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Mass flow, enrichment and potential environmental impacts of mercury in a preheater-precalciner cement plant using multiple mining and industrial wastes

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ABSTRACT

Cement plants (CPs) are one of the most important anthropogenic sources of mercury (Hg) emissions in China. Over 1000 cement production lines operate in China and use various raw materials; however, little data on Hg emissions is recorded on site. This study investigated a CP in Guizhou Province that uses multiple mining and industrial wastes as part of the circular economy policy. Among the various raw materials, carbide slag had the highest Hg content (2.6 mg/kg) and contributed half of the Hg input. High Hg concentration (27 mg/kg) in the kiln tail dust and a strong Hg enrichment factor (39) was found, which was determined as the ratio of total Hg accumulated within the clinker production process to the daily Hg input from raw materials and fuel. The clinker had negligible Hg (0.001 mg/kg), while the Hg in cement products (0.04 mg/kg) mostly came from additives and retarders. The estimated atmospheric emission factor of Hg from this CP was 161.5 mg Hg/t clinker, which was much higher than those of other CPs in Guizhou that employ low-Hg raw materials. A five-step sequential extraction experiment with kiln tail dust indicates that Hg mainly existed in fraction of F4 (73–96% of the total Hg, possibly as Hg_2Cl_2) and that some samples had high proportions of water-soluble Hg (up to 21% of the total), which may be easily released into surrounding water bodies and pose high environmental risks. Using low-Hg raw (or alternative raw) materials and conducting proper disposal of kiln tail dust will reduce the environmental risk of Hg from CPs.

1. Introduction

Mercury (Hg) is a global pollutant due to its toxicity and long-range transport and bioaccumulation characteristics (Krabbenhoft and Sunderland, 2013; Pirrone et al., 2010; Gerson et al., 2018). Since the Minamata disease outbreak in Japan in the 1950s, Hg has attracted much public attention (UNEP, 2013; World Health Organization, 1991; Li et al., 2021). Once deposited in aquatic systems by dry and wet deposition, atmospheric Hg may be methylated into methylmercury, which can accumulate in fish and, subsequently, be consumed by humans (Renzoni et al., 1998). Hence, quantifying and control Hg emissions from different sources is a premise to control Hg contamination. Cement plants was one important anthropogenic sources in modern society, according to the Global Mercury Assessment 2018, the cement industry contributed 233 tonnes to global atmospheric Hg emissions in 2015, listing as the third largest anthropogenic source and contributing 11% of the total anthropogenic emissions (UNEP, 2019).

China, as the world's largest cement producer and consumer, increased its cement production yield from 210 million tonnes (Mt) in 1990–2200 Mt in 2020, a ten-fold increase (National Bureau of Statistics of China, 1991, 2021). As a result, cement production has been the largest source of Hg emissions since 2009, with an increasing trend in China during the twenty-first century (Wu et al., 2016). Some previous studies investigated the atmospheric Hg emissions in China's cement industry. For example, Zhang et al. (2015) reported that the cement-related Hg emissions increased from 16.0 tonnes in 2000 to 98.3

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tonnes in 2010, and the annual average growth rate was 19.9% during 2000–2010. Similarly, Chen et al. (2020) revealed a rapid increase in cement-related mercury emissions and deposition in China during 2005–2015. The results showed a nearly two-fold increase in cement-related Hg emissions from 80 to 144 tonnes/year, as well as an increase in atmospheric deposition from 38 to 76 tonnes/year in China during 2005–2015 (Chen et al., 2020).

Currently, China has more than 1700 cement production lines and more than 95% of them use preheater-precalciner CPs (Cai et al., 2020). Prior to 2005, Chinese CPs were mostly based on shaft technology (Hua et al., 2016). With the stimulation of the current circular economy policy, huge amounts of industrial and mining solid wastes are used in cement production for their contents of calcium (Ca), silicon (Si), aluminium (Al) and iron (Fe). This can lead to changes in Hg loading, Hg behaviour inside the CP, and atmospheric Hg emissions. However, compared to other industrial facilities such as coal-fired power plants, the complex precalciner cement manufacturing process used in CPs results in complex Hg behaviour, such as contact between the flue gas and raw materials in the raw mill and the reuse of kiln tail dust. In previous studies, it was reported that Hg accumulates during the clinker production process in precalciner CPs according to the various types of conditions and CPs used (Li et al., 2019; Yang and thesis, 2014; Wang et al., 2014).

Besides atmospheric emissions, CPs may pose a potential environmental risk through other pathways, such as high-Hg-laden kiln tail dust (Li et al., 2019; Wang et al., 2014; Yang and thesis, 2014). Although capturing kiln tail dust can reduce Hg emissions to the atmosphere, improper treatment can lead to secondary contamination of terrestrial and aquatic environments. In some cases, the captured dust is disposed of in piles, quarries and landfills (Kersten et al., 2014). Determining the form of Hg existing in kiln tail ash could indicate its ability to be released to the environment and it could also provide evidence to explain the enrichment behaviour of Hg during the clinker production process. In addition, the mobility, toxicity and bioavailability of Hg are dependent on not only its total concentrations but also on its fractions (Jin et al., 2013; Yuan, 2009; 2010a, b). However, there has been little research on the speciation of Hg in kiln tail dust; only a few field studies have evaluated the behaviour of Hg inside precalciner CPs using different solid waste materials (Zheng et al., 2012).

Guizhou Province in southwest China is a karst region with abundant limestone resources and rapid economic growth. Its cement industry has actively developed in recent years. From 2005 to 2020, cement output increased sevenfold, reaching 110 Mt in 2020 (Bureau of Statistics of Guizhou Province, 2006; China Cement Association, 2021), and was entirely produced by precalciner kilns in recent few years. Moreover, Guizhou Province relies on coal-fired power generation, which, in 2019, produced 15.14 Mt of solid fly ash and 10.11 Mt of flue gas desulphurisation gypsum (Guizhou Yearbook Editorial Department. Chief Editor of Liang, 2020). These by-products are widely used in the cement manufacturing process. In addition, this province is a major mineral mining province, with some mines (such as basalt mines) producing various waste rocks. Furthermore, several chemical wastes, such as yellow phosphorous slag and carbide slag, are produced by local and regional chemical plants. All these resources are widely used in cement production. Therefore, this study was conducted to provide updated information on the behaviour of Hg inside the cement industry, which has changed in both production technology and raw material resources. All input and output solid materials from a precalciner CP were collected and examined. The aims of the current study are to (1) understand the Hg distribution inside this CP, (2) explore the degree of Hg enrichment in the precalciner CP and analyse the relevant mechanisms of enrichment, (3) reveal the fractions of Hg in kiln tail dust to verify the state and behaviour of Hg during the enrichment process and (4) evaluate the potential environmental risks of Hg associated with precalciner CPs. The results of this study help to understand the impacts of waste utilization on atmospheric Hg emissions from CPs and to assess the environmental risk of Hg-laden cement kiln dust.

2. Materials and methods

2.1. Description of the selected cement plant

The selected precalciner CP was located in the western part of Guizhou Province, which is its main coal-producing area. This CP had two production lines, each with a capacity of 4500 tonnes of clinker per day; one of these lines was investigated. The raw or alternative raw materials used in this CP included limestone (mainly $CaCO_3$), shale (mainly to provide Al and Si for cement production), beneficiation waste (waste rocks that provide a variety of trace elements), yellow phosphorus slag (mainly CaO and SiO_2), carbide slag (mainly $Ca(OH)_2$) and coal slag (providing Si, Ca, Al, Fe, Mn, etc.). Similarly, locally produced anthracitic coal, which formed in the late Permian, was used as fuel. This CP had been operating for about 5 years at the time of sampling.

The air pollution control devices (APCDs) used in this CP consisted of a fabric filter (FF) at the kiln head and a FF with selective non-catalytic reduction (SNCR) at the kiln tail (Fig. S1, Supporting Information). The FF was used to capture particulate matter and the SNCR was designed to control NOx emissions by injection of ammonium hydroxide at high-temperature zones (800–900 °C).

2.2. Sample collection, preparation and determination

In a precalciner CP, the cement production process has two parts: clinker production and clinker-to-cement production. The former involves high-temperature processes, while the latter is a low-temperature mixing process. Solid samples, including different raw materials (limestone, clay, etc.), coal, intermediate products (raw meal and kiln dust from APCDs), clinker, additives, retarder, and cement products, are collected simultaneously (about 1 kg per sample) 3–6 times per day. The specific sampling locations are shown in Fig. S1. The stack flue gas was not explicitly sampled in this study for technical reasons; however, data were provided by the factory, including the mass content of particulate matter in the stack flue gas and other material input and output information.

All solid samples, including the different raw materials, intermediate products, clinker, additives, retarder, and cement products, were air-dried and ground to particle sizes <0.15 mm. The US EPA Method 7473 was adopted to determine Hg concentrations in the solid samples, which involved heating them to 800 °C and measuring the released Hg^0 by cold vapour atomic absorption spectrophotometry (Milestone DMA80, Italy; detection limit = 0.1 μg/kg). Each solid sample was measured at least three times to obtain a mean value. The data of solid samples were determined based on their air-dried masses.

2.3. Sequential extraction of various fractions of Hg from kiln tail dust

Extraction was performed using a five-step sequential extraction procedure (Table S1) modified from Diao et al. (2018). This procedure classified the Hg fractions in solid samples as a water-soluble fraction (F1, mainly existing in $HgCl_2$, $HgSO_4$), an ion-exchangeable fraction (F2, Hg^{2+} absorbed forms), an acid-soluble fraction (F3, such as HgO, $HgSO_4$), an elemental fraction (F4, such as Hg^0 or Hg_2Cl_2) and a sulfide fraction (F5, HgS or m-HgS (metacinnabar)) (Diao et al., 2018).

In brief, about 1.0 g of kiln tail dust was taken for the extraction procedure and added into a centrifuge tube. Then, 20.0 mL of Milli-Q water (18.25 Ω) was added and shaken in an end-to-end shaker at 300 rpm at room temperature (25 °C). The extraction was then centrifuged at 4000 rpm for a least 30 min. The supernatant was transferred to a polyethylene bottle to maintain a constant volume after filtering through a 0.45 μm nylon filter to obtain fraction F1. The solid residue from each step was subjected to the next extraction step by adding a corresponding solvent to obtain fractions F2 to F5 as indicated in

Table S1. All the supernatant samples were supplemented with $SnCl_2$ for Hg reduction and the total Hg was quantified by cold vapour atomic fluorescence spectrometry (Brooks Rand MERX Model, USA).

2.4. Quality assurance and quality control

Quality assurance and quality control were checked using blanks, duplicate samples and certified reference materials. During the measurement of solid materials, certified reference materials of gypsum (NIST 2429), coal (NIST 1632 d), coal fly ash (NIST 1633c) and soil (GSS-5) were also analysed along with solid samples from the CP. The resulting recovery of Hg was in the range of 98–105%. During the experiment performing sequential extraction of various Hg fractions, certified reference materials of gypsum (NIST 2429) and coal fly ash (NIST 1633c) were also analysed. The proportion of total Hg recovered ranged from 84 to 92% (total Hg extracted in fractions 1–5 based on a single aqua regia extraction).

2.5. Calculations of enrichment factor and atmospheric emission factor

2.5.1. Enrichment factor

The *enrichment factor* is an index that depicts the degree of accumulation of a single element during the clinker production process. It was calculated according to the following equation (Li et al., 2019):

$$Enrichment\ factor = \frac{Total\ Hg\ inside\ the\ kiln\ system}{Input\ of\ Hg\ per\ day} = \frac{Total\ Hg\ in\ the\ raw\ meal\ fed\ to\ the\ kiln}{Daily\ input\ of\ Hg\ from\ raw\ materials\ and\ coal} \quad (1)$$

When the enrichment factor is close to unity, no Hg enrichment occurs in the system; while factors >1 indicate that Hg was enriched or retained during the process, with higher values indicating greater Hg enrichment.

2.5.2. Atmospheric emission factor

The atmospheric emission factor (EMF) is an index of Hg emissions from the kiln tail and kiln head in a precalciner CP. The EMF was calculated according to clinker production (units = mg/tonne clinker; Li et al., 2019; Cai et al., 2020):

$$EMF = \frac{M_{Hg} \times 1000}{M_{clinker}} \quad (2)$$

where M_{Hg} is the amount of Hg emitted into the atmosphere per day (g/d) and $M_{clinker}$ is the daily output of clinker (t/d).

3. Results and discussion

3.1. Mercury concentrations in various solid materials

The information on Hg concentration, material flow and Hg input/output during the clinker production process is shown in Table 1. Among the different raw materials and fuels, carbide slag had the highest Hg content (mean ± standard deviation, SD, = 2.61 ± 0.56 mg/kg; Table 1, Fig. 1). Limestone, on the contrary, was the main reactant material in clinker production and had a very low Hg concentration of 0.01 mg/kg

Table 1
Hg input and output during the clinker production process.

Hg input/output	Material		Hg concentration (Mean ± SD, mg/kg)	Material input or output (t/d)	Hg input or output (g/d)	Hg input or output percentage (%)
Hg input	Raw material	Limestone	0.01 ± 0.00 (n = 3)[a]	7960	88.3	10.44
		Shale	0.01 (n = 1)	52	0.7	0.08
		Beneficiation waste	0.28 ± 0.04 (n = 3)	494	138.8	16.41
		Yellow phosphorus slag	0.62 ± 0.03 (n = 3)	183	113.5	13.42
		Carbide slag	2.61 ± 0.56 (n = 3)	165	431.6	51.04
		Coal slag	0.05 ± 0.03 (n = 3)	45	2.2	0.26
	Fuel	Coal	0.11 ± 0.002 (n = 3)	649	70.6	8.34
	Sum				845.7	100
	Weighted average		0.089			
Intermediate products	Raw meal		3.83 ± 0.10 (n = 3)	8600	32,948	
	Kiln tail dust		27.49 ± 2.56 (n = 3)	260	7146	
Hg output	Kiln head dust		0.012	20	0.2	0.02
	Particulate mercury in stack flue gas at the kiln tail		0.24[b]	1046[c]	2.51	0.30
	Particulate mercury in stack flue gas at the kiln head		0.0002[b]	601[c]	0.001	<0.01
	Gaseous mercury emission from two stacks				839[e]	99.2[e]
	Clinker		0.001 ± 0.00 (n = 3)	5236	3.9	0.46
	Sum				845.6	100
Mercury emission factor	Excluded coal			148.0[d]		
	Included coal			161.5[d]		
Mercury enrichment factor	38.96					

[a] n = sample numbers.
[b] Hg concentration in flue gas (μg/m^3).
[c] Flue gas volume (10^4 m^3/d).
[d] EMF (mg/t clinker).
[e] Calculated mass balance.

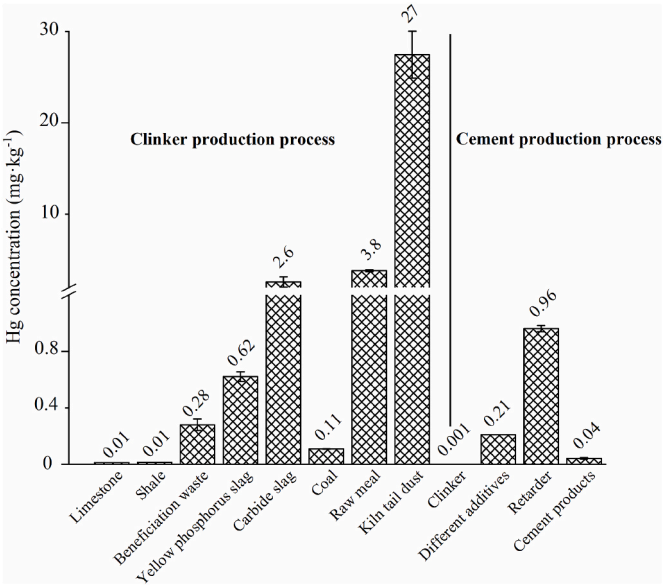

Fig. 1. Hg concentrations of different solid materials in the cement manufacturing process.

(Table 1), which is significantly lower than the average Hg content of limestone mines in China (0.042 mg/kg; Yang and thesis, 2014). The coal used as a fuel in this CP had a 0.11 mg/kg Hg content, which is one order of magnitude higher than that of limestone used in the same CP, but is similar to the average of world hard coal (0.10 mg/kg; Ketris and Yudovich, 2009) and slightly lower than the Chinese coal average (0.163 mg/kg; Dai et al., 2012). Other raw materials, including shale, beneficiation waste (waste rock), yellow phosphorus slag and coal slag, had low-to-medium Hg contents (0.01–0.62 mg/kg).

Due to the circulation and enrichment of Hg in the clinker production system, the concentrations of Hg in raw meal (3.83 ± 0.10 mg/kg) and kiln tail dust (27.49 ± 2.56 mg/kg) were several tens to hundreds of times higher than those in other materials except carbide slag (Fig. 1). This is consistent with previous studies on precalciner CPs that have reported strong Hg enrichment (Li et al., 2019; Wang et al., 2014; Yang and thesis, 2014). However, the Hg contents in raw meal and kiln tail dust differ among CPs, with the results of the present study being significantly higher than those of other studies from China and Europe (Table 2; Li et al., 2019; Wang et al., 2014; Yang and thesis, 2014; Mlakar et al., 2010; Kogut et al., 2021). The main possible reason is that this CP had a higher Hg load from the alternative materials and greater internal Hg accumulation.

Table 2
Hg concentrations in raw meal and kiln tail dust from different precalciner CPs.

Materials	Cement plant	Hg concentration (mg/kg)	Reference
Raw meal	CP #1 in Guizhou, China	3.83 ± 0.10	This study
	CP #2 in Guizhou, China	0.27 ± 0.02	Li et al. (2019)
	CP #3 in Guizhou, China	1.31 ± 0.25	Li et al. (2019)
	CP #4 in Sichuan, China	0.30 ± 0.003	Wang et al. (2014)
	CP #5 in Sichuan, China	0.037 ± 0.002	Wang et al. (2014)
	CP #6 in Slovenia	0.236	Mlakar et al. (2010)
	CP #7 in Europe	0.383	Kogut et al. (2021)
Kiln tail dust	CP #1 in Guizhou, China	27.49 ± 2.56	This study
	CP #2 in Guizhou, China	3.03 ± 0.49	Li et al. (2019)
	CP #3 in Guizhou, China	1.65 ± 0.14	Li et al. (2019)
	CP #4 in Sichuan, China	1.99 ± 0.95	Wang et al. (2014)
	CP #5 in Sichuan, China	0.43 ± 0.04	Wang et al. (2014)
	CP #6 in Slovenia	3.49	Mlakar et al. (2010)
	CP #7 in Europe	1.69	Kogut et al. (2021)

However, much lower Hg concentrations were found in the kiln head dust collected from the clinker cooler de-duster (0.012 mg/kg) and in the clinker (0.001 mg/kg; Fig. 1), indicating that almost all Hg in the raw meal evaporated during the calcination process. Thus, the higher Hg input did not lead to an increased Hg concentration in the clinker.

During the clinker-to-cement production process, the Hg concentrations in different additive materials (coal fly ash, coal slag, basalt and black rocks) and in the retarder (desulphurisation gypsum) ranged from 0.003 to 0.96 mg/kg, with the highest concentration found in desulphurisation gypsum (Table S2). The Hg level in cement products was 0.042 ± 0.005 mg/kg and was affected by the Hg levels in the additive materials and retarder. This is a similar level to those of other Chinese cements reported by Li et al. (2019; 0.022–0.029 mg kg^{-1}) and Wang et al. (2014; 0.035–0.061 mg kg^{-1}), probably as a result of the similar cement formulas used in China (such as the proportions of gypsum and coal fly ash).

3.2. Mass flow and enrichment of Hg during the cement manufacturing process

During the clinker production process, the input of Hg comes from raw materials and fuels, while its output is in the flue gas at the kiln tail and in the clinker. Information about the input and output of this system is shown in Fig. 2. The daily Hg input from raw materials (including coal) was 845.7 g/d, to which carbide slag contributed 51% despite only comprising 2% of the total daily mass of material input (7960 t/d). Limestone and coal contributed 11% and 8% of the Hg input, respectively. Other raw materials contributed 0.08–17% of the total Hg input (Fig. 2). Limestone has the highest daily average mass input (generally >80%), when the other raw materials have low Hg concentrations, limestone will contribute the most Hg to a precalciner CP (Li et al., 2019; Wang et al., 2014; Won and Lee, 2012). The high contribution of Hg from high-Hg-laden solid waste indicates that the content of Hg in non-essential raw materials needs to be regulated, especially when cement production uses a wide range of industrial wastes, some of which may contain high Hg concentrations and cause significant environmental and human health risks due to Hg atmospheric emissions (Cong et al., 2015; Wang et al., 2018).

During the clinker-to-cement production process, clinker and kiln head dust captured by the FF were mixed with additives (coal fly ash, coal slag, basalt and black stone; a total mass ratio of 13.4% of the cement products) and retarder (gypsum; a mass ratio of 4.4% of the cement products) to form the cement products. These additives had a weighted Hg content of 0.21 mg/kg and the retarder had a higher content of 0.96 mg/kg. Since the Hg concentrations in the clinker (0.001 mg/kg) and kiln head dust (0.012 mg/kg) were relatively low (Table 1), only a tiny amount of Hg (~4.2 g/d) from these two materials was incorporated into the cement. Thus, the Hg in the cement products was mainly derived from flue gas desulphurisation gypsum (59.1%) and fly ash (25.5%) from the coal-fired power plants. The clinker-to-cement process was a low-temperature mixing process with no Hg volatilisation anticipated; however, the weighted average Hg content (0.069 mg/kg) in different input materials during this process was substantially higher than that found in the cement products (0.042 mg/kg). This discrepancy might result from a proportion of the Hg in wet desulphurisation gypsum (up to 77%) being lost when it was dried at

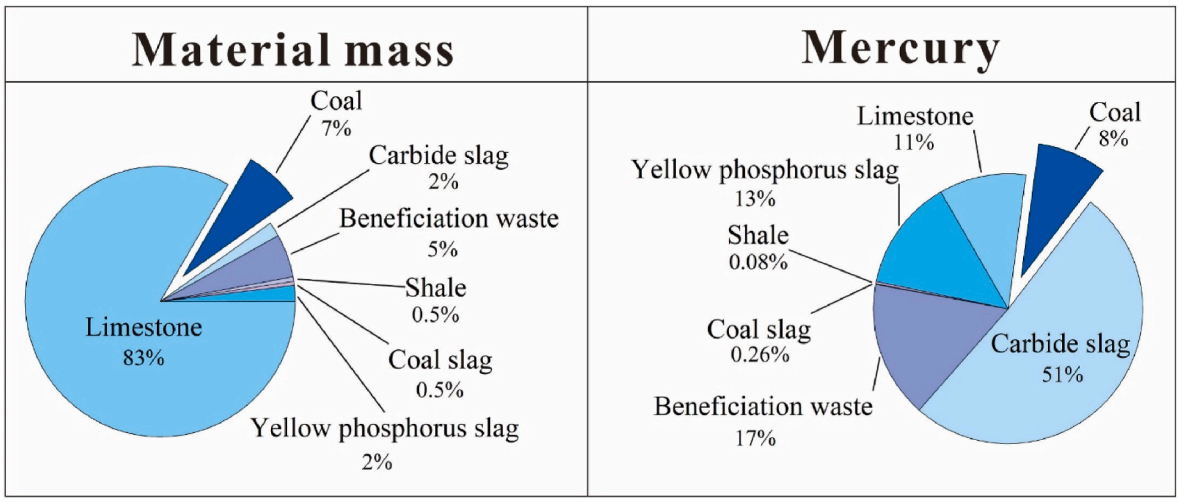

Fig. 2. Daily Hg input and mass input ratio of each raw material during the clinker production process.

temperatures of 150–200 °C before it was blended with clinker and other materials (Wang et al., 2022).

Accumulation and enrichment of Hg inside the clinker production system were evident. As shown in Fig. 3, the accumulation of Hg in the CP mainly occurred in the preheater-precalciner-rotary kiln system and was found in the particulate matter returned from that system, bringing most of the Hg back to the clinker production system. However, the Hg adsorbed on the particulate matter was captured by APCDs and mixed with raw materials, eventually becoming a raw meal that re-entered the preheater-precalciner-rotary kiln system during the clinker production process. When raw meal with a high Hg concentration entered the preheater-precalciner-rotary kiln system (at ~300–1450 °C), Hg evaporated and turned into gaseous mercury (Hg^0) that was discharged via flue gas (Schreiber et al., 2005). Because of their different boiling points, the different forms of Hg compounds are separated in different stages of the preheater. Some reports suggest that the adsorption of gaseous Hg on particulate matter would mostly occur between the first and second cyclones of the preheater (Mlakar et al., 2010). Only a small amount of Hg was fixed in the clinker as silicate ($HgSiO_3$ or $Hg_6Si_2O_7$), which was highly stable (Mlakar et al., 2010).

To analyse the degrees of Hg enrichment in preheater and precalciner CPs, the enrichment factors of four other CPs in China were compared (Fig. 4). This showed huge disparities (Fig. 4), with the highest enrichment factor (104) being for CP #3 in Guizhou, which was several to dozens of times those of the other CPs. Next was CP #1 of the present study (39), with the other CPs having approximately similar values ranging from 3.4 to 8.8. The behaviour of Hg in precalciner CPs is affected by various factors, such as the Hg contents of the raw materials and fuels, the collected kiln tail dust treatment method (shuttle or not), the type and efficiency of APCDs, the operating conditions, the CP running time (Renzoni et al., 2010; Sikkema et al., 2011; Senior et al., 2003, 2009; Li et al., 2019; Wang et al., 2016), and the Hg-absorption ability of the raw material mix.

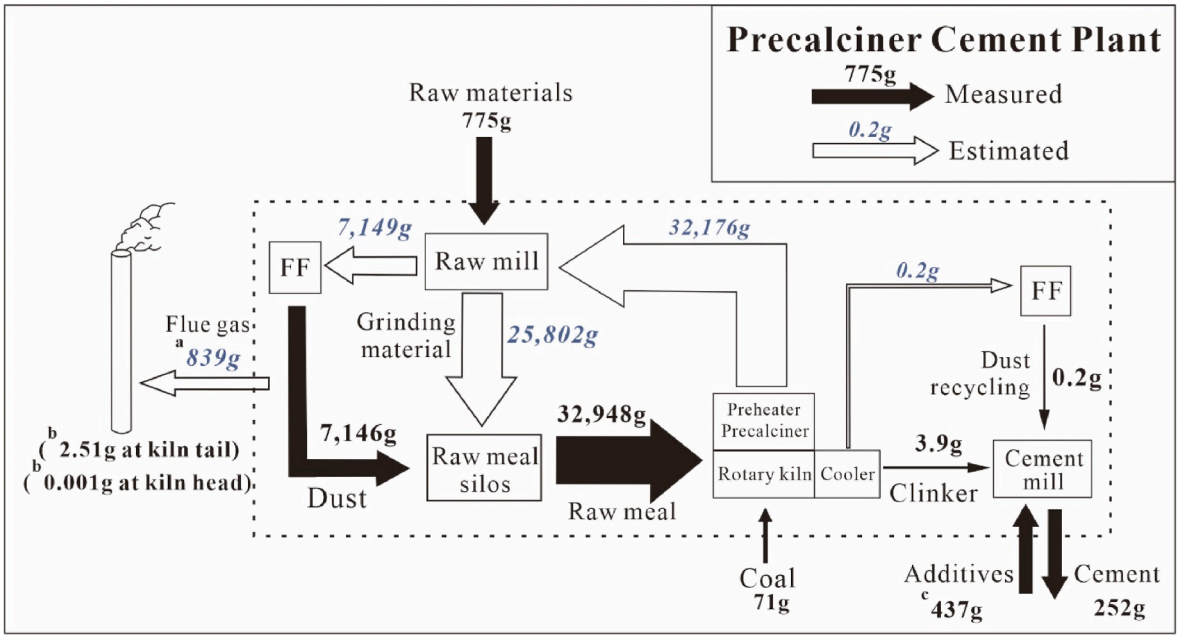

Fig. 3. Mass flow of Hg in the CP (per day). [a]. Gaseous mercury emitted from two stacks. [b] Particulate mercury emitted from two stacks. [c] This value includes possible atmospheric Hg emissions/losses.

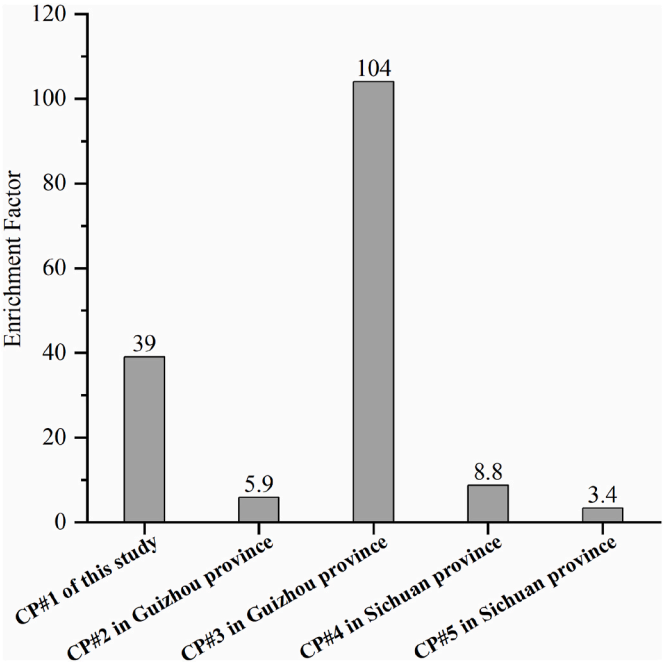

Fig. 4. Enrichment factors for mercury in different CPs in China (data for CPs #2 and #3 in Guizhou are from Li et al., 2019; data for CPs #3 and #4 in Sichuan Province are from Wang et al., 2016).

3.3. Potential environmental risks of cement plants

Previous studies show that precalciner CPs are in an enrichment stage in their initial 1.5 years of operation and produce low atmospheric Hg emissions (Li et al., 2019). However, in CPs run for more than 1.5 years, the atmospheric Hg emissions and Hg input can attain a dynamic equilibrium (Li et al., 2019; Cai et al., 2020). Consequently, the atmospheric Hg emissions in this study were estimated using this assumption. The mercury emission factor (EMF) of the studied CP was estimated to be 161.5 mg Hg/t clinker. This figure would be reduced to 148 mg Hg/t clinker if the contribution from the coal fuel was excluded. This value is significantly higher than the USA's Hg emission limits for existing and new CPs, which are 25 mg Hg/t clinker and 9.5 mg Hg/t clinker, respectively (USEPA, 2011). It is also much higher than the EMFs of CP #2 (76.1 mg Hg/t clinker) and CP #3 (1.8 mg Hg/t clinker) in Guizhou Province, which use low-Hg raw materials but have different lengths of operating time (Li et al., 2019). Once more, the figure obtained from this study is apparently higher than the national average (91 mg Hg/t clinker) based on a mass balance method from 60 cement production lines in China (Cui et al., 2021). Finally, the atmospheric Hg emissions were estimated to be 306 kg/y for this cement production line. Combining the data from the two other investigated CPs in Guizhou Province (Li et al., 2019), the cement industry emitted 7.12 t of Hg into atmosphere in 2020. However, it should be noted that this estimate is still too speculative; further onsite research in this province and at the national level is required to reduce this uncertainty.

Five-step sequential extraction was applied to the kiln tail dust to disclose the Hg fractions and possible environmental impacts. Besides three kiln tail dust samples (S1–S3) collected from the studied CP (CP #1), five other samples were collected from CPs in Guizhou (S4–S5 from CP #2 and S6–S8 from CP #3). The details of these two CPs are reported in our previous research (Li et al., 2019).

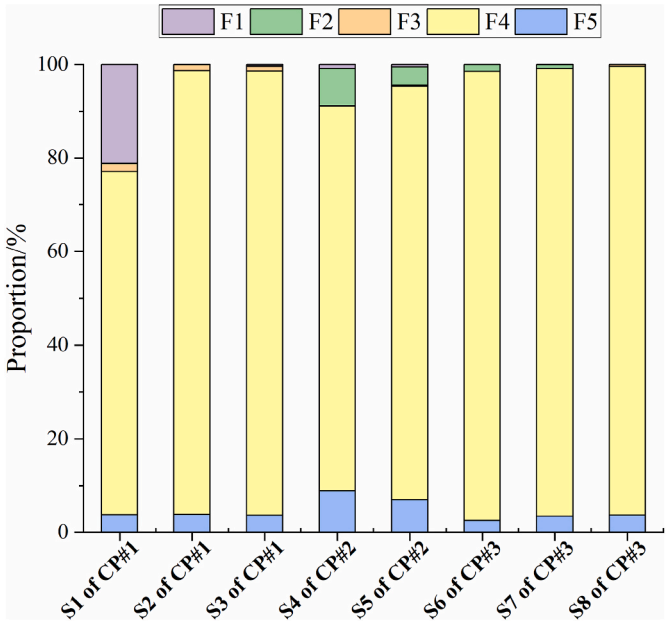

Fig. 5. Distribution patterns of mercury speciation in kiln tail dust from different CPs.

The results of the sequential extraction experiment are shown in Fig. 5 and indicate that the highest speciation of Hg (73–96%) occurred in fraction F4. The Hg speciation in other fractions were relatively low: 0.01–21.2% for F1, 0.03–7.97% for F2, 0.01–1.64% for F3, and 2.51–8.86% for F5. Fraction F4 occupied an absolutely dominant position in the kiln tail dust of the precalciner CPs, as shown in Fig. 5, and may mainly exist as Hg_2Cl_2, since chlorine is also highly enriched in the clinker production processes (Mlakar et al., 2010). Sulfide Hg was the second-most abundant fraction in most samples. Significantly, the proportions of water-soluble states in individual samples were relatively high, such as 21% in sample S1 (Fig. 5), and this form easily leaches into surface water and soil (Liu et al., 2021). The Hg in this fraction is labile and readily taken up plants and animals, exposing them to high environmental risks. Therefore, a standardised system should be established to systematically de-dust precalciner CPs and transfer and recycle that dust.

3.4. Implications

From this study, it can be seen that under the circular economy policy, CPs reuse large volumes of waste from other industries. Cement-related Hg contamination may occur when treating high-Hg-laden solid waste; however, the reuse of solid waste in CPs reduces waste disposal costs and reutilizes useful elements (Ca, Al, Fe, etc.), which is economically beneficial. Meanwhile, the high-temperature clinkerization process can solidify most other heavy metals into the clinker, such as Pb, Cd and Zn (Huang et al., 2021; Li et al., 2022), minimizing the environmental effects of releasing these elements. Hence, it is important to find ways to reduce the environmental impacts of volatile elements such as Hg. One way is to use low-Hg solid waste, another is to lower the Hg levels of high-Hg-laden solid waste before it is used.

4. Conclusions

Based on field investigations of a precalciner CP that used a variety of solid wastes as raw materials, it was found that Hg was significantly enriched during the clinker production process, with an enrichment factor as high as 39. Most raw materials and additives had low Hg contents, especially the main input material, limestone (0.01 mg/kg); while carbide slag, which comprised a small fraction of the material input (2%), doubled the Hg input. Elevated amounts of Hg were detected in raw meal (3.83 mg/kg) and kiln tail dust (27.49 mg/kg), and almost no Hg was found in the clinker (0.001 mg/kg). The estimated atmospheric emission factor of Hg from this CP was 161.5 mg Hg/t clinker, which is much higher than those of other CPs in Guizhou that used low-Hg-content raw materials. Therefore, cement-related Hg emissions should select appropriate raw materials with limited Hg contents to reduce atmospheric emissions. In addition, the experiment with sequential extraction of Hg fractions showed that Hg mainly existed in fraction F4 (possibly as Hg_2Cl_2), while some samples had high proportions of water-soluble (20%) and acid-soluble (8.9%) states, which can be easily released into water bodies and cause environmental harm.

Credit author statement

Zhonggen Li: Conceptualization, Investigation, Funding acquisition, Resources. **Yiming Huang**: Methodology, Software, Visualization. **Jinling Liu**: Resources, Writing – review & editing. **Guangyi Sun**: Methodology, Writing – review & editing. **Qingfeng Wang**: Investigation, Writing – review & editing. **Hanxi Xiao**: Methodology, Writing – review & editing. **Mingqin Huang**: Methodology.

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.

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Appendix A. Supplementary data

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