



Full Length Article

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

Qingfeng Wang^{a,b,*}, Dan Wang^a, Zhonggen Li^{a,*}, Leilei Fan^a, Leiming Zhang^d, Xinbin Feng^c

^a Department of Resources and Environment, Zunyi Normal College, Zunyi 563006, PR China

^b Key Laboratory of Endemic and Ethnic Diseases, Ministry of Education, Guizhou Medical University, Guiyang 550004, PR China

^c State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, PR China

^d Air Quality Research Division, Science and Technology Branch, Environment and Climate Change Canada, Toronto M3H 5T4, Canada



ARTICLE INFO

Keywords:

Hg emission
FGD gypsum
Thermal treatment
Wallboard production
Cement retarder

ABSTRACT

The thermal instability of most mercury (Hg) species in flue gas desulfurization (FGD) gypsum may lead to the release of large amounts of Hg into the atmosphere. In this study, gypsum samples were collected from 13 major coal-fired power plants (CFPPs) for evaluating the Hg thermal stability within a temperature range of 100–200 °C. Results indicated that the release ratio of Hg from FGD gypsum varied considerably among the CFPPs. Such significant differences were caused by different proportions of the major Hg compounds, especially of HgCl_x (HgCl₂ and Hg₂Cl₂), in the FGD gypsum samples. The release ratio appeared extremely sensitive to changes in the treatment temperature and duration. Wallboard manufacturing and its use as cement retarder are the leading causes of Hg emission (corresponding to greater than 95% of the total) during FGD gypsum resource utilization. The total average Hg emitted due to FGD gypsum resource utilization in China in 2017 was estimated to be 11.42 tons (ranging between 2.15 and 38.35 tons), which accounted for about 23.8 % (ranging between 4.6 and 79.8%) of the stack Hg emissions from CFPPs in that year. The results of this study indicate that the resource utilization processes of FGD gypsum are important Hg emission sources and that they should be considered with care in future emission control policies.

1. Introduction

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

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

of flue gas desulfurization (FGD) units increased from 90.6% to 95.9% during the same period [10,11].

These APCDs equipment can co-remove substantial Hg from the flue gas and capture it into solid byproducts like FGD gypsum [12–14]. In fact, denitrification equipment such as SCR could effectively oxidize Hg⁰ into Hg²⁺, reaching an average oxidation rate of 71% [15], and Hg²⁺ is easily removed by wet FGD devices [16]. The highest observed Hg removal efficiency (99%) was achieved by combining APCDs with SCR, fabric filter (FF), and WFGD (wet FGD) equipment [17]. In addition, the installation of APCDs drastically increases the output of FGD gypsum, which can be reused in the production of building materials (e.g., plastering gypsum, wallboard, concrete, and synthetic materials), for replacing natural gypsum as cement retarder, as well as in the land applications [11,18–20]. All of these uses may lead to the release of large amounts of Hg into the surrounding environment [21–26]. The amount of FGD gypsum produced from CFPPs in China increased from <10 million tons (Mt) in 2006 to approximately 110 Mt in 2019 [27], providing a potential secondary source of atmospheric Hg

* Corresponding authors at: Department of Resources and Environment, Zunyi Normal College, Pingan Road, Zunyi 563006, PR China.

E-mail addresses: qingfeng.424@163.com (Q. Wang), lizhonggencn@126.com (Z. Li).

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

The risk of Hg release during the FGD gypsum utilization process has been studied since 2005 [31,32]. In 2012, Yang et al. [33] warned that ignoring the emissions of Hg from CFPPs byproducts (including FGD gypsum) would lead to ineffective Hg control in CFPPs in China. Nevertheless, this topic is still scarcely studied. The majority of existing studies on estimating Hg emissions from CFPPs have focused only on Hg concentration and on the speciation of stack flue gas in relation to boiler types, coal characteristics, and the APCDs, among others [6,17,34–36]. In these studies, it was assumed that Hg was removed once it entered the byproducts. Previous studies [22,23,29,37], however, have proved that Hg (especially in the form of HgCl_x : either HgCl_2 or Hg_2Cl_2) can be released from FGD gypsum at temperatures even < 100 °C. Notably, thermal treatment is a necessary step in the main utilization pathways of FGD gypsum (e.g., used for wallboard production and as cement retarder) [30]. Thus, significant amounts of Hg are released during the wallboard manufacturing process (Hg release ratio between 2 and 92.8%) [22,24,29,31,32]. The cement industry has been the largest source of anthropogenic Hg emissions in China since 2009 [34]; therefore, it has received widespread attention [38,39]. However, few studies have focused on the release of Hg during the pretreatment process of FGD gypsum being used as cement retarder. Normally, FGD gypsum is directly mixed with clinker for grinding and, ultimately, producing cement. The Hg released during cement production processes is thought completely from the calcination process of the cement clinker and from fuel combustion [34,38,39]. However, when FGD gypsum is being used as cement retarder, it is usually too wet to be blended with other raw materials. Thus, it needs to be dried at a temperature between 40 and 400 °C [40]. During this process, Hg in FGD gypsum may release into the atmosphere. Additionally, Gustin and Ladwig [28] suggested that water addition is a dominant environmental factor promoting Hg release from FGD gypsum, they observed that up to 50% of the Hg was released into the atmosphere in 31 days. Zhu et al. [41] demonstrated that the Hg emission ratio from FGD gypsum can reach 2.65% during a 180-day experimental period in dark and room-temperature conditions and that Hg release can be greatly promoted by repeated wetting events. Diao et al. [42] and Hao [43] found that Hg can be released from FGD gypsum (up to 25.1–50.3%) during stacking at room temperature. It can be concluded that the high Hg content in FGD gypsum and its instability may lead to significant Hg emissions during the utilization of FGD gypsum.

In this study, FGD gypsums were collected from 13 major CFPPs in China, and the Hg release ratio from those samples during different thermal treatment processes was evaluated. Moreover, the main Hg species contained in the gypsum samples were identified, and the total amount of Hg released from the FGD gypsum resource utilization processes in China was estimated. The findings of this study may fill the current knowledge gap about Hg emission control in CFPPs and can lay the foundation for the whole-life management of Hg emissions from CFPPs in China.

2. Methodology

2.1. Sample collection

FGD gypsum samples were collected from 13 CFPPs: 12 in the Guizhou Province, southwestern China (CFPPs 1–12 #), and 1 in Tangshan City, Hebei Province, northern China (CFPP 13#). The sampling sites of CFPPs 1–11# were described in one of our previous studies [44], although they were indicated with different CFPP numbers (Fig. S1). The site of CFPP 12# is in Qianxi County, western Guizhou

Province. Information about the boiler type and its capacity, the APCDs, and the Hg content in the gypsum samples is given in Table S1. Each gypsum sample was obtained by mixing at least 9 subsamples collected within 2 days at the same site.

Notably, owing to the ultra-low emission retrofit in China since 2014, most CFPPs in the country have similar pollutant control equipment [45] (e.g., SCR, electrostatic precipitator (ESP) or ESP + FF, and WFGD). A comprehensive study of the gypsum in typical CFPPs within a specified area like Guizhou is expected to provide an approximate view of current Hg emissions from CFPPs in China.

2.2. Thermal treatment tests

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

In China, the resource utilization processes of FGD gypsum are mainly used for wallboard production and as cement retarder. For the wallboard production, FGD gypsum first needs to be dried (at temperatures < 128 °C) to remove any free moisture, and then to be calcined (128–163 °C), to produce $\beta\text{-CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$. Subsequently, it has to be mixed with water and several additives to form a slurry, which can be extruded between two sheets of paper to form a wet board. Afterward, the wet board is conveyed on a conveyor belt, cut to the designed length, and dried at 94–203 °C to remove any free moisture [24]. The whole process from FGD gypsum drying to the output of final products lasts about 1–2 h. For the purpose of being used as cement retarder (Fig S2), FGD gypsum needs to be pretreated typically under a temperature range of 120–200 °C for 1 h to make it dry enough [40,46] (Fig. S2). Our survey results, which included more than 35 domestic manufacturers of gypsum drying equipment in China, showed that the normal thermal treatment of FGD gypsum consists in drying it at 150 °C for 30–60 min. Hence, our laboratory simulations were carried out at temperatures of 100, 150, and 200 °C, over periods of 20, 40, 80, and 120 min. Notably, each sample was treated three times in parallel.

2.3. Temperature-programmed Hg decomposition (Hg-TPD) analysis

Hg-TPD is an important tool for identifying Hg species in gypsum [22,29,37,47–49] by comparing Hg thermal release curves of FGD gypsum samples with that of different Hg standard substances and gypsum mixtures under the same procedure of pyrolysis. Hg-TPD analyses were carried out using the same lab device described in one of our previous studies [29]: a certain amount of gypsum sample was put into a temperature-programmed tube furnace, and the flow rate of the carrier gas was kept at 1 L/min. The thermal release profiles of different Hg standards of Hg_2Cl_2 , HgCl_2 , black HgS, red HgS, HgO, Hg_2SO_4 , and HgSO_4 , that mixed with 800 °C preheated gypsum in this study are shown in Fig. S3. The decomposition temperature of the Hg standards follows this order: $\text{Hg}_2\text{Cl}_2 < \text{HgCl}_2 < \text{black HgS} < \text{red HgS} < \text{Hg}_2\text{SO}_4 < \text{HgO} < \text{HgSO}_4$. This sequence is consistent with those reported in previous studies [22,23,50].

2.4. Method for estimating the amount of released Hg

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

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

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

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

2.5. Analysis methods, quality assurance, and quality control

The total Hg content in gypsum was determined using a Direct Mercury Analyzer (Milestone DMA-80, Italy). The sample pretreatment and measurement methods were all described in one of our previous studies [44]. Briefly, the gypsum samples were air-dried, ground into small pieces (<0.150 mm), and subjected to pyrolysis. Subsequently, the Hg in the gypsum was selectively trapped in a gold amalgamator, released by heating, and measured by atomic absorption spectrometry [51]. Quality control measures, including method blanks, triplicates, matrix spikes, and reference materials, were also previously described [44]. The relative standard deviation (RSD) of the duplicate Hg concentration results in this study was always $<5\%$.

3. Results and discussion

3.1. Hg release during the thermal treatment

Fig. 1 depicts the thermal release ratio of Hg from FGD gypsum during thermal treatment at different temperatures for 40 min. The data refer to samples collected from 13 important CFPPs in China. The Hg release ratio varied greatly among CFPPs and increased drastically with the thermal treatment temperature. For example, the average ratio increased from $6.35 \pm 4.88\%$ under thermal treatment conditions of 100°C to $16.61 \pm 8.91\%$ under 150°C , and to $35.50 \pm 17.30\%$ under 200°C for 40 min. The highest ratio ($77.37 \pm 2.28\%$) was obtained for CFPPs 2# under 200°C for 40 min. This ratio was about 10 times the lowest ($8.43 \pm 5.64\%$), obtained for CFPPs 3# under 100°C . Thus, the

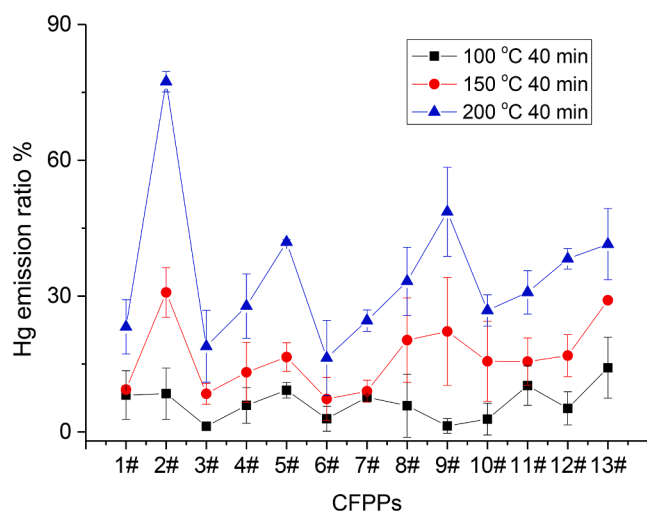


Fig. 1. Hg release ratio of different FGD gypsums treated with various temperatures for 40 min.

treatment temperature appears as a key factor affecting the thermal release of Hg from FGD gypsum.

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

3.2. Hg-TPD of FGD gypsum

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

3.3. Relationship between Hg species and the release ratio

According to Fig. S3, HgCl_x is most likely the main Hg species released during the FGD gypsum resource utilization process since it is the least stable Hg compound in gypsum. FGD gypsum with the highest Hg release ratio may also be the one with the highest HgCl_x proportion, and the relationship between the ratios of the main Hg species (i.e., HgCl_x and HgS) and the Hg release ratio (150°C , 40 min) is shown in

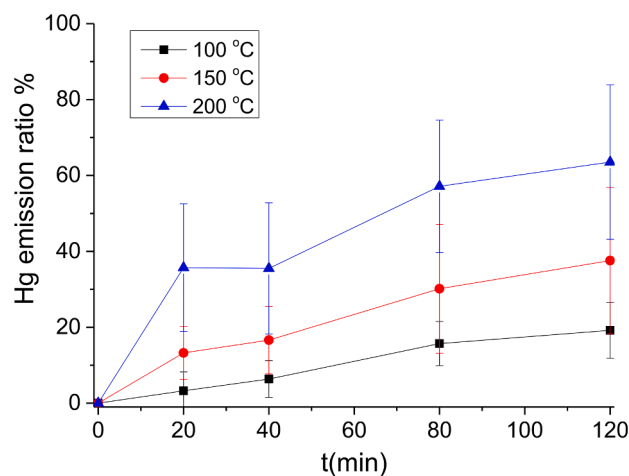


Fig. 2. Average Hg release ratio of FGD gypsum from 13 CFPPs during the thermal treatments with different durations and temperatures.

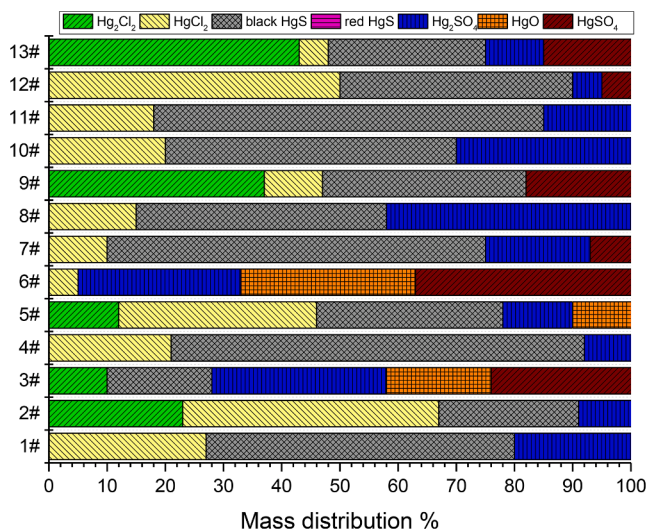


Fig. 3. Mass distributions of different Hg compounds in gypsum samples from 13 CFPPs.

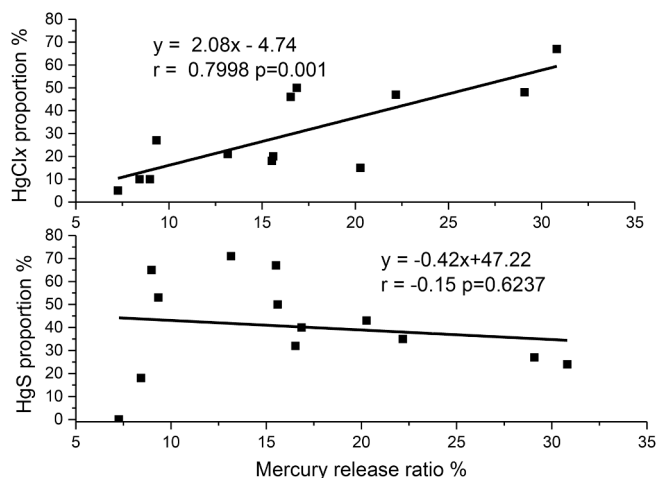


Fig. 4. Correlations between the release ratio of Hg from gypsum and the proportions of the main Hg species in gypsum.

Fig. 4. The Hg release ratio showed a strong positive correlation with the proportion of HgCl_x ($r = 0.7998$, $p = 0.001$) in gypsum, but no significant correlation with that of HgS ($r = -0.15$, $p = 0.6237$), this confirmed that HgCl_x is the main Hg compound released during the FGD gypsum resource utilization processes that involved thermal treatment. These findings are consistent with those of Liu et al. [22] and one of our previous studies [44], in which Cl was one of the most important elements affecting the Hg content in gypsum.

The above information suggests that different Hg compounds in gypsum are the main reason for the great differences observed in the FGD Hg release ratios. Since HgCl_x was the main compound released during the thermal treatment process, a high proportion of HgCl_x is expected to result in an increase in the Hg release ratio. For example, the gypsum from CFPP 2# had the highest Hg release ratio (30.82%, 150 °C, 40 min) as well as the highest HgCl_x proportion (67%). In comparison, the gypsum from CFPP 6# had the lowest Hg release ratio and a relatively low HgCl_x proportion (about 6%).

3.4. Estimation of the amount of Hg released from FGD gypsum during the resource utilization processes

3.4.1. Uncertainties in the estimation of Hg emissions

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

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

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

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

The Hg emission ratio along the different utilization pathways was also a determining factor for Hg releasing. Due to the different thermal treatment purposes, the treatment temperature and time during distinct FGD gypsum utilization processes vary greatly. A previous report [30] indicated that wallboard production (24.3 Mt, 27.8%) and being used as cement retarder (60 Mt, 68.3%) accounted for about 96% of the total reuse amount of FGD gypsum in China in 2014. These values were very different from those for the United States, where wallboard production accounted for 54%, and cement/concrete/asphalt production counted only <8% of the total reuse amount of FGD gypsum in 2016 [56]. Since the largest proportion of FGD gypsum used for building materials production was wallboard production [11,19], the Hg emission ratio from wallboard production can be approximated as the average Hg emission ratio from building material production. Liu et al. [22] simulated the Hg release during wallboard production by heating gypsum samples in a reactor tube, increasing the temperature from room conditions to 163 °C, and then maintaining it at 163 °C for 1 h. The release ratio was estimated to be 30.8%. In one of our previous studies [29], we simulated the same process under a temperature of 163 °C for 2 h, obtaining an emission ratio of 48.3%. Other reports [31,32] indicated that wallboard production could be normally conducted within a temperature range of 160–180 °C, and the release ratio can reach 58%. In this study, by maintaining a temperature of 150 °C for 2 h, we obtained an average release ratio (φ_w) of 37.6%, the minimum value (13.25%) was obtained by maintaining a temperature of 150 °C for 20 min, while the maximum (63.52%) was obtained by maintaining a temperature of 200 °C for 2 h (see Fig. 2). A previous study suggested [22] that the thermal treatment of FGD gypsum as cement retarder can be similar to that for wallboard production. However, since these thermal treatments have different purposes, their treatment temperatures and durations are considerably different. We considered an average release ratio (φ_c) of 16.61% (obtained by maintaining a temperature of 150 °C for 40 min) (Fig. 2). This value is comprised between the minimum value (6.35%) was obtained by maintaining a temperature of 100 °C for 40 min and the maximum value (42.13%) by maintaining a temperature of 200 °C for 60 min [40] (see Fig. 2). For the land applications, specific data on the ratio of Hg released into the atmosphere from FGD gypsum are still lacking,

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

however, significant release amounts are expected [57,58]. Zhu et al. [41] found that the Hg release rates in the dark at room temperature varied between 0.31 and 2.65% during 180-day period tests. Moreover, temperature, UV radiation, and solid moisture content were all suspected to significantly enhance the release of Hg. Diao et al. [42] confirmed that Hg could be released from gypsum in significant amounts under room temperature in 10 days, the release ratio ranged between 1.5 and 15.3% in the dark and between 0.7 and 25.1% under UV irradiation. Gustin and Ladwig [28] and Hao [43] indicated that the Hg release ratio ranged from 9% to 50% in 31 days and from 15.8% to 51% in 38 days. Overall, these results suggest that the release ratio of Hg from FGD gypsum during prolonged land application processes may be quite high compared to that during the brief thermal treatments included in resource utilization processes. As the FGD gypsum commonly directly used in the land applications under room temperature, in this study, we assumed an average ratio of 15.3% [42], ranging between 0.31 and 51% according to previous studies [41,43].

Regarding the utilization amount (ratio) of FGD gypsum in each utilization category, a previous report [30] showed that industrial byproduct gypsum (including FGD gypsum, phospho-gypsum, and titanium gypsum) used for wallboard (24.3 Mt, 27.8%) and cement retarder (60 Mt, 68.3%) production accounted for 96% of the total reuse amount of byproduct gypsum in China in 2014. Additionally, Li [59] showed that the reuse amount of industrial byproduct gypsum in 2018 was 23.1 Mt (18.6%) for wallboard production and 81 Mt for being used as cement retarder (65.3%). In this study, we assumed that, on average, 25% (20–30%) of FGD gypsum would be used for building materials production (mainly wallboard production) (γ_w), 70% (60–80%) for being used as cement retarder (γ_c), and 5% (2–8%) for land applications (γ_l). Notably, the ratios of FGD gypsum used for wallboard production and land applications increased from 2005 to 2019 due to national policies [60] and the promotion of FGD gypsum for soil improvement [61]. In summary, all the parameters related to the release of Hg from

FGD gypsum are listed in Table 2 [27,30,43,59,62].

3.4.2. Amount of Hg released from FGD gypsum utilization processes

Fig. 5a and Table S2 show how the amount of Hg released during FGD resource utilization has increased in the last decade. This has been mainly the result of a rapid increase in FGD gypsum production. The estimated annual average Hg release amount was only 0.17 tons (ranging between 0.03 and 0.56 tons) in 2005. This figure increased to around 10 tons in 2012, maintained this level until 2017, and then increased to 13.75 tons (ranging between 2.60 and 46.18 tons) in 2019. Comparable Hg release amounts resulted from the process of building materials production (mainly wallboard, 5.92 tons) and being used as cement retarder (7.43 tons) (Fig. 5b), although double of the amount of FGD gypsum was used in the latter process. A previous study [6] suggested that the total amount of Hg emitted from CFPPs into the atmosphere in China in 2017 reached 48 tons. The estimated total amount of Hg released during FGD utilization processes in 2017 was 11.42 tons (ranging between 2.15 and 38.35 tons), which accounted for about 23.8% (ranging between 4.6 and 79.8%) of the total Hg emissions from CFPPs in China. Atmospheric Hg emissions from CFPPs in the country are expected to decrease to 2.4 tons by 2030 [45]; however, the amount of Hg released from FGD utilization processes may actually increase by that time, while this has not been taken into account in previous emission estimates. In addition, FGD gypsum is only one of the important flue gas control byproducts. As a matter of fact, other flue gas control byproducts (e.g., fly ash) may emit even more Hg than gypsum during their utilization process [27]. These secondary emission sources of Hg should be carefully considered in future emission estimates and policymaking.

4. Conclusions

The huge production amount of FGD gypsum and its high resource

Table 2
Production amount, utilization ways, and estimated Hg content in 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 (511–1036)	10 ^{a,b}	25 ^{d,e} (20–30)	37.56 (13.25–63.52)	70 ^{d,e} (60–80)	16.61 (6.35–42.13)	5 ^{d,e} (2–8)	15.3 (0.31–51)
2006	17 ^{a,b}		20 ^{a,b}						
2007	34.95 ^{a,b}		33 ^{a,b}						
2008	43 ^{a,b}		45 ^{a,b}						
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						

m is the annual production amount of FGD gypsum in China (Mt) and α is the proportion of resource utilization of FGD gypsum. γ_w , γ_c , and γ_l are the proportions of FGD gypsum being used for building material (mainly wallboard) production, being used as cement retarder, and being used in land applications, respectively; moreover, φ_w , φ_c , and φ_l are the estimated Hg release ratios along the same three pathways.

a. NBSC, 2016 [62]; b. Hao, 2017 [43]; c. MEE, 2019 [27]; d. NDRC, 2014 [30]; e. Li, 2019 [59].

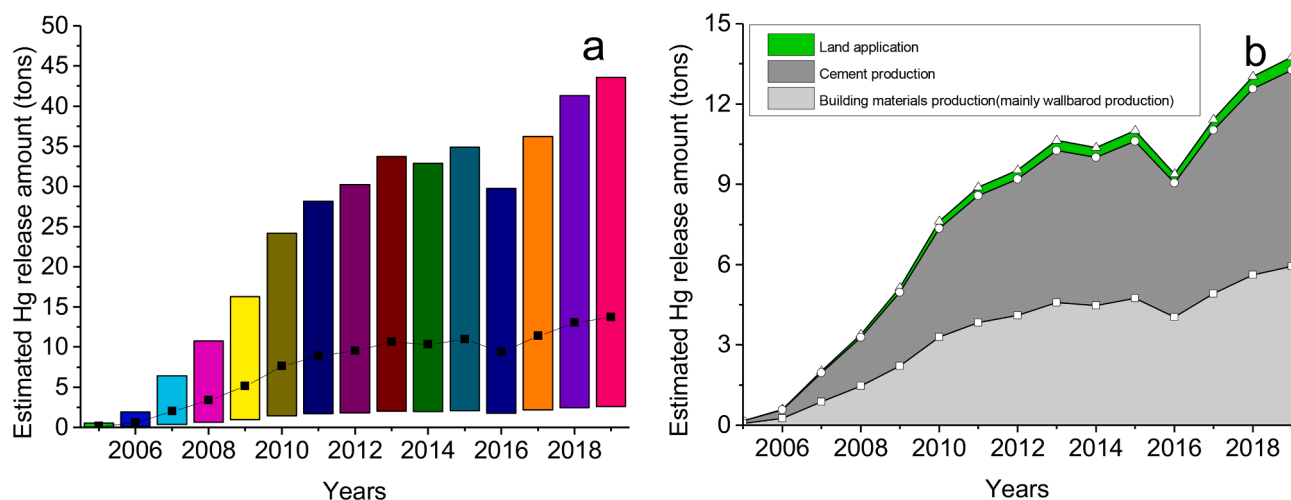


Fig. 5. Estimated annual Hg release amounts from FGD gypsum utilization in China: (a) total, with columns showing the annual ranges, and (b) for different resource utilization processes.

utilization ratio make the release of Hg from FGD gypsum an important issue in China. In this study, FGD gypsum was collected from 13 typical CFPPs in China to evaluate the Hg emissions along the main resource utilization pathways, including wallboard production and being used as cement retarder. Our results indicated that the amount of Hg released from FGD gypsum is closely linked to the heating temperature and the duration of the simulated resource utilization processes. The average Hg release ratio when the samples were subjected to 100 °C for 20 min was only $3.25 \pm 4.96\%$, but it dramatically increased to $63.52 \pm 20.37\%$ when the samples were subjected to 200 °C for 120 min. Under a typical resource utilization treatment temperature range (between 100 and 200 °C), the release of Hg from FGD gypsum can be mainly attributed to the decomposition of HgCl_x (HgCl_2 and Hg_2Cl_2). The Hg release amount from the process of wallboard production and being used as cement retarder have increased substantially in the last decade and reached to a total of 11.42 tons in 2017 that corresponding to about 1/4 of the total atmospheric emissions (48 tons) from CFPPs in China. This suggests that the release of Hg from FGD gypsum during resource utilization processes cannot be ignored since it may seriously undermine the current efforts to control Hg emissions from CFPPs in China.

CRedit authorship contribution statement

Qingfeng Wang: Methodology, Investigation, Data curation, Formal analysis, Writing – original draft. **Dan Wang:** Investigation, Software, Visualization. **Zhonggen Li:** Conceptualization, Writing – review & editing. **Leilei Fan:** Investigation. **Leiming Zhang:** Writing – review & editing. **Xinbin Feng:** Conceptualization, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge the support of the National Natural Science Foundation of China (Nos.41967044, 21707141); Zunyi Science and Technology Bureau, Zunyi Normal University Joint Science and Technology Research and Development Fund Project (Nos. Zun Shi Ke He [2018]07); Zunyi Normal College 2017 Academic New Seedling Cultivation and Innovation Exploration Project (Nos. Qian Ke He Ping Tai Ren Cai [2017]5727-8); Zunyi Normal College Service Local

Industrial Revolution Project (Nos. Zunshi CXY[2021]09). This study was also supported by the project of Key Laboratory of Endemic and Ethnic Diseases, Ministry of Education, Guizhou Medical University and the Talent Base for Environmental Protection and Mountain Agricultural in Chishui River Basin. We would like to thank TopEdit (www.tope-ditsci.com) for English language editing of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2021.122898>.

References

- [1] Liu Y, Wang Q, Mei R, Wang H, Weng X, Wu Z. Mercury re-emission in flue gas multipollutants simultaneous absorption system. *Environ Sci Technol* 2014;48(23):14025–30.
- [2] Bernhoft RA. Mercury Toxicity and Treatment: A Review of the Literature. *Int J Env Res Pub He* 2012;2012.
- [3] Jiang GB, Shi JB, Feng XB. Mercury pollution in China. *Environ Sci Technol* 2006;40(12):3672–8.
- [4] Crespo-Lopez ME, Augusto-Oliveira M, Lopes-Araújo A, Santos-Sacramento L, Yuki Takeda P, Macchi BdM, et al. Mercury: What can we learn from the Amazon? *Environ Int* 2021;146:106223.
- [5] Wu Z, Ye H, Shan Y, Chen B, Li J. A city-level inventory for atmospheric mercury emissions from coal combustion in China. *Atmos Environ* 2020;223.
- [6] Liu K, Wang S, Wu Q, Wang L, Ma Q, Zhang L, et al. A Highly Resolved Mercury Emission Inventory of Chinese Coal-Fired Power Plants. *Environ Sci Technol* 2018;52(4):2400–8.
- [7] Oberschelp C, Pfister S, Raptis CE, Hellweg S. Global emission hotspots of coal power generation. *Nat Sustain* 2019;2(2):113–21.
- [8] Bogacki J, Marcinowski P, Majewski M, Zawadzki J, Sivakumar S. Alternative approach to current eu bat recommendation for coal-fired power plant flue gas desulfurization wastewater treatment. *Processes* 2018;6(11):229.
- [9] Liu X, Gao X, Wu X, Yu W, Chen L, Ni R, et al. Updated hourly emissions factors for chinese power plants showing the impact of widespread ultralow emissions technology deployment. *Environ Sci Technol* 2019;53(5):2570–8.
- [10] CEC(China electricity council), 2019. China power industry annual development report. China Architecture & Building Press: 169-184 (in Chinese).
- [11] Liu S, Liu W, Jiao F, Qin W, Yang C. Production and resource utilization of flue gas desulfurized gypsum in China - A review. *Environ Pollut* 2021;288.
- [12] Liu S, Hao H, Jia W, Cao Y, Chen C. Effects of ultralow-emission retrofitting on mercury emission from a coal-fired power plant. *Energ Fuel* 2020;34(6):7502–8.
- [13] Zhao S, Duan Y, Yao T, Liu M, Lu J, Tan H, et al. Study on the mercury emission and transformation in an ultra-low emission coal-fired power plant. *Fuel* 2017;199:653–61.
- [14] Zhang Y, Yang J, Yu X, Sun P, Zhao Y, Zhang J, et al. Migration and emission characteristics of Hg in coal-fired power plant of China with ultra low emission air pollution control devices. *Fuel Process Technol* 2017;158:272–80.
- [15] Zhang L, Wang S, Wu Q, Wang F, Lin CJ, Zhang L, et al. Mercury transformation and speciation in flue gases from anthropogenic emission sources: a critical review. *Atmos Chem Phys* 2016;16(4):2417–33.
- [16] Wang S. Near-zero air pollutant emission technologies and applications for clean coal-fired power. *Engineering* 2020;6(12):1408–22.

- [17] Zhang L, Wang S, Wang L, Wu Y, Duan L, Wu Q, et al. Updated Emission Inventories for Speciated Atmospheric Mercury from Anthropogenic Sources in China. *Environ Sci Technol* 2015;49(5):3185–94.
- [18] Wang Z, Pan L, Yang F. Comprehensive utilization of FGD gypsum resources in coal fired power plants. *Chem Indust Press* 2018;31–4 (in Chinese).
- [19] Zhang Y, Wang Y, Zhou J, Jiayi L, Tong L. Basic characteristics and comprehensive utilization of FGD gypsum. *IOP Conf Series: Earth Environ Sci* 2020;510.
- [20] Li J, Zhuang X, Querol X, Font O, Moreno N. A review on the applications of coal combustion products in China. *Int Geol Rev* 2018;60(5–6):671–716.
- [21] Sun M, Cheng G, Lu R, Tang T, Baig SA, Xu X. Characterization of Hg^0 re-emission and Hg^{2+} leaching potential from flue gas desulfurization (FGD) gypsum. *Fuel Process Technol* 2014;118:28–33.
- [22] Liu X, Wang S, Zhang L, Wu Y, Duan L, Hao J. Speciation of mercury in FGD gypsum and mercury emission during the wallboard production in China. *Fuel* 2013;111:621–7.
- [23] Zhu Z, Zhuo Y, Fan Y, Wang Z. Fate of mercury in flue gas desulfurization gypsum determined by Temperature Programmed Decomposition and Sequential Chemical Extraction. *J Environ Sci* 2016;43:169–76.
- [24] Marshall J, Blythe GM, Richardson M. Fate of mercury in synthetic gypsum used for wallboard production, Topical Report, Task 4 Wallboard Plant Test Results; 2007. Medium: ED: USG Corporation.
- [25] Wen B, Li L, Duan Y, Zhang Y, Shen J, Xia M, et al. Zn, Ni, Mn, Cr, Pb and Cu in soil-tea ecosystem: The concentrations, spatial relationship and potential control. *Chemosphere* 2018;204:92–100.
- [26] Zhang Y, Ren Y, Liu BL, Zhang ZH. Comprehensive utilization status of sintering flue gas desulfurization gypsum. *Bull Chin Ceram Soc* 2015;34:3563–7 (in Chinese with English abstract).
- [27] MEE. National annual report on prevention and control of environmental pollution by solid waste in large and medium cities. Beijing: Ministry of Ecology and Environment of the People's Republic of China (MEE), 2015–2019 (in Chinese).
- [28] Gustin M, Ladwig K. Laboratory investigation of hg release from flue gas desulfurization products. *Environ Sci Technol* 2010;44(10):4012–8.
- [29] Wang Q, Liu Y, Wu Z. Laboratory study on mercury release of the gypsum from the mercury coremoval wet flue gas desulfurization system with additives. *Energy Fuels* 2018;32(2):1005–11.
- [30] NDRC (National Development and Reform Commission). Annual report on comprehensive utilization of resources in China. *China Econ Trade Herald* 2014; 30:49–56 (in Chinese).
- [31] Kairies CL, Schroeder KT, Cardone CR. Mercury in gypsum produced from flue gas desulfurization. *Fuel* 2006;85(17):2530–6.
- [32] Heebink LV, Hassett DJ. Mercury release from FGD. *Fuel* 2005;84(11):1372–7.
- [33] Yang Y, Huang Q, Wang Q. Ignoring emissions of Hg from coal ash and desulfurized gypsum will lead to ineffective mercury control in coal-fired power plants in China. *Environ Sci Technol* 2012;46(6):3058.
- [34] Wu Q, Wang S, Li G, Liang S, Lin C-J, Wang Y, et al. Temporal trend and spatial distribution of speciated atmospheric mercury emissions in China during 1978–2014. *Environ Sci Technol* 2016;50(24):13428–35.
- [35] Wang SX, Zhang L, Li GH, Wu Y, Hao JM, Pirrone N, et al. Mercury emission and speciation of coal-fired power plants in China. *Atmos Chem Phys* 2010;10(3): 1183–92.
- [36] Zhang L, Wang S, Meng Y, Hao J. Influence of mercury and chlorine content of coal on mercury emissions from coal-fired power plants in China. *Environ Sci Technol* 2012;46(11):6385–92.
- [37] Rallo M, Lopez-Anton MA, Perry R, Maroto-Valer MM. Mercury speciation in gypsums produced from flue gas desulfurization by temperature programmed decomposition. *Fuel* 2010;89(8):2157–9.
- [38] Cai X, Cai B, Zhang H, Chen L, Zheng C, Tong P, et al. Establishment of high-resolution atmospheric mercury emission inventories for Chinese cement plants based on the mass balance method. *Environ Sci Technol* 2020;54(21):13399–408.
- [39] Kogut K, Górecki J, Burmistrz P. Opportunities for reducing mercury emissions in the cement industry. *J Clean Prod* 2021;293.
- [40] Guo XL, Shi HS. Thermal treatment and utilization of flue gas desulfurization gypsum as an admixture in cement and concrete. *Constr Build Mater* 2008;22(7): 1471–6.
- [41] Zhu Z-W, Zhuo Y-Q, Fan Y-M, Wang Z-P. Mechanism of mercury vapor release from flue gas desulfurization gypsum. *Fuel Process Technol* 2017;156:485–90.
- [42] Diao X, Yuan C-G, Wu J, Gui B, Zhang K, Zhang C. Mercury release and fraction transformation during desulfurization gypsum aging process (UV irradiation). *Fuel* 2018;217:522–8.
- [43] Hao Y. Geochemical characteristics and potential risks of heavy metals in desulfurization gypsum from coal-fired power plants (Ph.D. Thesis), Shanghai: Shanghai University; 2017 (in Chinese).
- [44] Wang Q, Wang D, Li Z, Zhang L, Feng X. Mercury in desulfurization gypsum and its dependence on coal properties in coal-fired power plants. *Fuel* 2021;293.
- [45] Wu Q, Wang S, Liu K, Li G, Hao J. Emission-limit-oriented strategy to control atmospheric mercury emissions in coal-fired power plants towards the implementation of Minamata Convention. *Environ Sci Technol* 2018;52(19): 11087–93.
- [46] Li Y, Wu JH, Hao B, Liu DC. Heat treatment process of the flue gas desulfurization gypsum and its influence on the properties of cement. *Appl Mech Mater* 2012;214: 40–4.
- [47] Chang L, Zhang Y, Liu H, Peng R, Yu X, Zhao Y, et al. Migration and identification of mercury species in wet flue gas desulfurization system using temperature programmed decomposition. *J Clean Prod* 2020;276.
- [48] Pavlin M, Popović A, Jačimović R, Horvat M. Mercury fractionation in gypsum using temperature desorption and mass spectrometric detection: Mass spectrometric approach to mercury fractionation in FGD gypsum. *Open Chem* 2018;16(1):544–55.
- [49] Sedlar M, Pavlin M, Jačimović R, Stergarsek A, Frkal P, Horvat M. Temperature fractionation (TF) of Hg compounds in gypsum from wet flue gas desulfurization system of the coal fired thermal power plant (TPP). *Amer J Anal Chem* 2015;6(12): 18.
- [50] Lopez-Anton MA, Yuan Y, Perry R, Maroto-Valer MM. Analysis of mercury species present during coal combustion by thermal desorption. *Fuel* 2010;89(3):629–34.
- [51] Fostier AH, Melendez-Perez JJ. Assessment of direct mercury analyzer to quantify mercury in soils and leaf samples. *J Brazil Chem Soc* 2013;24(11):1880–6.
- [52] Rumayor M, Díaz-Somoano M, López-Antón MA, Ochoa-González R, Martínez-Tarazona MR. Temperature programmed desorption as a tool for the identification of mercury fate in wet-desulfurization systems. *Fuel* 2015;148:98–103.
- [53] Chang L, Zhao Y, Zhang Y, Yu X, Li Z, Gong B, et al. Mercury species and potential leaching in sludge from coal-fired power plants. *J Hazard Mater* 2021;403.
- [54] Zheng C, Xu L, Liu S, Wang L, Liang C, Zhao H, et al. Speciation and thermal stability of mercury in solid products from ultralow emission air pollution control devices. *Energy Fuels* 2018;32(12):12655–64.
- [55] Hao Y, Wu S, Pan Y, Li Q, Zhou J, Xu Y, et al. Characterization and leaching toxicities of mercury in flue gas desulfurization gypsum from coal-fired power plants in China. *Fuel* 2016;177:157–63.
- [56] Koralegedara NH, Pinto PX, Dionysiou DD, Al-Abed SR. Recent advances in flue gas desulfurization gypsum processes and applications – A review. *J Environ Manage* 2019;251.
- [57] Wang K, Orndorff W, Cao Y, Pan W. Mercury transportation in soil via using gypsum from flue gas desulfurization unit in coal-fired power plant. *J Environ Sci* 2013;25(9):1858–64.
- [58] Shock SS, Noggle JJ, Bloom N, Yost LJ. Evaluation of potential for mercury volatilization from natural and FGD gypsum products using flux-chamber tests. *Environ Sci Technol* 2009;43(7):2282–7.
- [59] Li Y. Development status and trend of gypsum industry. *Sulphuric Acid Industry* 2019;11. 1–7+13 (in Chinese).
- [60] Yang D, Yang Z. Current situation of comprehensive utilization of desulfurized gypsum in China. *Sulphuric Acid Industry* 2018;9:4–8 (in Chinese).
- [61] Zhao Y, Wang S, Li Y, Liu J, Zhuo Y, Zhang W, et al. Long-term performance of flue gas desulfurization gypsum in a large-scale application in a saline-alkali wasteland in northwest China. *Agric Ecosyst Environ* 2018;261:115–24.
- [62] NBSC (National Bureau of Statistics of China). *China Statistical Yearbook*. Beijing: China Statistics Press; 2016 (in Chinese).