

1 **Utilization of desulfurization gypsum potentially impairs the**
2 **efforts for reducing Hg emissions from coal-fired power plants in**
3 **China**

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11 Abstract

12 The thermal instability of most mercury (Hg) species in flue gas
13 desulfurization (FGD) gypsum may lead to the release of large amounts of
14 Hg into the atmosphere. In this study, gypsum samples were collected from
15 13 major coal-fired power plants (CFPPs) for evaluating the Hg thermal
16 stability within a temperature range of 100 - 200 °C. Results indicated that
17 the release ratio of Hg from FGD gypsum varied considerably among the
18 CFPPs. Such significant differences were caused by different proportions
19 of the major Hg compounds, especially of HgCl_x (HgCl₂ and Hg₂Cl₂), in
20 the FGD gypsum samples. The release ratio appeared extremely sensitive
21 to changes in the treatment temperature and duration. Wallboard
22 manufacturing and its use as cement retarder are the leading causes of Hg
23 emission (corresponding to > 95% of the total) during FGD gypsum
24 resource utilization. The total average Hg emitted due to FGD gypsum
25 resource utilization in China in 2017 was estimated to be 11.42 tons
26 (ranging between 2.15 - 38.35 tons), which accounted for about 23.8 %
27 (ranging between 4.6 - 79.8%) of the stack Hg emissions from CFPPs in
28 that year. The results of this study indicate that the resource utilization

29 processes of FGD gypsum are important Hg emission sources and that they
30 should be considered with care in future emission control policies.

31 Keywords: Hg emission; FGD gypsum; thermal treatment; wallboard
32 production; cement retarder

33

34 **1. Introduction**

35 Mercury (Hg) is a highly toxic heavy metal, which is persistent in the
36 natural environment and biologically accumulates [1, 2]. For these reasons,
37 it has been listed as a priority pollutant for control by many national and
38 international organizations [3]. It was estimated that nearly 19 million
39 people worldwide were at risk of Hg exposure in 2015 [4], demonstrating
40 that Hg pollution is a global public health challenge.

41

42 Coal-fired power plants (CFPPs) are major emitters of Hg and other toxic
43 pollutants and greenhouse gases, in China and globally [5-8]. Since 2014,
44 the retrofit of ultra-low emission (ULE) technology in CFPPs has become
45 mandatory in China for controlling the emissions of particulate matter,
46 sulfur dioxide (SO₂), and nitrogen oxides (NO_x) [9] from this industrial
47 sector. This action has promoted the installation of numerous air pollution
48 control devices (APCDs) in CFPPs in recent years [10]. The installed
49 proportion of denitrification equipment (e.g., selective catalytic reduction
50 (SCR), selective non-catalytic reduction (SNCR) equipment) increased
51 from 49.4% in 2013 to 92.6% in 2018, while that of flue gas desulfurization

52 (FGD) units increased from 90.6% to 95.9% during the same period [10,
53 11].

54

55 These APCDs equipment can co-remove substantial Hg from the flue gas
56 and capture it into solid byproducts like FGD gypsum [12-14]. In fact,
57 denitrification equipment such as SCR could effectively oxidize Hg^0 into
58 Hg^{2+} , reaching an average oxidation rate of 71% [15], and Hg^{2+} is easily
59 removed by wet FGD devices [16]. The highest observed Hg removal
60 efficiency (99%) was achieved by combining APCDs with SCR, fabric
61 filter (FF), and WFGD (wet FGD) equipment [17]. In addition, the
62 installation of APCDs drastically increases the output of FGD gypsum,
63 which can be reused in the production of building materials (e.g., plastering
64 gypsum, wallboard, concrete, and synthetic materials), for replacing
65 natural gypsum as cement retarder, as well as in the land applications [11,
66 18-20]. All of these uses may lead to the release of large amounts of Hg
67 into the surrounding environment [21-26]. The amount of FGD gypsum
68 produced from CFPPs in China increased from less than 10 million tons
69 (Mt) in 2006 to approximately 110 Mt in 2019 [27], providing a potential

70 secondary source of atmospheric Hg emissions [21, 28, 29]. The resource
71 utilization ratio of FGD gypsum in China dramatically increased from less
72 than 10% in 2005 to about 75% in 2012 and has remained constant since
73 then [10]. According to the 2014 report of the National Development and
74 Reform Commission of China [30], the gypsum used for wallboard
75 production and as cement retarder accounted for about 96% of the total
76 reuse amount.

77

78 The risk of Hg release during the FGD gypsum utilization process has been
79 studied since 2005 [31, 32]. In 2012, Yang et al. [33] warned that ignoring
80 the emissions of Hg from CFPPs byproducts (including FGD gypsum)
81 would lead to ineffective Hg control in CFPPs in China. Nevertheless, this
82 topic is still scarcely studied. The majority of existing studies on estimating
83 Hg emissions from CFPPs have focused only on Hg concentration and on
84 the speciation of stack flue gas in relation to boiler types, coal
85 characteristics, and the APCDs, among others [6, 17, 34-36]. In these
86 studies, it was assumed that Hg was removed once it entered the byproducts.
87 Previous studies [22, 23, 29, 37], however, have proved that Hg (especially

88 in the form of HgCl_x : either HgCl_2 or Hg_2Cl_2) can be released from FGD
89 gypsum at temperatures even $<100\text{ }^\circ\text{C}$. Notably, thermal treatment is a
90 necessary step in the main utilization pathways of FGD gypsum (e.g., used
91 for wallboard production and as cement retarder) [30]. Thus, significant
92 amounts of Hg are released during the wallboard manufacturing process
93 (Hg release ratio between 2-92.8%) [22, 24, 29, 31, 32]. The cement
94 industry has been the largest source of anthropogenic Hg emissions in
95 China since 2009 [34]; therefore, it has received widespread attention [38,
96 39]. However, few studies have focused on the release of Hg during the
97 pretreatment process of FGD gypsum being used as cement retarder.
98 Normally, FGD gypsum is directly mixed with clinker for grinding and,
99 ultimately, producing cement. The Hg released during cement production
100 processes is thought completely from the calcination process of the cement
101 clinker and from fuel combustion [34, 38, 39]. However, when FGD
102 gypsum is being used as cement retarder, it is usually too wet to be blended
103 with other raw materials. Thus, it needs to be dried at a temperature
104 between $40 - 400\text{ }^\circ\text{C}$ [40]. During this process, Hg in FGD gypsum may
105 release into the atmosphere. Additionally, Gustin and Ladwig [28]

106 suggested that water addition is a dominant environmental factor
107 promoting Hg release from FGD gypsum, they observed that up to 50% of
108 the Hg was released into the atmosphere in 31 days. Zhu et al. [41]
109 demonstrated that the Hg emission ratio from FGD gypsum can reach 2.65%
110 during a 180-day experimental period in dark and room-temperature
111 conditions and that Hg release can be greatly promoted by repeated wetting
112 events. Diao et al. [42] and Hao [43] found that Hg can be released from
113 FGD gypsum (up to 25.1 - 50.3%) during stacking at room temperature. It
114 can be concluded that the high Hg content in FGD gypsum and its
115 instability may lead to significant Hg emissions during the utilization of
116 FGD gypsum.

117

118 In this study, FGD gypsums were collected from 13 major CFPPs in China,
119 and the Hg release ratio from those samples during different thermal
120 treatment processes was evaluated. Moreover, the main Hg species
121 contained in the gypsum samples were identified, and the total amount of
122 Hg released from the FGD gypsum resource utilization processes in China
123 was estimated. The findings of this study may fill the current knowledge

124 gap about Hg emission control in CFPPs and can lay the foundation for the
125 whole-life management of Hg emissions from CFPPs in China.

126

127 **2. Methodology**

128 **2.1 Sample collection**

129 FGD gypsum samples were collected from 13 CFPPs: 12 in the Guizhou
130 Province, southwestern China (CFPPs 1-12 #), and 1 in Tangshan City,
131 Hebei Province, northern China (CFPP 13#). The sampling sites of CFPPs
132 1-11# were described in one of our previous studies [44], although they
133 were indicated with different CFPP numbers (Fig. S1). The site of CFPP
134 12# is in Qianxi County, western Guizhou Province. Information about the
135 boiler type and its capacity, the APCDs, and the Hg content in the gypsum
136 samples is given in Table S1. Each gypsum sample was obtained by mixing
137 at least 9 subsamples collected within 2 days at the same site.

138

139 Notably, owing to the ultra-low emission retrofit in China since 2014, most
140 CFPPs in the country have similar pollutant control equipment [45] (e.g.,
141 SCR, electrostatic precipitator (ESP) or ESP+FF, and WFGD). A

142 comprehensive study of the gypsum in typical CFPPs within a specified
143 area like Guizhou is expected to provide an approximate view of current
144 Hg emissions from CFPPs in China.

145

146 **2.2 Thermal treatment tests**

147 Thermal treatment tests were conducted to simulate the heat treatment of
148 FGD gypsum during the resource utilization processes. The thermal
149 treatment of FGD gypsum included the following steps: 0.2 g of FGD
150 gypsum were placed in a porcelain crucible, then positioned in a preheated
151 electric blast oven (Shanghai Yiheng 9000, ± 1 °C) to a specified
152 temperature. After a certain time, the porcelain crucible was removed from
153 the oven and cooled down under room conditions. Afterward, the treated
154 FGD gypsum was weighed, and the Hg concentration was measured.

155

156 In China, the resource utilization processes of FGD gypsum are mainly
157 used for wallboard production and as cement retarder. For the wallboard
158 production, FGD gypsum first needs to be dried (at temperatures < 128 °C)
159 to remove any free moisture, and then to be calcined (128 - 163 °C), to

160 produce β -CaSO₄•1/2 H₂O. Subsequently, it has to be mixed with water
161 and several additives to form a slurry, which can be extruded between two
162 sheets of paper to form a wet board. Afterward, the wet board is conveyed
163 on a conveyor belt, cut to the designed length, and dried at 94 - 203 °C to
164 remove any free moisture [24]. The whole process from FGD gypsum
165 drying to the output of final products lasts about 1 - 2 h. For the purpose of
166 being used as cement retarder (Fig S2), FGD gypsum needs to be pretreated
167 typically under a temperature range of 120 - 200 °C for 1 h to make it dry
168 enough [40, 46] (Fig. S2). Our survey results, which included more than
169 35 domestic manufacturers of gypsum drying equipment in China, showed
170 that the normal thermal treatment of FGD gypsum consists in drying it at
171 150 °C for 30 - 60 min. Hence, our laboratory simulations were carried out
172 at temperatures of 100, 150, and 200 °C, over periods of 20, 40, 80, and
173 120 min. Notably, each sample was treated three times in parallel.

174

175 **2.3 Temperature-programmed Hg decomposition (Hg-TPD) analysis**

176 Hg-TPD is an important tool for identifying Hg species in gypsum [22, 29,
177 37, 47-49] by comparing Hg thermal release curves of FGD gypsum

178 samples with that of different Hg standard substances and gypsum mixtures
179 under the same procedure of pyrolysis. Hg-TPD analyses were carried out
180 using the same lab device described in one of our previous studies [29]: a
181 certain amount of gypsum sample was put into a temperature-programmed
182 tube furnace, and the flow rate of the carrier gas was kept at 1 L/min. The
183 thermal release profiles of different Hg standards of Hg₂Cl₂, HgCl₂, black
184 HgS, red HgS, HgO, Hg₂SO₄, and HgSO₄, that mixed with 800°C
185 preheated gypsum in this study are shown in Fig. S3. The decomposition
186 temperature of the Hg standards follows this order: Hg₂Cl₂ < HgCl₂ < black
187 HgS < red HgS < Hg₂SO₄ < HgO < HgSO₄. This sequence is consistent
188 with those reported in previous studies [22, 23, 50]

189

190 **2.4 Method for estimating the amount of released Hg**

191 The resource utilization processes of FGD gypsum performed in China are
192 mainly divided into three aspects: (1) used for building materials
193 production (mainly for wallboard production), (2) being used as cement
194 retarder, and (3) used for land applications such as agricultural practice,
195 soil stabilization and mining reclamation [11, 18, 19]. The amount of Hg

196 released during these processes is affected by the Hg content of the FGD
197 gypsum, the amount of reused FGD gypsum, and the Hg release ratio. The
198 total amount of Hg (M_{em}) released during FGD resource utilization
199 processes in China can be estimated based on the following equation:

$$200 \quad M_{em} = c_g m \alpha (\gamma_w \varphi_w + \gamma_c \varphi_c + \gamma_l \varphi_l) \quad (\text{Eq. 1})$$

201 , where c_g is the Hg content in FGD gypsum, m is the annual production
202 amount of FGD gypsum in China, and α is the proportion of resource
203 utilization of FGD gypsum; moreover, γ_w , γ_c , and γ_l are the proportions of
204 FGD gypsum used for the production of building materials (mainly
205 wallboard production), as cement retarder, and for land applications,
206 respectively, while φ_w , φ_c , and φ_l are the estimated Hg emission ratios along
207 the same three pathways.

208

209 **2.5 Analysis methods, quality assurance, and quality control**

210 The total Hg content in gypsum was determined using a Direct Mercury
211 Analyzer (Milestone DMA-80, Italy). The sample pretreatment and
212 measurement methods were all described in one of our previous studies
213 [44]. Briefly, the gypsum samples were air-dried, ground into small pieces

214 (< 0.150 mm), and subjected to pyrolysis. Subsequently, the Hg in the
215 gypsum was selectively trapped in a gold amalgamator, released by heating,
216 and measured by atomic absorption spectrometry [51]. Quality control
217 measures, including method blanks, triplicates, matrix spikes, and
218 reference materials, were also previously described [44]. The relative
219 standard deviation (RSD) of the duplicate Hg concentration results in this
220 study was always < 5%.

221

222 **3. Results and discussion**

223 **3.1 Hg release during the thermal treatment**

224 Fig. 1 depicts the thermal release ratio of Hg from FGD gypsum during
225 thermal treatment at different temperatures for 40 min. The data refer to
226 samples collected from 13 important CFPPs in China. The Hg release ratio
227 varied greatly among CFPPs and increased drastically with the thermal
228 treatment temperature. For example, the average ratio increased from 6.35
229 $\pm 4.88\%$ under thermal treatment conditions of $100\text{ }^{\circ}\text{C}$ to $16.61 \pm 8.91\%$
230 under $150\text{ }^{\circ}\text{C}$, and to $35.50 \pm 17.30\%$ under $200\text{ }^{\circ}\text{C}$ for 40 min. The highest
231 ratio ($77.37 \pm 2.28\%$) was obtained for CFPPs 2# under $200\text{ }^{\circ}\text{C}$ for 40 min.

232 This ratio was about 10 times the lowest ($8.43 \pm 5.64\%$), obtained for
233 CFPPs 3# under $100\text{ }^{\circ}\text{C}$. Thus, the treatment temperature appears as a key
234 factor affecting the thermal release of Hg from FGD gypsum.

235

236 The thermal treatment duration is another important factor affecting Hg
237 release. In fact, as shown in Fig. 2, the Hg release ratio of FGD gypsum
238 increased drastically with the thermal treatment time. In particular, the
239 average Hg release ratio increased from $3.25 \pm 4.96\%$ to $19.20 \pm 7.35\%$,
240 from $13.25 \pm 6.97\%$ to $37.56 \pm 19.25\%$, and from $35.7 \pm 16.8\%$ to $63.52 \pm$
241 20.37% under treatment temperatures of $100\text{ }^{\circ}\text{C}$, $150\text{ }^{\circ}\text{C}$, and $200\text{ }^{\circ}\text{C}$,
242 respectively, when the thermal treatment time increased from 20 to 120
243 min. The thermal release ratios at $100\text{ }^{\circ}\text{C}$, $150\text{ }^{\circ}\text{C}$, and $200\text{ }^{\circ}\text{C}$ (estimated
244 by one-variable linear regression) were $1.69\% / 10\text{ }^{\circ}\text{C}$ ($y = 0.169x + 0.131$,
245 $r = 0.989$), $2.99\% / 10\text{ }^{\circ}\text{C}$ ($y = 0.299x + 3.965$, $r = 0.978$), and $4.69\% /$
246 $10\text{ }^{\circ}\text{C}$ ($y = 0.469x + 13.99$, $r = 0.908$), respectively.

247

248 **3.2 Hg-TPD of FGD gypsum**

249 The Hg thermal release profiles of the FGD gypsum samples from different
250 CFPPs are shown in Fig. S4. Notably, these profiles vary greatly, indicating
251 that different Hg compounds exist in the FGD gypsum samples of different
252 CFPPs. Using the Peak Fit 4.12 software, the proportions of different Hg
253 forms in FGD gypsum were calculated by comparing them with the release
254 profiles of Hg standards (Fig. S3). The data in Fig. 3 show that the
255 dominant Hg species in the FGD gypsum samples were HgCl_x (Hg₂Cl₂ and
256 HgCl₂), HgS, and Hg_xSO₄ (Hg₂SO₄ and HgSO₄). In particular, HgCl_x was
257 the main Hg species in CFPPs 2#, 5#, 9#, 12#, and 13#, accounting for
258 about 67%, 46%, 47%, 50%, and 48% of the total Hg, respectively.
259 Meanwhile, HgS was the main Hg species in CFPPs 1#, 4#, 7#, 10#, and
260 11#, accounting for about 53%, 71%, 65%, 50%, and 67% of the total Hg,
261 respectively. Hg_xSO₄ was the main Hg species in CFPPs 3#, 6#, and 8#,
262 accounting for about 54%, 65%, and 42% of the total Hg, respectively. And
263 HgO accounted for only 18%, 10%, and 30% of the total Hg in CFPPs 3#,
264 5#, and 6#, respectively. Accordingly, previous studies [22, 23, 42, 52-54]
265 have reported that HgCl₂, HgS, HgO, and Hg_xSO₄ are primary Hg
266 compounds in FGD gypsum.

267

268 **3.3 Relationship between Hg species and the release ratio**

269 According to Fig. S3, HgCl_x is most likely the main Hg species released
270 during the FGD gypsum resource utilization process since it is the least
271 stable Hg compound in gypsum. FGD gypsum with the highest Hg release
272 ratio may also be the one with the highest HgCl_x proportion, and the
273 relationship between the ratios of the main Hg species (i.e., HgCl_x and HgS)
274 and the Hg release ratio (150 °C, 40 min) is shown in Fig. 4. The Hg release
275 ratio showed a strong positive correlation with the proportion of HgCl_x (r
276 = 0.7998, $p = 0.001$) in gypsum, but no significant correlation with that of
277 HgS ($r = -0.15$, $p = 0.6237$), this confirmed that HgCl_x is the main Hg
278 compound released during the FGD gypsum resource utilization processes
279 that involved thermal treatment. These findings are consistent with those
280 of Liu et al. [22] and one of our previous studies [44], in which Cl was one
281 of the most important elements affecting the Hg content in gypsum.

282

283 The above information suggests that different Hg compounds in gypsum
284 are the main reason for the great differences observed in the FGD Hg

285 release ratios. Since HgCl_x was the main compound released during the
286 thermal treatment process, a high proportion of HgCl_x is expected to result
287 in an increase in the Hg release ratio. For example, the gypsum from CFPP
288 2# had the highest Hg release ratio (30.82%, 150 °C, 40 min) as well as the
289 highest HgCl_x proportion (67%). In comparison, the gypsum from CFPP
290 6# had the lowest Hg release ratio and a relatively low HgCl_x proportion
291 (about 6%).

292

293 **3.4 Estimation of the amount of Hg released from FGD gypsum during** 294 **the resource utilization processes**

295 **3.4.1 Uncertainties in the estimation of Hg emissions**

296 Uncertainties in the estimated Hg emissions from FGD gypsum are mainly
297 derived from the indeterminacy of the Hg content in gypsum, the average
298 Hg emission ratio, and the utilization amount (ratio) of FGD gypsum along
299 each utilization pathway.

300 The Hg content in gypsum (c_g) was estimated according to the following
301 equation [44]:

$$302 \quad c_g = -188.65 + 2.40c_{Cl} + 1.12c_{Hg} \quad (\text{Eq. 2})$$

303 , where c_{Cl} and c_{Hg} are the Cl content (mg/kg) and the Hg content ($\mu\text{g}/\text{kg}$)
304 in coal (obtained from different sources). The reported Hg and Cl contents
305 in coal and the estimated Hg content in FGD gypsum in China are shown
306 in Table 1. Notably, the estimated Hg content in FGD gypsum (according
307 to Eq. 1 and based on the Hg and Cl contents in coal obtained in a previous
308 study [17]) were 511 and 1036 $\mu\text{g}/\text{kg}$, respectively. These results are
309 somewhat consistent with those of Hao et al. [55] (in which the average
310 and median Hg contents calculated based on samples from 70 power plants
311 distributed in 20 Chinese provinces were 891 $\mu\text{g}/\text{kg}$ and 629 $\mu\text{g}/\text{kg}$,
312 respectively) and Liu et al. [22] (in which the average Hg content
313 calculated based on samples from 9 Chinese power plants was 963 $\mu\text{g}/\text{kg}$).
314 In this study, the average Hg content in Chinese flue gas gypsum was
315 assumed to be 805 ± 268 $\mu\text{g}/\text{kg}$ (with values ranging between 511-1036
316 $\mu\text{g}/\text{kg}$), this was calculated as the average of two estimated data (511 $\mu\text{g}/\text{kg}$
317 and 1036 $\mu\text{g}/\text{kg}$) and reported data (891 $\mu\text{g}/\text{kg}$).

318

319 The Hg emission ratio along the different utilization pathways was also a
320 determining factor for Hg releasing. Due to the different thermal treatment

321 purposes, the treatment temperature and time during distinct FDG gypsum
322 utilization processes vary greatly. A previous report [30] indicated that
323 wallboard production (24.3 Mt, 27.8%) and being used as cement retarder
324 (60 Mt, 68.3%) accounted for about 96% of the total reuse amount of FDG
325 gypsum in China in 2014. These values were very different from those for
326 the United States, where wallboard production accounted for 54%, and
327 cement/concrete/asphalt production counted only less than 8% of the total
328 reuse amount of FDG gypsum in 2016 [56]. Since the largest proportion of
329 FDG gypsum used for building materials production was wallboard
330 production [11, 19], the Hg emission ratio from wallboard production can
331 be approximated as the average Hg emission ratio from building material
332 production. Liu et al. [22] simulated the Hg release during wallboard
333 production by heating gypsum samples in a reactor tube, increasing the
334 temperature from room conditions to 163 °C, and then maintaining it at
335 163 °C for 1 h. The release ratio was estimated to be 30.8%. In one of our
336 previous studies [29], we simulated the same process under a temperature
337 of 163 °C for 2 h, obtaining an emission ratio of 48.3%. Other reports [31,
338 32] indicated that wallboard production could be normally conducted

339 within a temperature range of 160 - 180 °C, and the release ratio can reach
340 58%. In this study, by maintaining a temperature of 150 °C for 2 h, we
341 obtained an average release ratio (φ_w) of 37.6%, the minimum value
342 (13.25%) was obtained by maintaining a temperature of 150 °C for 20 min,
343 while the maximum (63.52%) was obtained by maintaining a temperature
344 of 200 °C for 2 h (see Fig. 2). A previous study suggested [22] that the
345 thermal treatment of FGD gypsum as cement retarder can be similar to that
346 for wallboard production. However, since these thermal treatments have
347 different purposes, their treatment temperatures and durations are
348 considerably different. We considered an average release ratio (φ_c) of 16.61%
349 (obtained by maintaining a temperature of 150 °C for 40 min) (Fig. 2). This
350 value is comprised between the minimum value (6.35%) was obtained by
351 maintaining a temperature of 100 °C for 40 min and the maximum
352 value (42.13%) by maintaining a temperature of 200 °C for 60 min [40] (see
353 Fig. 2). For the land applications, specific data on the ratio of Hg released
354 into the atmosphere from FGD gypsum are still lacking, however,
355 significant release amounts are expected [57, 58]. Zhu et al. [41] found that
356 the Hg release rates in the dark at room temperature varied between 0.31 -

357 2.65% during 180-day period tests. Moreover, temperature, UV radiation,
358 and solid moisture content were all suspected to significantly enhance the
359 release of Hg. Diao et al. [42] confirmed that Hg could be released from
360 gypsum in significant amounts under room temperature in 10 days, the
361 release ratio ranged between 1.5 - 15.3% in the dark and between 0.7 - 25.1%
362 under UV irradiation. Gustin and Ladwig [28] and Hao [43] indicated that
363 the Hg release ratio ranged from 9% to 50% in 31 days and from 15.8% to
364 51% in 38 days. Overall, these results suggest that the release ratio of Hg
365 from FGD gypsum during prolonged land application processes may be
366 quite high compared to that during the brief thermal treatments included in
367 resource utilization processes. As the FGD gypsum commonly directly
368 used in the land applications under room temperature, in this study, we
369 assumed an average ratio of 15.3% [42], ranging between 0.31 and 51%
370 according to previous studies [41, 43].

371

372 Regarding the utilization amount (ratio) of FGD gypsum in each utilization
373 category, a previous report [30] showed that industrial byproduct gypsum
374 (including FGD gypsum, phospho-gypsum, and titanium gypsum) used for

375 wallboard (24.3 Mt, 27.8%) and cement retarder (60 Mt, 68.3%)
376 production accounted for 96% of the total reuse amount of byproduct
377 gypsum in China in 2014. Additionally, Li [59] showed that the reuse
378 amount of industrial byproduct gypsum in 2018 was 23.1 Mt (18.6%) for
379 wallboard production and 81 Mt for being used as cement retarder (65.3%).
380 In this study, we assumed that, on average, 25% (20 - 30%) of FGD gypsum
381 would be used for building materials production (mainly wallboard
382 production) (γ_w), 70% (60 - 80%) for being used as cement retarder (γ_c),
383 and 5% (2 - 8%) for land applications (γ_l). Notably, the ratios of FGD
384 gypsum used for wallboard production and land applications increased
385 from 2005 to 2019 due to national policies [60] and the promotion of FGD
386 gypsum for soil improvement [61]. In summary, all the parameters related
387 to the release of Hg from FGD gypsum are listed in Table 2 [27, 30, 43, 59,
388 62].

389

390 **3.4.3 Amount of Hg released from FGD gypsum utilization processes**

391 Fig. 5a and Table S2 show how the amount of Hg released during FGD
392 resource utilization has increased in the last decade. This has been mainly

393 the result of a rapid increase in FGD gypsum production. The estimated
394 annual average Hg release amount was only 0.17 tons (ranging between
395 0.03 - 0.56 tons) in 2005. This figure increased to around 10 tons in 2012,
396 maintained this level until 2017, and then increased to 13.75 tons (ranging
397 between 2.60 - 46.18 tons) in 2019. Comparable Hg release amounts
398 resulted from the process of building materials production (mainly
399 wallboard, 5.92 tons) and being used as cement retarder (7.43 tons) (Fig.
400 5b), although double of the amount of FGD gypsum was used in the latter
401 process. A previous study [6] suggested that the total amount of Hg emitted
402 from CFPPs into the atmosphere in China in 2017 reached 48 tons. The
403 estimated total amount of Hg released during FGD utilization processes in
404 2017 was 11.42 tons (ranging between 2.15 - 38.35 tons), which accounted
405 for about 23.8 % (ranging between 4.6 - 79.8%) of the total Hg emissions
406 from CFPPs in China. Atmospheric Hg emissions from CFPPs in the
407 country are expected to decrease to 2.4 tons by 2030 [45]; however, the
408 amount of Hg released from FGD utilization processes may actually
409 increase by that time, while this has not been taken into account in previous
410 emission estimates. In addition, FGD gypsum is only one of the important

411 flue gas control byproducts. As a matter of fact, other flue gas control
412 byproducts (e.g., fly ash) may emit even more Hg than gypsum during their
413 utilization process [27]. These secondary emission sources of Hg should
414 be carefully considered in future emission estimates and policymaking.

415

416 **4. Conclusions**

417 The huge production amount of FGD gypsum and its high resource
418 utilization ratio make the release of Hg from FGD gypsum an important
419 issue in China. In this study, FGD gypsum was collected from 13 typical
420 CFPPs in China to evaluate the Hg emissions along the main resource
421 utilization pathways, including wallboard production and being used as
422 cement retarder. Our results indicated that the amount of Hg released from
423 FGD gypsum is closely linked to the heating temperature and the duration
424 of the simulated resource utilization processes. The average Hg release
425 ratio when the samples were subjected to 100 °C for 20 min was only 3.25
426 \pm 4.96%, but it dramatically increased to 63.52 \pm 20.37% when the samples
427 were subjected to 200 °C for 120 min. Under a typical resource utilization
428 treatment temperature range (between 100 - 200 °C), the release of Hg

429 from FGD gypsum can be mainly attributed to the decomposition of HgCl_x
430 (HgCl_2 and Hg_2Cl_2). The Hg release amount from the process of wallboard
431 production and being used as cement retarder have increased substantially
432 in the last decade and reached to a total of 11.4 tons in 2017 that
433 corresponding to about 1/4 of the total atmospheric emissions (48 tons)
434 from CFPPs in China. This suggests that the release of Hg from FGD
435 gypsum during resource utilization processes cannot be ignored since it
436 may seriously undermine the current efforts to control Hg emissions from
437 CFPPs in China.

438

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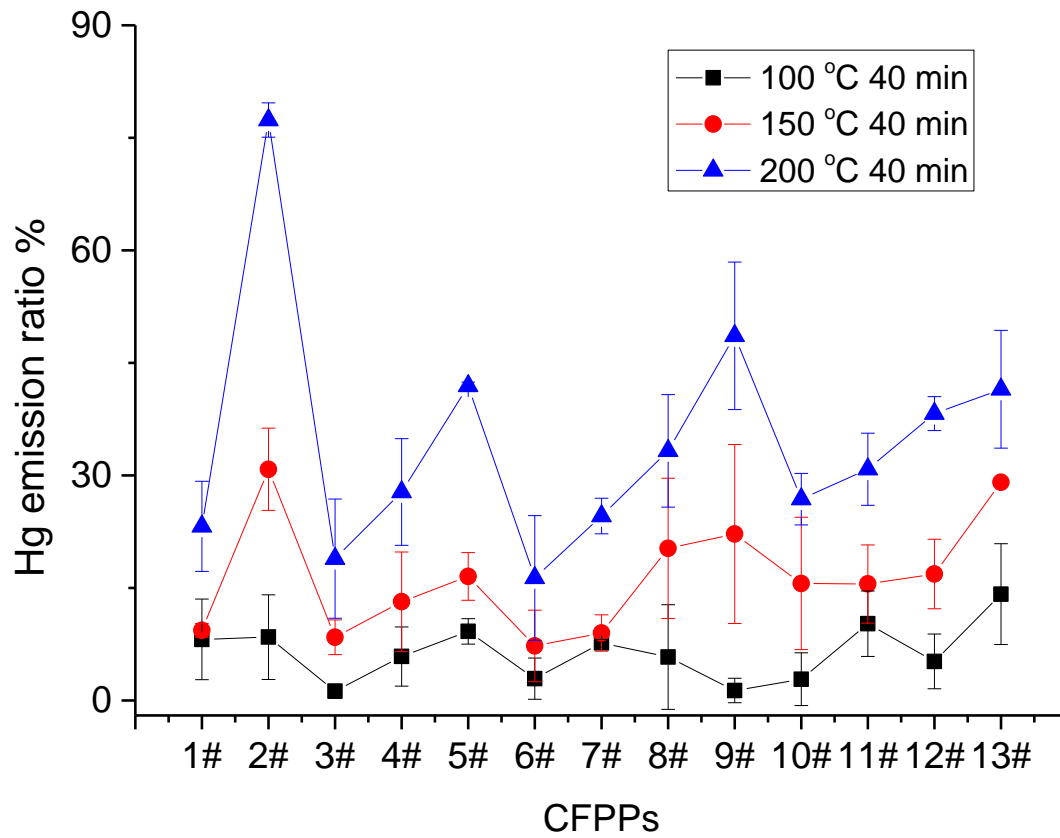
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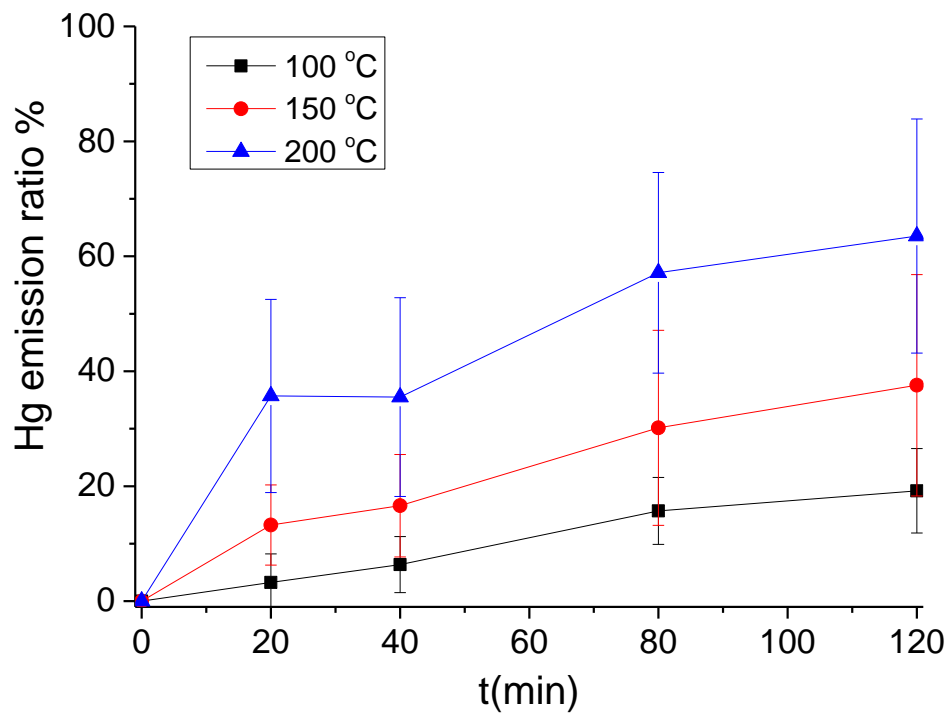
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653 Fig. 1 Hg release ratio of different FGD gypsums treated with various

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temperatures for 40 minutes

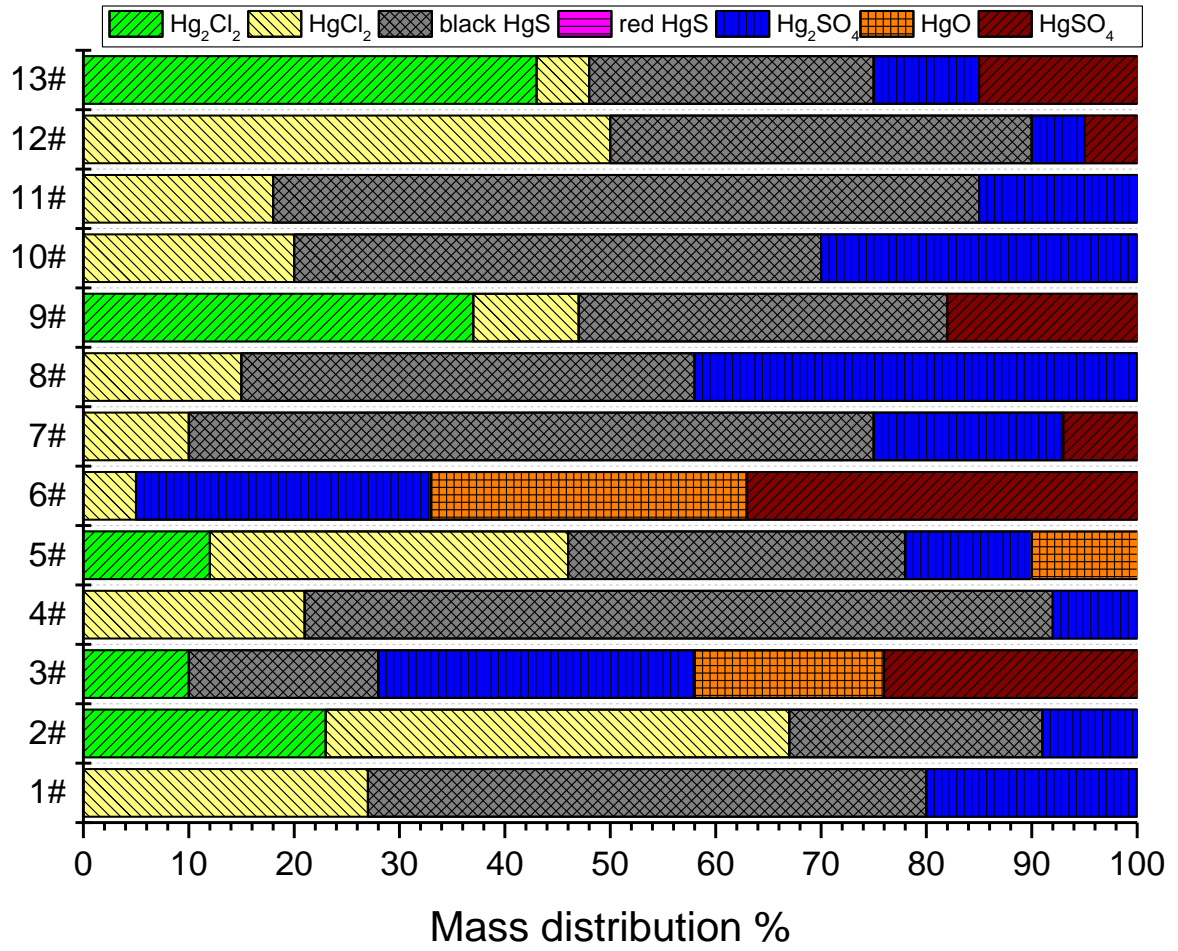
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657 Fig. 2 Average Hg release ratio of FGD gypsum from 13 CFPPs during

658 the thermal treatments with different durations and temperatures



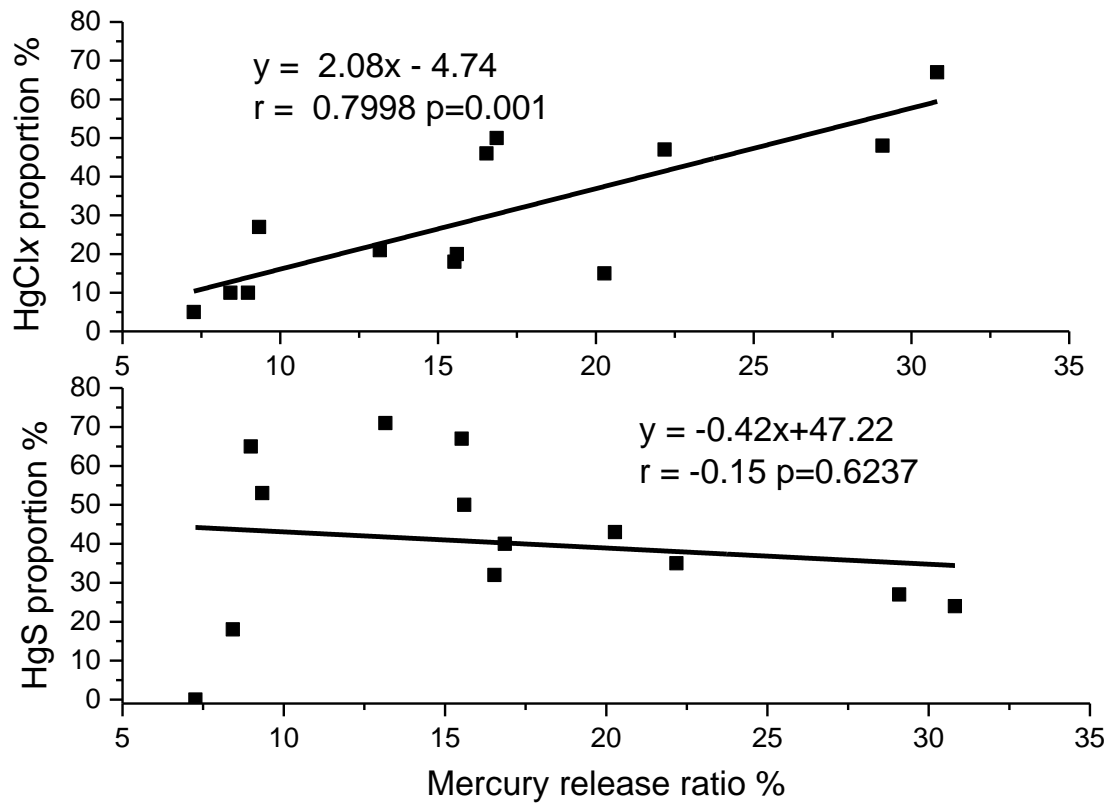
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661 Fig. 3 Mass distributions of different Hg compounds in gypsum samples

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from 13 CFPPs

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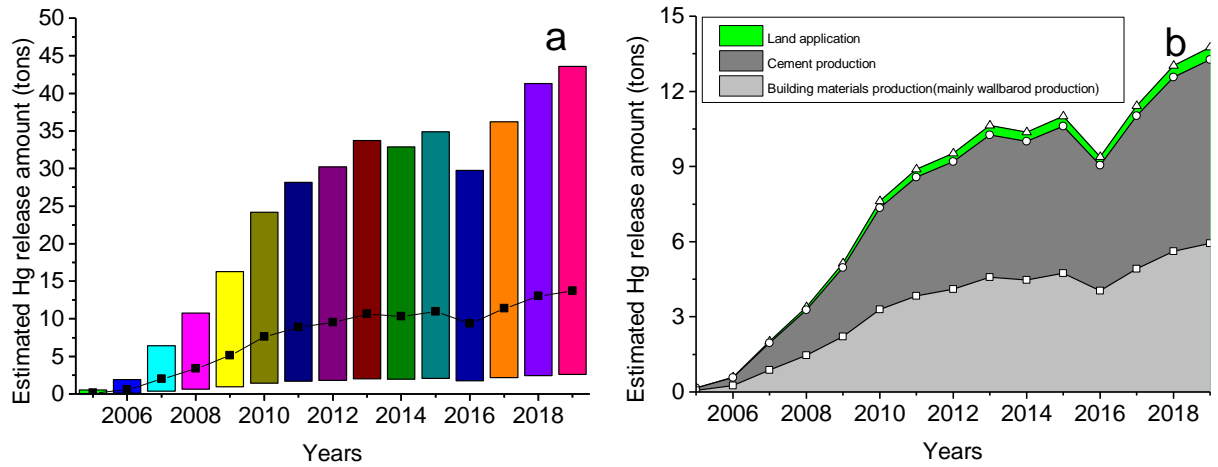


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665 Fig. 4 Correlations between the release ratio of Hg from gypsum and the

666 proportions of the main Hg species in gypsum

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Fig. 5 Estimated annual Hg release amounts from FGD gypsum utilization in China: (a) total, with columns showing the annual ranges, and (b) for different resource utilization processes

674 Table 1 Reported Hg and Cl contents in coal and estimated Hg content in

675 FGD gypsum in China

Data source	Zhang et al. (2012) [36] (a)		USGS data [36] (b)		Reported contents in gypsum (Hao et al. 2016) [54]	Estimated contents in gypsum ($\mu\text{g}/\text{kg}$)		Average ($\mu\text{g}/\text{kg}$)
	Hg content in coal ($\mu\text{g}/\text{kg}$)	Cl content in coal (mg/kg)	Hg content in coal ($\mu\text{g}/\text{kg}$)	Cl content in coal (mg/kg)		a	b	
National average	170	260	159	436	868	511	1036	805 ± 268

676

677 Table 2 Production amount, utilization ways, and estimated Hg content in
 678 FGD gypsum in China

Years	m (Mt)	c_g ($\mu\text{g}/\text{kg}$)	$\alpha\%$	$\gamma_w\%$	$\varphi_w\%$	$\gamma_c\%$	$\varphi_c\%$	$\gamma_l\%$	$\varphi_l\%$
2005	9.44 ^{a,b}	805	10 ^{a,b}	25 ^{d,e}	37.56	70 ^{d,e}	16.61	5 ^{d,e}	15.3
2006	17 ^{a,b}	(511 -	20 ^{a,b}	(20 -	(13.25	(60-	(6.35 -	(2 -	(0.31
2007	34.95 ^{a,b}	1036)	33 ^{a,b}	30)	-	80)	42.13)	8)	- 51)
2008	43 ^{a,b}		45 ^{a,b}		63.52)				
2009	52.3 ^{a,b}		56 ^{a,b}						
2010	63.01 ^{a,b}		69 ^{a,b}						
2011	72.41 ^{a,b}		70 ^{a,b}						
2012	75.5 ^{a,b}		72 ^{a,b}						
2013	71.8 ^{a,b}		84.5 ^{a,b}						
2014	70.88 ^{a,b}		83.4 ^{a,b}						
2015	72.7 ^c		86.3 ^c						
2016	66.4 ^c		80.6 ^c						
2017	84.9 ^c		76.7 ^c						
2018	100.0 ^c		74.3 ^c						
2019	110.0 ^c		71.3 ^c						

679 m is the annual production amount of FGD gypsum in China (Mt) and α is the
 680 proportion of resource utilization of FGD gypsum. γ_w , γ_c , and γ_l are the proportions of
 681 FGD gypsum being used for building material (mainly wallboard) production, being
 682 used as cement retarder, and being used in land applications, respectively; moreover,
 683 φ_w , φ_c , and φ_l are the estimated Hg release ratios along the same three pathways.
 684 a. NBSC, 2016 [62]; b. Hao, 2017 [43]; c. MEE, 2019 [27]; d. NDRC, 2014 [30]; e. Li,
 685 2019 [59].