaction). The Hg^{2+} from homogeneous oxidation was determined conducting

167 a test with the resin-bed downstream the reactor without any sorbent, whereas the

168 heterogeneous Hg^{2+} is the Hg retained in the resin-bed which is placed downstream the

169 reactor in a test with the sorbent. All balances were ensured to be accurately closed. Five

170 pieces of thermocouples (K type) were placed in the most important/critical points of the

171 device (one of the thermocouples was situated near the sorbent sample inside the tube) to

172 make sure that there was no cold or overheated zone (with mercury losses or damage of

173 the tubes, respectively). Each of the variables (five temperatures, Hg^0 signal from the

174 VM3000 analyser and gas flow rates measured and controlled by the MFCs) were

175 continuously registered/recorded in the computer by a LabView software. The effect of

176 temperature was evaluated testing the capture efficiencies of the sorbents at temperatures

177 of 120 ºC, 150 ºC and 200 ºC. The duration of the mercury retention experiments was up

178 to 600 min.

179 **3. Results and discussion**

180 *3.1. Characterization of the sorbents*

181 Table 1 shows the physical and chemical characterization of mineral-based sorbents and

182 ACs. The specific surfaces and porous textural characteristics of the sorbents indicate that

183 the raw mineral sorbents have lower BET surface and micropore volume than the samples

184 of ACs (raw-AC and sulphur-AC). Both Ekobent (Eb) and Minsorb DX (M) sorbents

185 show better textural properties in comparison with the Eco-dry (Ec) sorbent as indicate

186 their higher BET surfaces. Eb sorbent has relatively higher content of TiO_2, Fe_2O_3 and

187 Al_2O_3 than sorbents M and Ec. Sorbent M has the highest content of calcium (expressed

188 as oxide). Main differences between raw-AC and sulphur-AC samples are their BET

189 surface and sulphur content. Such characteristics have a considerable effect on mercury

190 adsorption, being sulphur-AC sorbent more suitable for mercury capture (higher BET

191 surface and higher content of sulphur).

192

193 **Table 1**. Physical and chemical characterization of mineral-based sorbents and ACs.

	M	**Eb**	**Ec**	**Raw AC**	**Sulfur-AC**
LOI (wt% db)	13.0	5.50	3.00	81.9	88.3
SiO_2 (wt% db)	55.0	54.0	75.0	-	6.90
MgO (wt% db)	20.0	3.00	1.00	-	0.54
Al_2O_3 (wt% db)	8.00	16.0	10.0	-	7.60
CaO (wt% db)	6.00	2.50	2.00	-	0.91
Fe_2O_3 (wt% db)	3.00	14.0	6.00	-	5.70
TiO_2 (wt% db)	1.50	5.00	1.00	-	0.24
Elem. S (wt% db)	-	-	-	<0.50	2.50
S_{BET} ($m^2 \cdot g^{-1}$)	132	94.0	18.0	142	560
S_{meso} ($m^2 \cdot g^{-1}$)	97.0	66.0	12.0	55.0	-
V_{micro} ($mm^3 liq \cdot g^{-1}$)	19.0	15.0	3.10	43.0	-

194

195 Table 2 displays the content of the chemical-promoters (sulphur, chloride and bromide)

196 in each mineral-based sorbent after the impregnation procedures. The content of sulphur

197 corresponding to the impregnated sorbent (M+S), determined both by XRF method and

198 elemental analysis was 2.7 (w/w)%. The content of chloride in the impregnated bentonite

199 (Eb+Cl) sample was 1.5 (w/w)% (corresponding to 2.29 (w/w)% of $FeCl_3$). The content

200 of bromide in the impregnated sorbent Eco-dry (Ec+Br), determined by ion

201 chromatography, was 3.8 (w/w)%.

202 **Table 2.** Content of chemical-promoters after impregnation procedures

Sorbent (matrix)	Chemical-promoter	Final content (w/w)%
M+S (zeolite)	Sulphur	2.7 (sulphur)
Eb+Cl (bentonite)	$FeCl_3$	1.5 (chloride)
Ec+Br (diatomaceous earth)	$CaBr_2$	3.8 (bromide)

203

204 *3.2. Mercury removal experiments*

205 Both original and impregnated mineral-based sorbents were subjected to synthetic

206 atmospheres containing mercury using the laboratory-scale device. First experiments

207 were carried out under inert atmosphere (N_2) to evaluate if there was any interaction

208 between Hg^0 vapours and the non-impregnated sorbents. Table 3 shows the percentages

209 of mercury captured by the sorbent (Hg_{cap}), the oxidized mercury (Hg^{2+} out) in gas phase,

210 which was determined by the mentioned sorption/capture in the suitable ion exchanger

211 resin (Dowex), and the mercury that remained as elemental mercury (Hg^0 out) in the

212 simulated gas stream. The total amount of oxidized mercury (Hg^{2+}) in the gas stream in

213 this case was resulting only from the heterogeneous interaction (gas-sorbent) because no

214 homogeneous oxidation (gas-gas) occurs in N_2 atmosphere. The original sorbents M, Eb

215 and Ec (non-impregnated) showed a negligible mercury capture (< 0.7%) and low Hg

216 oxidation rates (Hg^{2+} out< 3.4%).

217 **Table 3.** Percentages of mercury captured, heterogeneous mercury oxidation and

218 elemental mercury corresponding to the original sorbents (M, Eb and Ec) under inert

219 atmosphere (N_2).

	M	Eb	Ec
Hg_{cap} (s) (%)	0.3	0.7	0.4
Hg^{2+} out (g) (%)	2.4	2.4	3.4
Hg^0 out (g) (%)	97.4	97.6	96.2

220

221 The comparison between these three non-impregnated sorbents (Table 3) displayed that

222 Eb (bentonite basis) has the highest percentage of Hg captured (0.7%) probably due to its

223 relatively higher content of TiO_2, Fe_2O_3 and Al_2O_3. These compounds have been

224 demonstrated to be relatively efficient in Hg^0 oxidation (Dunham *et al.*, 2003; Galbreath

225 *et al.*, 2005). Mercury oxidized on the surface of the sorbent could be adsorbed on CaO

226 surface (Kim *et al.*, 2009). In the case of sample M (zeolite-based), the mechanism of

227   capture by this kind of solid matrix is recognized as ion-exchange and it was found to be

228   rapid and reversible (Chojnacki *et al.*, 2004). It must be taken in mind that mercury could

229   be oxidized on the solid surface and then partially desorbed into the gas stream. In the

230   three cases, most of the mercury remained in the gas phase as Hg^0 (Hg^0 out > 96%),

231   reflecting the low mercury retention capacities of the raw sorbents. This fact led the

232   authors to perform the chemical impregnations in an attempt to improve the mercury
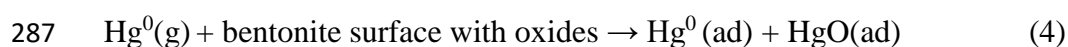
233   retention capacities.

234   The obtained distribution percentages of Hg^0 out (g), Hg^{2+} out (g) and Hg_{cap} were

235   completely different when impregnated sorbents were subjected to the retention

236   experiments in a simulated dry-MSWI atmosphere. The Hg-sorption breakthrough curves

237   obtained in this study (Hg^0 (g) inlet concentration 100 $\mu g/m^3$) are presented in Figure 2.

238   The difference between the total Hg ($[Hg^0]$out/$[Hg^0]$in=1) and the curve values

239   ($[Hg^0]$out/$[Hg^0]$in) is the content of oxidized form of mercury (Hg^{2+} out) and the mercury

240   captured by the sorbent (Hg_{cap}). It can be shown that the curves corresponding to Ec+Br

241   have higher slope suggesting its lower retention and oxidation capacity in comparison

242   with the other two sorbents. Table 4 shows the obtained percentages of mercury

243   distribution at 150 ºC for both non-impregnated (M, Eb and Ec) and impregnated (M+S,

244   Eb+Cl, Ec+Br) sorbents in the simulated dry-MSWI atmosphere**.** As it was already

245   mentioned, Hg^{2+} out is the result of both homogeneous and heterogeneous oxidation.

246   Authors had determined that homogeneous mercury oxidation in the same atmosphere

247   (dry-MSWI) was 55 ± 5% which is mainly due to the influence of HCl. It can be shown,

248   that the impregnation of Ec sorbent by $CaBr_2$ (Ec+Br) did not improve significantly the

249   sorption results. Chemical impregnation by $CaBr_2$ slightly decreased Hg^0 (out) from 35%

250   to 31%. This fact suggests that Hg could be oxidized on the sorbent surface via formation

251   of $HgBr_2$ and then, $HgBr_2$ could be desorbed again into the flue gas stream due to the low

252   desorption temperature of $HgBr_2$ (110±9 ºC) (Rumayor *et al.*, 2013), lower than $HgCl_2$

253   desorption temperature and lower than the working temperature (150 ºC). Another

254   important factor is the low BET surface and the lack of fine porous structure in the Ec

255   sorbent for an efficient retaining of volatile components. Otherwise, both M and Eb

256   sorbents after their chemical impregnations (M+S and Eb+Cl) exhibited a considerable

257   mitigation of Hg^0 (out), from 38% and 26% to 16% and 15%, respectively. M

258   impregnated with sulphur (M+S) was able to capture 10% of the total Hg in five hours,

259   with fair remaining capacity for further capturing of mercury vapours. The overall capture

260   mechanism combined probably two mechanisms: chemisorption of elemental mercury

261   with direct reaction of Hg^0 with elemental sulphur (+ sulphur compounds formed due to

262   interaction with model flue gas) and sorption of $HgCl_2$ on the surface of pores with slow

263   chemical conversion into HgS. The reactions between the elemental sulphur and mercury

264   vapours Hg^0 and the reaction between $HgCl_2$ and sulphur (sulphides) can be

265   schematically described (with simplifications) (Granite *et al.*, 1998):

266     $Hg^0(g) + S(s,l) \rightarrow HgS(ad)$ (1)

267     $HgCl_2(g) \rightarrow HgCl_2(ad)$ (2)

268     $HgCl_2(ad) + S(s,l) + CaS(s) \rightarrow HgS(ad) + CaCl_2(s)$ (3)

269   Elemental sulphur has diverse allotropes (S_2, S_4, S_6 and S_8) and it was suggested that

270   shorter allotrope promoters, S_2 and S_6, are more reactive than the longer allotrope

271   promoter S_8 (Korpiel and Vidic, 1998) because the terminal sulphur atoms are supposed

272   to be the active sites for mercury capture. From an environmental point of view, HgS is

273   the preferred chemical form of mercury for long-term storage of solid residues because it

274   provides an efficient barrier for leaching (Graydon *et al.*, 2009; Rumayor *et al.*, 2015).

275 The results obtained with Eb showed that its chemical promotion by $FeCl_3$ (Eb-Cl)

276 improved mercury capture, respect the non-impregnated sorbent (Eb), from 4.5% to 6.4%.

277 It is remarkable that the mineral matrix of Eb presents more oxidation capacity than either

278 M or Ec. When non-impregnated Eb was tested in MSW-incineration, Hg^0 (out) was 26%

279 in comparison with M (38.5%) and Ec (35%). As it was previously discussed, the

280 characteristics of Eb matrix (richer in TiO_2, Fe_2O_3 and Al_2O_3), favour Hg heterogeneous

281 oxidation. The chemical impregnation by $FeCl_3$ improves the oxidation of mercury via

282 formation of $HgCl_2$ based on the Mars–Maessen mechanism (Eq. 4-7) (Qi *et al.*, 2015).

283 However, as in the case of $HgBr_2$, mercury chloride (II) ($HgCl_2$) begins to be thermally

284 unstable around 120 ºC which means that it could be afterwards partly desorbed again

285 into the flue gas (Eq. 5) making easier to be captured in the case of flue gas desulfurization

286 scrubber solutions.

287 $$Hg^0(g) + \text{bentonite surface with oxides} \rightarrow Hg^0(ad) + HgO(ad) \qquad (4)$$

288 $$Cl^- + Hg^0(ad) + HgO(ad) \rightarrow HgCl(ad) \qquad (5)$$

289 $$HgCl(ad) + Cl^- \rightarrow HgCl_2(ad) \qquad (6)$$

290 $$HgCl_2(ad) \rightarrow HgCl_2(g) \qquad (7)$$

291

292 **Table 4.** Percentages of mercury captured, heterogeneous and homogeneous mercury

293 oxidized and elemental mercury corresponding to the original sorbents in dry-MSWI

294 atmosphere at 300 min.

	M	M+S	Eb	Eb+Cl	Ec	Ec+Br
Hg_{cap} (%)	0.2	9.7	4.5	6.4	0.9	1.1
Hg^{2+} out (%)	61.3	74.4	69.4	78.1	64.2	67.9
Hg^0 out (%)	38.5	15.9	26.1	15.5	34.9	31.0

295   The Hg^0out (g) removal extent using the mineral-based sorbents were compared at

296   temperatures of 120 ºC, 150 ºC and 200 ºC. As it was expected, the results given in Figure

297   3 shows that the average Hg^0 (out) removal efficiency decreased slightly with an increase

298   in temperature. Sorbents M+S and Eb+Cl exhibited better efficiencies in terms of Hg^0out

299   (g) reduction. At 120 ºC the values of Hg^0out (g) obtained in presence of M+S and Eb+Cl

300   were about 10% while in the presence of Ec+Br sorbent Hg^0out (g) was 28%. The Hg^0out

301   (g) percentages using Eb+Cl at 120ºC and 150 ºC were similar to those percentages

302   corresponding with M+S. However at higher temperatures (200 ºC), it can be shown a

303   reduction of the efficiency of Eb+Cl (Hg^0out (g)=30%) in comparison with M+S (Hg^0out

304   (g)=20%). These results were expected due to the volatility of formed Hg compounds

305   which suggests a combination of chemisorption and physisorption process. It must be

306   taken into account that at higher temperatures (in presence of oxygen) SO_2 is partly

307   oxidized to SO_3, and in the case of presence of water vapours, they could result in H_2SO_4

308   that may be adsorbed on the surface of the sorbents. This effect together with adsorption

309   effects of CO_2 inhibit mercury adsorption, as there could be a competition for the same

310   surface binding sites (López-Antón *et al.*, 2015). On the other hand, depending on sorbent

311   nature, the adsorbed SO_3/H_2SO_4 can contribute to better sorption of mercury in the form

312   of sulphates.

313   Two samples of activated carbons (Raw-AC and Sulphur-AC) were tested under the same

314   atmospheres (N_2 and MSWI) to compare their mercury retention properties/capacities

315   with those obtained with the impregnated mineral sorbents (Table 5). Raw-AC displayed

316   lower retention capacity than the three samples of impregnated mineral-based sorbents

317   and the Sulphur-AC. On one hand, it must be taken into consideration that Raw-AC has

318   negligible content of sulphur in comparison with either sulphur-AC or the impregnated

319   zeolite M+S. On the other hand, BET surface of raw-AC (142 $m^2 \cdot g^{-1}$) is relatively low

14

which may disfavour Hg retention. In contrast, as it was expected, sulphur-AC showed

the best mercury retention capacity in 10 hours (102.1 ± 10 mg·kg^{-1}) due to its remarkable

sulphur content (2.5%), highest BET surface and highest volume of micropores

(suggesting higher presence of active sites for mercury capture). Impregnated zeolite was

able to capture 52.4 ± 9 mg·kg^{-1} in 10 hours which represents a significant step forward for

the developing of non-carbon based sorbents for mercury capture in Waste-to-Energy

facilities. A reduction of Hg^{0}out (g) up to 8.6% was achieved using M+S sorbent under

dry-MSW atmosphere whereas Ec+Br and Eb+Br sorbents reached percentages of Hg^{0}out

(g) of 31.1% and 14.5%, respectively.

Table 5. Retention capacities of the sorbents obtained at 150 ^{o}C (600 min)

Sorbent	Hg captured (mg·kg^{-1})	Hg^{0}out (g) (%)	Hg captured (mg·kg^{-1})	Hg^{0}out (g) (%)
	N$_2$	N$_2$	MSWI	MSWI
M+S	<1	90.3	52.4 ± 9*	8.6*
Ec+Br	2.4 ± 0.3	89.2	4.5 ± 0.9	31.1
Eb+Cl	17.5 ± 1	81.7	18.5 ± 5	14.5
Raw-AC	<1	91.3	5 ± 0.4	30.4
Sulphur-AC	43 ± 4	25.3	102.1 ± 10*	0.0*

*unsaturated sorbents at 600 min

4. Conclusions

The results obtained in this work confirm that impregnated mineral-based sorbents could

be a versatile alternative to the common ACs. The highest mercury removal efficiency

and capture capacity by mineral-based sorbents was achieved by a commercial, zeolite-

337 based sorbent impregnated with sulphur (M+S). This study suggests that the interaction

338 mechanism of mercury in this case occurs via formation of HgS. Furthermore, from an

339 environmental point of view, HgS is the most suitable (non-hazardous) chemical form of

340 mercury for long-term storage of the spent-sorbent residues as it affords an effective

341 barrier against leaching in comparison with the Hg chemical form resulting from other

342 chemical-promoters such as $FeCl_3$ and $CaBr_2$. The highest mercury heterogeneous

343 oxidation was achieved with a bentonite-based sorbent (Eb, Eb+Cl) due to its higher

344 content of TiO_2, Fe_2O_3 and Al_2O_3 that could favour Hg oxidation on the sorbent surface.

345 The higher the temperature, the lower the efficiency of Hg capture (in the temperature

346 range of 120 – 200 ºC) which means higher emissions of mercury (Hg^0 out). A

347 commercial activated carbon (sulphur-AC) showed the highest mercury retention

348 capacity (102.1 ± 10 mg·kg^{-1}) during the first 10 hours of sorption because of its

349 remarkable high sulphur content (2.5%) and good textural properties (high BET surface

350 and volume of micropores) which indicate high presence of active sites for mercury

351 capture. Nevertheless, the retention capacity obtained in 10 hours using the impregnated

352 zeolite sorbent (M+S), 52.4 ± 9 mg·kg^{-1}, under the same conditions represents a significant

353 step forward for the further development of non-carbon sorbents for mercury capture in

354 Waste-to-Energy facilities.

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Figure captions

Figure 1. Schematic diagram of the lab-scale device for Hg-capture experiments.
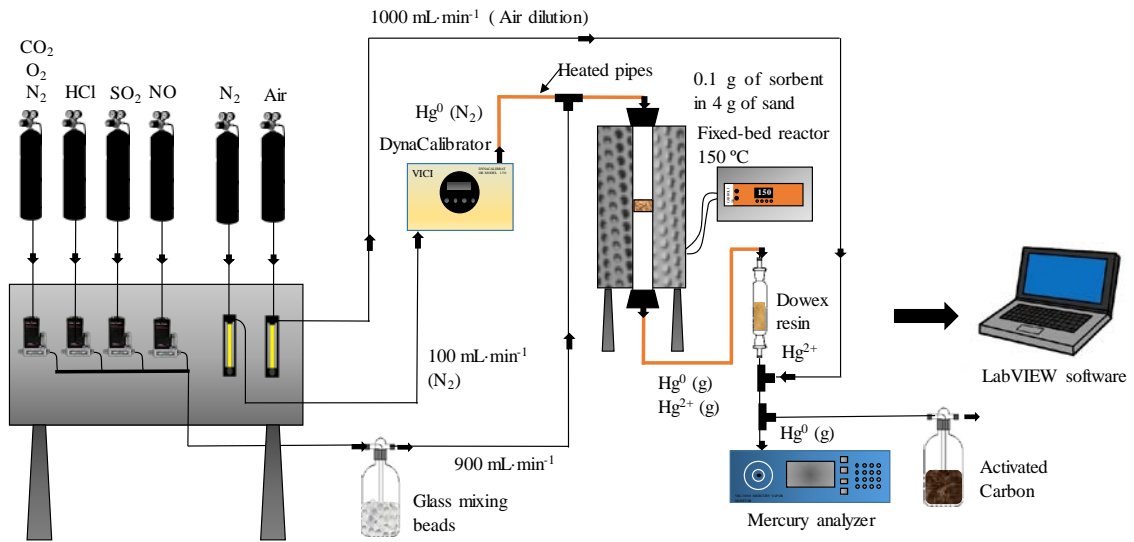
Figure 2. Relative output concentrations of mercury ($[Hg^0\text{-out}/Hg^0\text{-in}]$) obtained for the three impregnated mineral sorbents (M+S, Eb+Cl and Ec+Br) in the two model gas atmospheres: (N_2) and model atmosphere corresponding to dry flue gas from MSWI (dry-MSWI) ($Hg^0in=100\mu g\cdot m^{-3}$, T=150 ºC).

Figure 3. Influence of temperature on mercury captured (Hg^0out (%)) by impregnated sorbents M+S, Eb+Cl and Ec+Br.
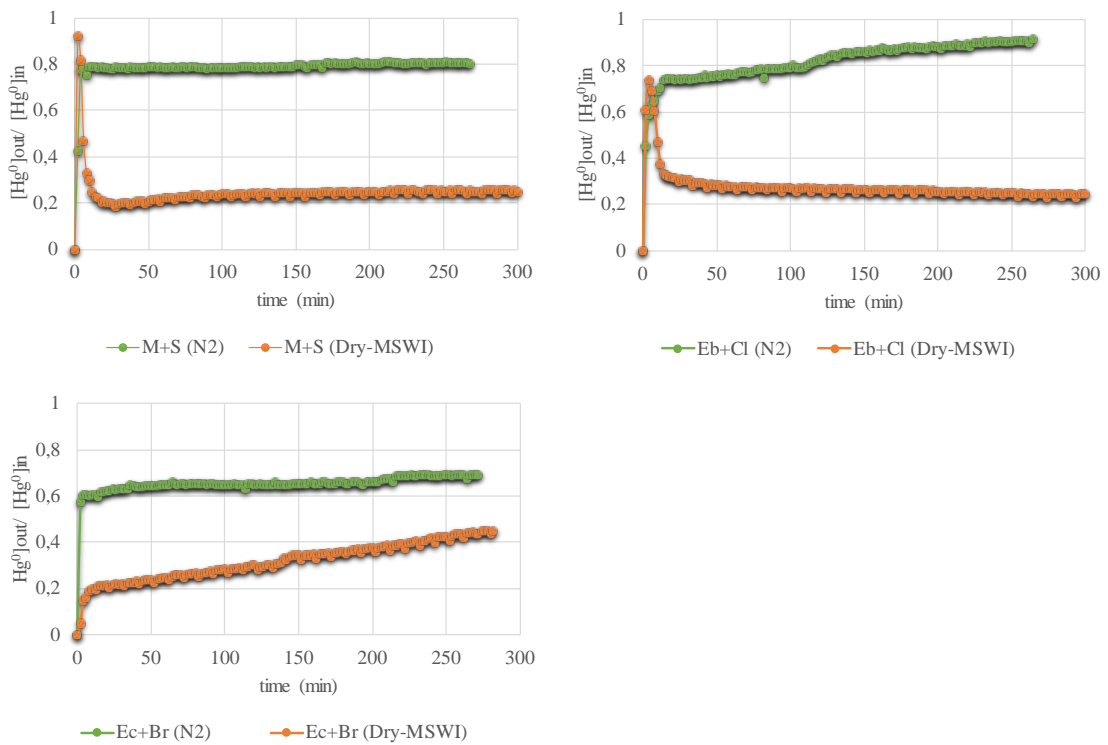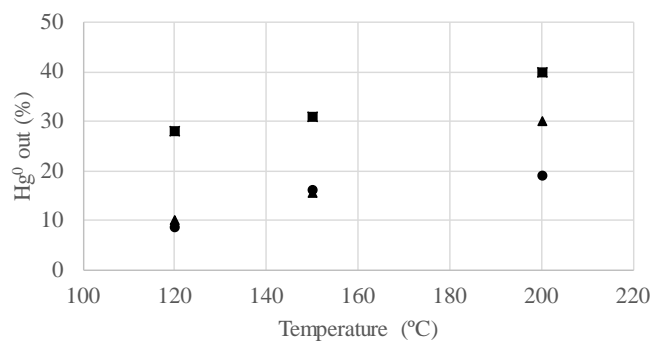
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Figure 1.

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478　**Figure 2.**

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480　**Figure 3.**

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