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Fate of Lead and Cadmium in Precalciner Cement Plants and Their Atmospheric Releases

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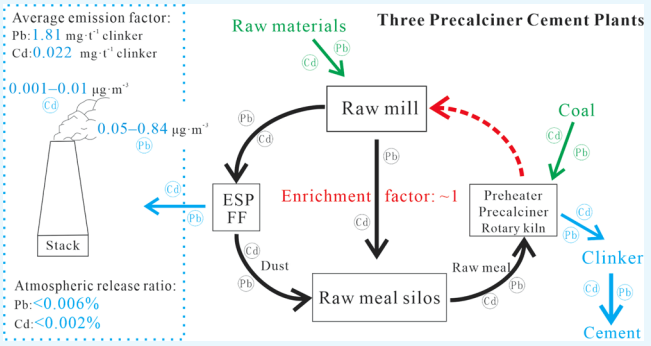
ABSTRACT: Disclosing the fate of lead (Pb) and cadmium (Cd) during the cement production process is the key to control their atmospheric emissions, which have not attracted much attention yet. In this study, three precalciner cement plants (CPs) using different raw materials in Guizhou Province in Southwest China were investigated. It showed that the concentrations of Pb and Cd in different raw materials and the associated total metal input of these materials were different among CPs; the behavior of Pb and Cd were almost the same during the clinker production process that there has been no accumulation of these two elements inside the system, and nearly all input of Pb and Cd were discharged by the clinker. Although the temperature of clinkerization was pretty high of 1450 °C, the atmospheric emission ratio of both metals was negligible (<0.006% for Pb and <0.002% for Cd of the total output, respectively); the main reason might be that the two elements were incorporated into the minerals of clinker, either as silicate or sulfate. The long-term environmental impacts of some high Pb- and Cd-laden clinkers and cement need to be monitored and evaluated.



1. INTRODUCTION

The manufacturing of cement involves the calcining of raw materials in a kiln to produce clinker;[1] it is thus an energy-consuming industry; at the same time, a range of atmospheric pollutants, such as particulate matters (PM) and heavy metals, as well as greenhouse gas CO_2, would be released into the ambient atmosphere during this high-temperature process.[2−6] Therefore, the environmental impact of the cement industry, especially the heavy metal emissions concerning their toxicity and persistency, has received more and more attention.[7,8]

Nriagu and Pacyna[9] estimated the atmospheric emissions of 16 trace metals from the cement plants (CPs) in the world and found the emission varied considerably for each element due to the large uncertainties in the emission factors (EMFs). In order to reduce the atmospheric emissions of heavy metals from CPs and eliminate their negative environmental impacts, the fate of heavy metals in CPs should be clarified first. However, aside from Hg, which has been studied with a couple of field investigations,[7,10,11] research on other metals is relatively scarce. As two toxic and semi-volatile heavy metals, lead (Pb) and cadmium (Cd) can volatilize during the simulated clinker sintering process at 1450 °C,[12,13] while they were found to be not totally volatilized in the rotary kiln, with the resultant clinker containing considerable content of Pb (16.8 mg·kg^{-1}) and Cd (3.1 mg·kg^{-1}) in filed investigation,[14] and the loss of Pb and Cd in CPs with precalciner process was in the range of 39−57% by comparing the concentrations of Pb and Cd in raw meal and clinker.[15] However, Cd was mainly discharged via the flue gas dust, while the emissions of Pb were dependent on the process conditions of some industrial process.[16] Hence, the behavior of Pb and Cd inside the CPs could be more complicated than thought. In addition, due to the lack of information of Pb and Cd contents in different raw materials and the intermediate products, it is still not clear about the detailed behaviors of Pb and Cd during the clinker and cement production process.[17,18] Furthermore, the estimation of atmospheric emissions of Pb and Cd from CPs would be vital to assess the environmental impacts of this industry.[4,19−21]

China has been the largest producer of cement in the world for more than three decades, and now, it produces more than one half of the world's total cement products.[22] The dominant production technique for cement in China has changed from using shaft kilns before 2000 to precalciner kilns, or suspension pre-heater kilns, since 2010.[5] Guizhou Province in Southwest China is one important cement production base in China due

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Table 1. Pb Concentration in Different Materials during the Entire Production of the Studied CPs

materials			Pb concentration (mean ± SD, mg·kg^{-1})		
			CP #1	CP #2	CP #3
material inputs during the clinker production	raw materials	limestone	319 ± 243 (n = 3)[a]	5.8 ± 4.7 (n = 3)[a]	2.9 ± 0.7 (n = 3)[a]
		sandstone	7.9 ± 0.9 (n = 3)	[b]	[b]
		shale	35 ± 14 (n = 3)	11.4 ± 2.0 (n = 3)	14.4
		coal gangue	50 ± 2 (n = 2)	[b]	[b]
		iron-rich materials	52 ± 3 (n = 3)	1619 ± 70 (n = 3)	[b]
		beneficiation waste	[b]	[b]	12.1 ± 1.1 (n = 2)
		yellow phosphorus slag	[b]	[b]	21.1 ± 2.8 (n = 3)
		carbide slag	[b]	[b]	9.9 ± 2.5 (n = 2)
		coal slag	[b]	[b]	19.4 ± 0.9 (n = 3)
	fuel	coal	17 ± 4 (n = 2)	13.1 ± 0.6 (n = 3)	8.6 ± 0.6 (n = 3)
	weighted mean		244.7	36.2	4.36
intermediate products	raw meal		251 ± 15 (n = 3)	32 ± 1 (n = 3)	5.0 ± 0.1 (n = 3)
	kiln tail dust		527 ± 73 (n = 6)	30 ± 5 (n = 6)	6.0 ± 0.3 (n = 3)
	kiln head dust		234 ± 55 (n = 3)	117 ± 23 (n = 3)	23.2
	stack flue gas at the kiln tail		0.84[c]	0.16[c]	0.05[c]
	stack flue gas at the kiln head		0.21[c]	0.54[c]	0.33[c]
material during the clinker to cement production	additives	fly ash of CFPPs	133 ± 25 (n = 2)	22 ± 11 (n = 3)	51.8 ± 0.2 (n = 3)
		desulfurization gypsum	14 ± 14 (n = 3)	1.7 ± 0.05 (n = 3)	1.2 ± 0.04 (n = 3)
		limestone	319 ± 243 (n = 3)	5.8 ± 4.7 (n = 3)	[b]
		bottom ash of CFPPs	[b]	[b]	19.4 ± 0.9 (n = 3)
		basalt	[b]	[b]	6.7 ± 0.2 (n = 3)
		black stone	[b]	[b]	14.5 ± 1.1 (n = 3)
	weighted mean		141.6	12.3	30.0
	clinker		407 ± 7 (n = 3)[a]	42 ± 3 (n = 3)[a]	8.1 ± 0.3 (n = 3)[a]
	cement products		542 ± 57 (n = 4)	40 ± 8 (n = 6)	11.1 ± 1.4 (n = 6)

[a]n is the sample numbers. [b]Not applicable. [c]Unit in μg·m^{-3} for Pb concentration in flue gas.

to its rich limestone and coal deposits, and the cement output in this province has increased by 7 times during 2005−2018 and accounted for 5% of the national total in 2018.[23−25] Our previous studies revealed the distinctive Hg emission levels from different precalciner CPs in Guizhou and found Hg was enriched and accumulated inside the clinker production process and Hg isotope signals of this source was different from other important sources, for example, non-ferrous smelters.[7,26] In this study, three precalciner CPs (CP #1, CP #2, and CP #3) in Guizhou Province are systematically investigated; these three CPs all have a preheater and precalciner process and with a capacity of 4500−5000 tonnes clinker each line per day; the basic information of the instigated CPs is shown in Table S1. All input/output solid materials in the entire production process had been collected and analyzed, and the sampling locations are illustrated in Figure 7. The aims are to (1) detect the Pb and Cd concentrations in all materials during the entire production process; (2) find out whether there has been an enrichment of Pb and Cd inside the clinker production process; (3) quantify the atmospheric EMFs and the total atmospheric emissions of these two pollutants from CPs in Guizhou Province and the whole country; (4) assess the potential environmental impacts of Pb and Cd flowing through the cement production process. To the best of our best knowledge, this is the first detailed report on the two elements during the whole cement production process in China. Hence, results from this study will provide important basic information to reveal the fate of Pb and Cd during the precalciner cement production and the factors that control Pb and Cd emissions in CPs, which are needed to assess the possible impacts of Pb and Cd pollution caused by CPs.

2. RESULTS AND DISCUSSION

2.1. Concentrations of Pb and Cd in Different Solid Materials. The concentrations of solid materials in precalciner CPs are discussed in three parts, for example, different raw materials and coal, intermediate products (raw meal and kiln dust), and materials in clinker to cement production process. The detailed information about the concentrations of Pb and Cd in these materials are shown in Tables 1 and 2, respectively. In addition, their daily material input and output are provided in Table S2 of Supporting Information.

2.1.1. Raw Materials and Coal. Large variations in the Pb and Cd concentrations in different raw materials and coal were observed for these three CPs (Tables 1 and 2). Especially, the concentrations of Pb and Cd in limestone (319 ± 243 mg·kg^{-1} for Pb; 5.5 ± 0.2 mg·kg^{-1} for Cd) of CP #1 were much higher than that of the other two CPs (5.8 ± 4.7 mg·kg^{-1} for Pb, 0.02 ± 0.02 mg·kg^{-1} for Cd in CP #2; 2.9 ± 0.7 mg·kg^{-1} for Pb, and 0.04 ± 0.01 mg·kg^{-1} for Cd in CP #3), with the latter two cases having similar contents of Cd as previous reports (0.030−0.065 mg·kg^{-1}).[27] The high Pb and Cd concentrations in limestone found in CP #1 might be related to the oolitic limestone, which has been found to contain high levels of heavy metals due to geological reasons, and as high as 4.9 mg·kg^{-1} of Cd concentration was found in oolitic limestone in Europe,[28,29] which was comparable to CP #1 of this study (5.5

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Table 2. Cd Concentration in Different Materials during the Entire Production of the Studied CPs

materials			Cd concentration (mean ± SD, mg·kg^{-1})		
			CP #1	CP #2	CP #3
material inputs during the clinker production	raw materials	limestone	5.49 ± 0.20 (n = 3)[a]	0.02 ± 0.02 (n = 3)[a]	0.04 ± 0.01 (n = 3)[a]
		sandstone	0.03 ± 0.002 (n = 3)	[b]	[b]
		shale	0.19 ± 0.01 (n = 3)	0.53 ± 0.28 (n = 3)	0.16
		coal gangue	7.85 ± 0.64 (n = 2)	[b]	[b]
		iron-rich materials	0.87 ± 0.03 (n = 3)	10.06 ± 0.92 (n = 3)	[b]
		beneficiation waste	[b]	[b]	1.5 ± 0.04 (n = 2)
		yellow phosphorus slag	[b]	[b]	0.26 ± 0.8 (n = 3)
		carbide slag	[b]	[b]	0.28 ± 0.5 (n = 2)
		coal slag	[b]	[b]	0.23 ± 0.3 (n = 3)
	fuel	coal	0.11 ± 0.01 (n = 2)	0.08 ± 0.01 (n = 3)	0.10 ± 0.01 (n = 3)
	weighted mean		4.26	0.24	0.13
intermediate products	raw meal		5.02 ± 0.15 (n = 3)	0.23 ± 0.01 (n = 3)	0.15 ± 0.03 (n = 3)
	kiln tail dust		7.00 ± 0.32 (n = 6)	0.20 ± 0.02 (n = 6)	0.16 ± 0.04 (n = 3)
	kiln head dust		6.53 ± 1.19 (n = 3)	0.44 ± 0.05 (n = 3)	0.26
	stack flue gas at the kiln tail		0.01[c]	0.001[c]	0.001[c]
	stack flue gas at the kiln head		0.01[c]	0.002[c]	0.004[c]
material during the clinker to cement production	additives	fly ash from CFPPs	2.23 ± 0.54 (n = 2)	0.30 ± 0.14 (n = 3)	1.94 ± 0.02 (n = 3)
		desulfurization gypsum	0.30 ± 0.30 (n = 3)	0.02 ± 0.01 (n = 3)	0.05 ± 0.01 (n = 3)
		limestone	5.49 ± 0.20 (n = 3)	0.02 ± 0.02 (n = 3)	[b]
		bottom ash from CFPPs	[b]	[b]	0.23 ± 0.03 (n = 3)
		basalt	[b]	[b]	0.20 ± 0.01 (n = 3)
		black stone	[b]	[b]	0.26 ± 0.07 (n = 3)
	weighted mean		2.43	0.15	1.01
	clinker		6.88 ± 0.23 (n = 3)	0.31 ± 0.01 (n = 3)	0.33 ± 0.08 (n = 3)
	cement products		7.14 ± 0.04 (n = 4)	0.32 ± 0.06 (n = 6)	0.35 ± 0.06 (n = 6)

[a]n is the sample numbers. [b]Not applicable. [c]Unit in μg·m^{-3} for Cd concentration in flue gas.

± 0.2 mg·kg^{-1}). Moreover, iron-rich materials from nonferrous smelters used in CP #2 contained astonishing high Pb (1619 ± 70 mg·kg^{-1}) and Cd (10.06 ± 0.92 mg·kg^{-1}) compared to other raw materials (Tables 1 and 2), which were about 100 times higher than other raw materials. Pb and Cd in coal and most other raw materials possessed low concentrations in the three CPs (<50 mg·kg^{-1} for Pb and <0.3 mg·kg^{-1} for Cd), with except of coal gangue and beneficiation waste that contained moderate Cd concentrations (1.5−7.8 mg·kg^{-1}).

2.1.2. Intermediate Products. Pb and Cd concentrations in intermediate products, which includes raw meal and dust captured from the air pollution control devices (APCDs) at kiln tail, are shown in Figure 1 and Tables 1 and 2. Pb and Cd concentrations in intermediate products of CP #1 were also much higher than that of CPs #2 and #3, which was consistent with the variation of Pb and Cd contents in limestone (Figure 1).

In CP #1, the concentration of Pb and Cd in raw meal (251 ± 15 mg·kg^{-1} of Pb; 5.0 ± 0.2 mg·kg^{-1} of Cd) were roughly equal to that in raw mix materials (weight mean: 244.7 mg·kg^{-1} of Pb; 4.26 mg·kg^{-1} of Cd) but significantly lower than that in kiln tail dust (527 ± 73 mg·kg^{-1} of Pb; 7.0 ± 0.3 mg·kg^{-1} of Cd) and in clinker (407 ± 7 mg·kg^{-1} of Pb; 6.88 ± 0.23 mg·kg^{-1} of Cd). In CP #2, there was a tiny gap in the concentrations of Pb and Cd in raw meal (32 ± 1 mg·kg^{-1} of Pb; 0.23 ± 0.01 mg·kg^{-1} of Cd), in kiln tail dust (30 ± 5 mg·kg^{-1} of Pb; 0.20 ± 0.02 mg·kg^{-1} of Cd), and in raw mix materials and coal (36.2 mg·kg^{-1} of Pb; 0.24 mg·kg^{-1} of Cd), and all of them were lower than that in clinker (42 ± 3 mg·kg^{-1} of Pb; 0.31 ± 0.01 mg·kg^{-1} of Cd). Similarly, the Pb and Cd contents in raw meals (5.0 ± 0.1 mg·kg^{-1} of Pb; 0.15 ± 0.03 mg·kg^{-1} of Cd) and in kiln tail dust (6.0 ± 0.3 mg·kg^{-1} of Pb; 0.16 ± 0.04 mg·kg^{-1} of Cd) were almost indistinguishable, and both of them were slightly higher than that in raw mix materials (4.36 mg·kg^{-1} of Pb; 0.13 mg·kg^{-1} of Cd) but lower than that in clinker (8.1 ± 0.3 mg·kg^{-1} of Pb; 0.33 ± 0.08 mg·kg^{-1} of Cd). The much higher metal concentration found in clinker than that of raw meal might be related to the mass

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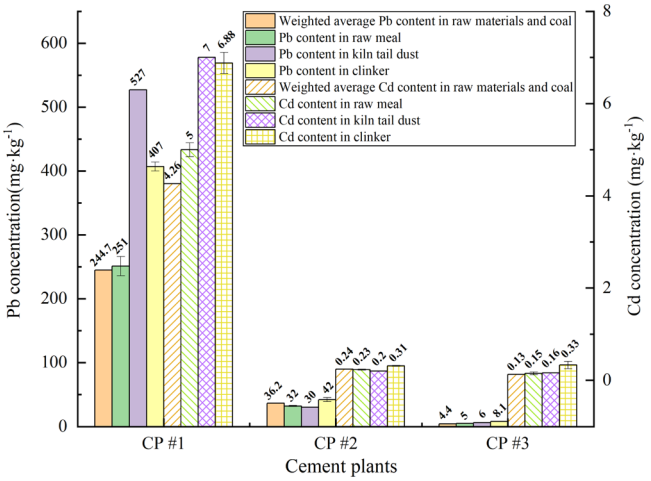

Figure 1. Comparison of the Pb and Cd concentration in different solid materials during the clinker production process in three CPs.

reduction (ca. 1.6:1 for raw meal to clinker) during the clinker production,[30] and the slightly higher metal concentration in kiln tail dust than raw meal indicates the capture of metal in flue gas within the raw mill and detained by the dust collector, which was consistent with the research of Wang et al.[31] It should be noted that the concentration of Pb and Cd in raw meal of CP #1 has exceeded the reference limits of metals in raw meal in China (GB 30760—2014),[32] which has a limit of 67 mg·kg^{-1} for Pb and 1 mg·kg^{-1} for Cd, while raw meal of CPs #2 and #3 was within this limit.

2.1.3. Materials in Clinker-to-Cement Production Process. During the clinker-to-cement production process, the input materials were clinker, dust captured by APCDs at kiln head, additives, and retarder, while the output was the kiln head stack gas and cement products. The concentrations of Pb and Cd in kiln head dust, clinker, and cement products of CP #1 were also much higher than those of CPs #2 and #3. The contents of Pb and Cd in kiln head dust (average 124.7 mg·kg^{-1} of Pb; 2.4 mg·kg^{-1} of Cd) was generally similar to that in clinker (average 152.7 mg·kg^{-1} of Pb; 2.5 mg·kg^{-1} of Cd) (Tables 1 and 2). Fly ash of coal fired power plants (CFPPs) used in the three CPs as additives contained much higher concentrations of Pb (68.9 mg·kg^{-1} on average) and Cd (1.49 mg·kg^{-1} on average) than that of gypsum. In the last, Pb and Cd concentrations in cement products (average 197.7 mg·kg^{-1} of Pb; 2.6 mg·kg^{-1} of Cd) were increased slightly compared to that of the clinker (Tables 1 and 2).

Pb and Cd in clinker and cement products were compared in this study and others (Table 3). Pb contents in clinker (408 ± 7 mg·kg^{-1}) and cement (542 ± 57 mg·kg^{-1}) in CP #1 of this study were approximately 100 times higher than that of a CP in Nigeria (4.4 mg·kg^{-1} in clinker; 3.9 mg·kg^{-1} in cement) and CP in United States of America (3 mg·kg^{-1} in cement),[33] and similarly, Cd contents in clinker and cement products of CP #1 were 10−100 times higher than other CPs. Pb contents of cement products in CP #3 (11.1 ± 1.4 mg·kg^{-1}) were only one ninth of that of a CP in South Korea (91 mg·kg^{-1}),[34] and Cd in cement products of CP #2 (0.32 ± 0.06 mg·kg^{-1}) were only a quarter of a CP in Peninsular Malaysia (1.3 mg·kg^{-1}, Table 3).[35]

Moreover, the reference limit of Pb in clinker in China was 100 mg·kg^{-1} and that of Cd was 1.5 mg·kg^{-1} (GB 30760—2014);[32] thus, CP #1 exceeded the standard both for Pb and Cd, while CPs #2 (42 ± 3 mg·kg^{-1} of Pb; 0.31 ± 0.01 mg·kg^{-1} of Cd) and #3 (8.1 ± 0.3 mg·kg^{-1} of Pb; 0.33 ± 0.08 mg·kg^{-1} of Cd) were within the standard. Therefore, the limestone and iron-rich materials with low heavy metal concentrations were recommended to be the preferred materials to produce clinker. Otherwise, the cement products with high heavy metal concentrations deserved further research considering their possible impact on the environment and human health.

Table 3. Comparison of Pb and Cd Concentrations in Clinker and Cement Products of Different CPs

		concentration (mg·kg^{-1})		
materials	CPs	Pb	Cd	references
clinker	CP #1 (Guizhou province, China)	408	6.9	this study
	CP #2 (Guizhou province, China)	42	0.3	this study
	CP #3 (Guizhou province, China)	8.1	0.3	this study
	CP in Nigeria	4.4	0.5	33
	CP in Beijing, China	16.8	3.1	14
cement	CP #1 (Guizhou province, China)	542	7.1	this study
	CP #2 (Guizhou province, China)	40	0.3	this study
	CP #3 (Guizhou province, China)	11	0.4	this study
	CP in Nigeria	3.9	0.6	33
	CP in USA	3	0.05	33
	CP in South Korea	91	1.3	34
	CP in Peninsular Malaysia	71	1.3	35

2.2. Atmospheric Emissions of Pb and Cd. Surprisingly, the Pb and Cd concentrations of stack flue gas in CP #1 were close to that of two other CPs. This might be caused by the high PM removals by electrostatic precipitator (ESP) or ESP-combined fabric filter (FF) and most Pb and Cd in flue gas were attached to the PMs in the lower temperature range (<200 °C). We compared the concentrations of Pb and Cd in this study and other previous studies, and the results are shown in Table 4. The concentrations of Pb in stack flue gas in the three CPs were 0.05−0.84 μg·m^{-3} (average 0.36 μg·m^{-3}, Table 1), while that of Cd were 0.001−0.01 μg·m^{-3} (average 0.005 μg·m^{-3}; Table 2). Since the cement industry emission standards do not have separate restrictions on Pb and Cd, the emission limit for inorganic chemical industry was selected

Table 4. Comparison of Pb and Cd Concentration in Stack Flue Gas of Different Studies

metals	concentration (μg·m^{-3})	references
Pb	0.05−0.84	this study
	0.72	38
	34	37
	0.3−88	39
	2.26−893	40
	0.65−50.4	41
Cd	0.001−0.01	this study
	0.04	38
	14.6	37
	0.1−37	39
	0.19−0.83	40
	0.02−0.3	41

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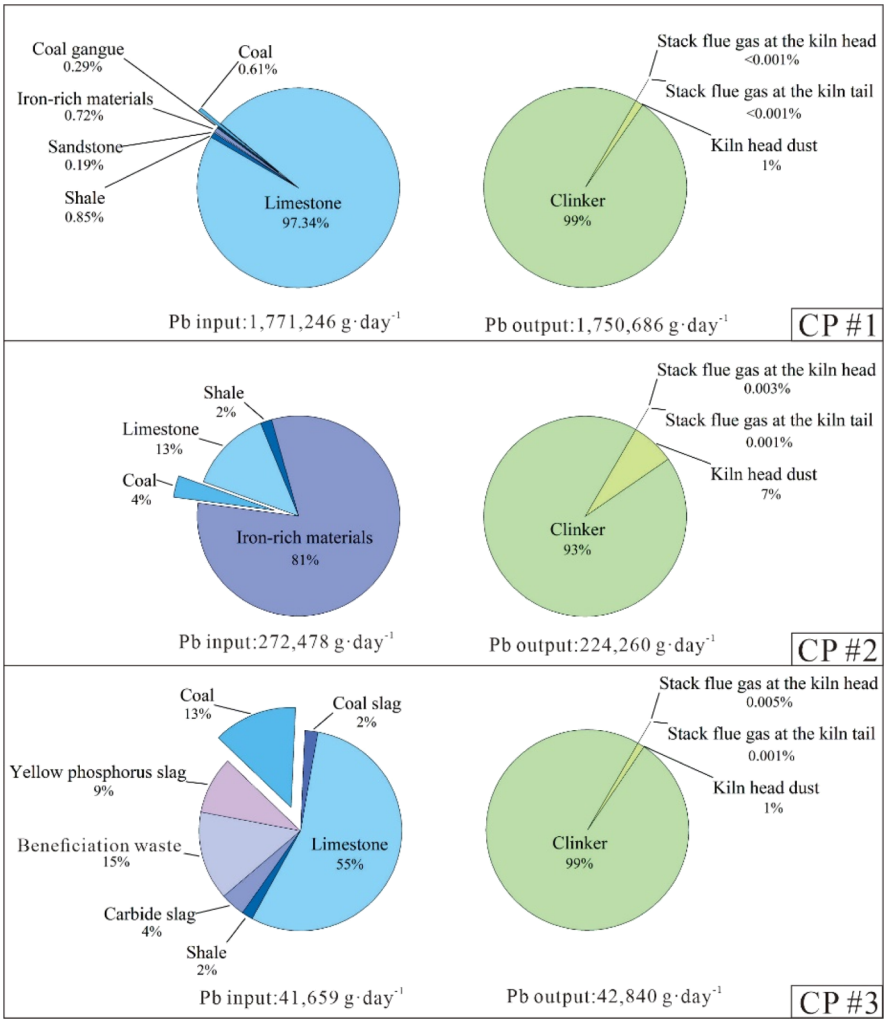

Figure 2. Daily Pb input and output during the clinker production process of the three CPs.

for comparison and all concentrations of the stack flue gas in the three CPs were below this standard limit (2 mg·m^{-3} of Pb, 0.5 mg·m^{-3} of Cd) (GB 31573—2015).[36] Furthermore, they were also much lower than most contents investigated by previous studies such as CP in India (34 μg·m^{-3} of Pb, 14.6 μg·m^{-3} of Cd; Table 4).[37] However, Pb and Cd contents of flue gas in our study were close to the results investigated by Yan et al.[38] (0.72 ± 0.01 μg·m^{-3} of Pb, 0.04 ± 0.01 μg·m^{-3} of Cd; Table 4).

To quantify the atmospheric emissions of Pb and Cd from CPs, the atmospheric EMFs of Pb and Cd from CPs were established to estimate the emissions from kiln tail/head based on eqs 5 and 6, and the results are shown in Table S3. The difference in emissions between kiln tail and kiln head was not significant as other volatile elements, such as Hg.[7]

The average daily production capacity of the three CPs studied was 4500−5000 tonnes clinker·day^{-1} line^{-1} (Table S1), and the atmospheric Pb emission was estimated to be 3.08 kg·yr^{-1} on average per cement production line by using EMF_1 of Pb (average: 1.81 mg Pb·tonne^{-1} clinker). Similarly, the atmospheric Cd emission was 0.038 kg·yr^{-1} on average per cement production line by using EMF_1 of Cd (average: 0.022 mg Cd·tonone^{-1} clinker) (Table S3).

The production of clinker in Guizhou Province in 2018 was 8.03 × 10^7 tonnes,[42] and the total provincial atmospheric Pb emission of cement industry in 2018 was estimated to be 145.3 kg·yr^{-1}, while Cd emission was estimated to be 1.77 kg·yr^{-1} on average, which was much lower than the emissions from CFPPs in the same province (430 kg·yr^{-1} of Pb; 51.4 kg·yr^{-1} of Cd).[43,44]

Moreover, the production of clinker in the whole country was 1.43 × 10^9 tonnes in 2018;[45] thus, the total national atmospheric Pb emission was 2.58 tonnes·yr^{-1}, while Cd was around 31 kg·yr^{-1}. The values of Pb and Cd emissions obtained in this study were much lower than previous research results,[5] which gave the annual Pb emissions of 259−1129 tonnes·yr^{-1} and Cd emissions of 5.7−26.3 tonnes·yr^{-1} from Chinese CPs in 1980−2012. Similarly, Shao et al.[19] estimated that Cd emission from Chinese CPs in 2010 to be 19 tonnes, which was also much higher than this study.

2.3. Mass Balance of Pb and Cd during the Cement Production Process. Limestone was the main material for clinker production, which accounted for 75−83% of the raw material mass of the three CPs studied (Table S2), while, other raw materials, for example, shale, sandstone, coal gangue, iron-rich materials, beneficiation waste, and bottom ash from CFPPs, as well as coal accounted for 7−10% of the raw material mass (Table S2). Combined with the metal concentration in different input/output materials (Tables 1 and 2) and the associated material mass flow (Table S2), the

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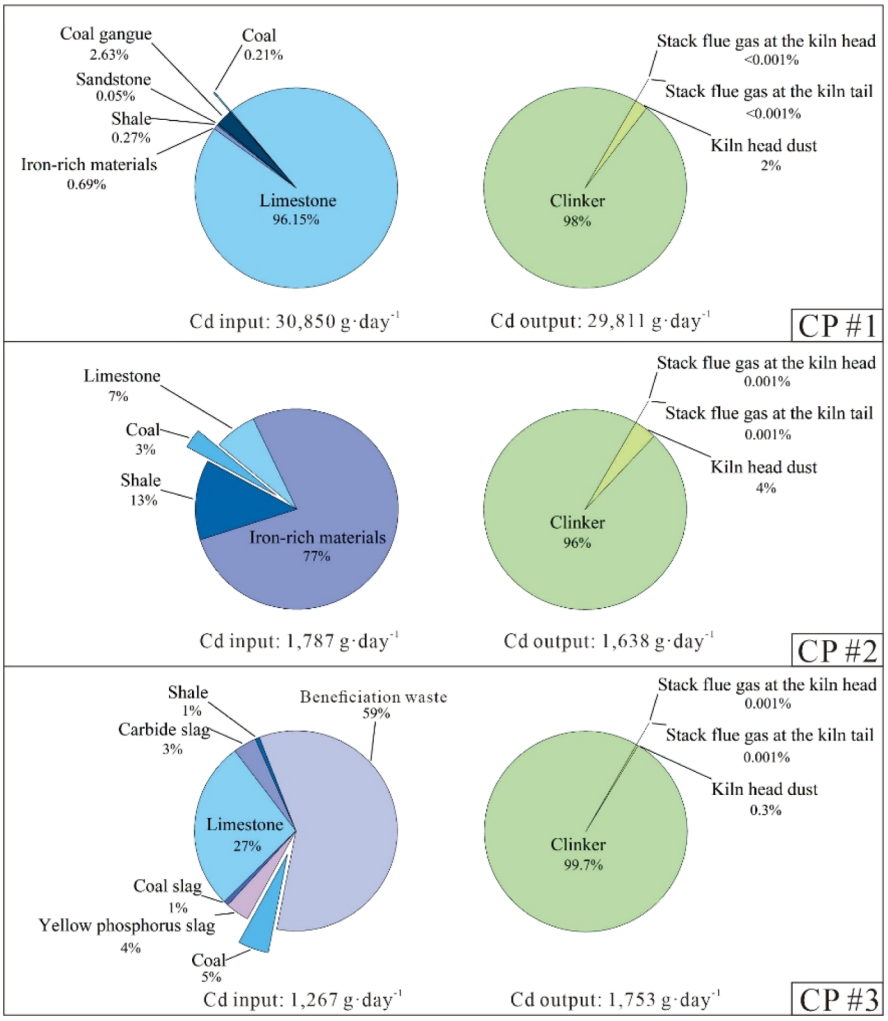

Figure 3. Daily Cd input and output during the clinker production process of the three CPs.

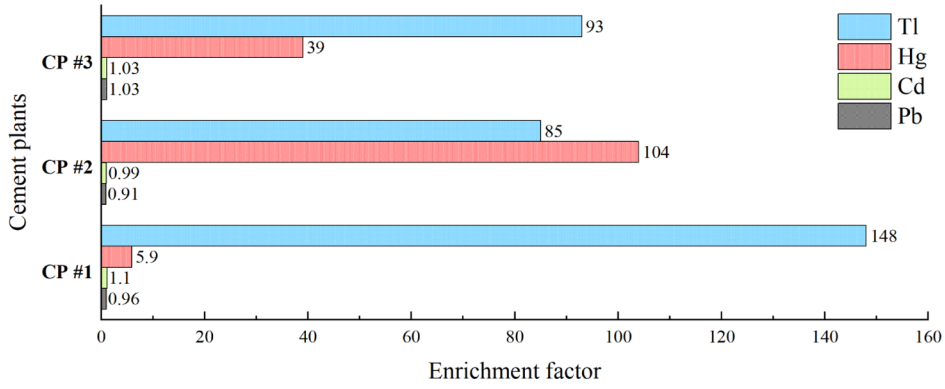

Figure 4. Enrichment factors of different heavy metals in the three CPs (Hg in CP #3 is internal unpublished data, Tl in the three CPs are quoted from ref 46 and Hg in CPs #1 and #2 are quoted from ref 7; re-use this figure with permission from Elsevier).

proportion of each material in the Pb and Cd input and output during the clinker production process is calculated (Figures 2 and 3). The detailed information of input and output of Pb and Cd flow during the whole cement production process in each CPs are shown in Figures 5 and 6.

Limestone in CP #1 and iron-rich materials in CP #2, which contained ultra-high Pb and Cd contents, completely dominated the input volume of Pb and Cd (Figures 2 and 3). In CP #2, the iron-rich material contributed more than three quarters of Pb and Cd input, albeit it only accounts for 2% of total mass material (Table S2). In CP #3, high Cd content of beneficiation waste accounted for more than half of the Cd input (59%), while limestone accounted for most of the Pb input (55%). As for the output of Pb and Cd, the clinker accounts for almost all the Pb and Cd output in the three CPs (93−99.7%). Meanwhile, the daily input and output of Pb and Cd during the clinker production process are roughly equal in three CPs (Figures 2 and 3), which indicates that almost all Pb

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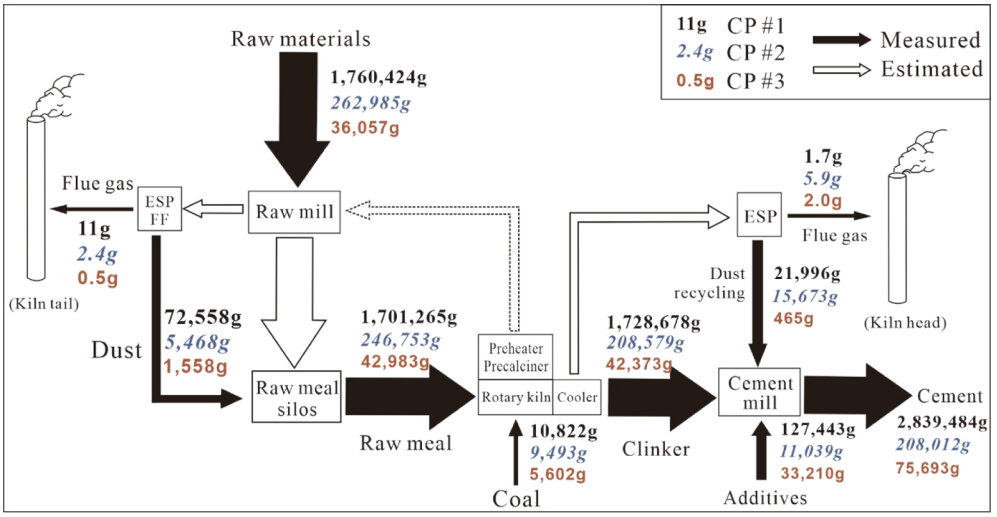

Figure 5. Mass flow of Pb in three CPs. (Values are based on one day).

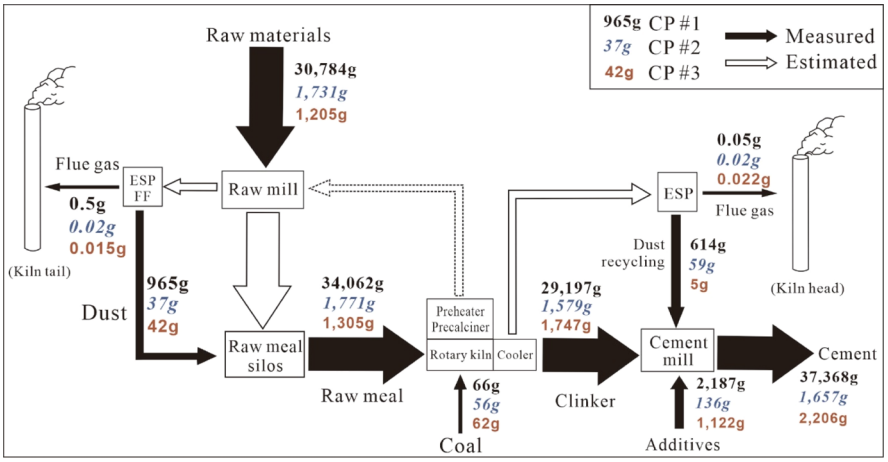

Figure 6. Mass flow of Cd in three CPs. (Values are based on one day).

and Cd input from different raw materials and fuels were ended up in the clinker. Moreover, low levels of Pb and Cd in flue gases resulted in minimal atmospheric emissions.

The output/input ratios of Pb in the clinker production and clinker-to-cement production were 95 and 118% on average of three CPs (Figures 2 and 5), respectively. Similarly, the output/input ratios of Cd in the clinker and clinker-to-cement production were 109 and 119% (Figures 3 and 6). Meanwhile, the enrichment factors of Pb and Cd from three CPs were established based on eq 4. The results are shown in Figure 4, and the enrichment factors of Pb and Cd in three CPs were all around 1, in particular, the enrichment factors of Pb were 0.96, 0.91, and 1.03, while those of Cd were 1.1, 0.99, and 1.03 in CP #1, CP #2, and CP #3, respectively. However, the enrichment factors of Hg and Tl in the three CPs were 5.9, 104, and 39[7] and 148, 85, and 93,[46] respectively (Figure 4). The high enrichment factors of Tl and Hg indicated the obvious enrichment in the system of CPs; thus, close to 1 of enrichment factor of Pb and Cd in this study suggests Pb and Cd were roughly balanced during the clinker productions, namely, the daily Pb or Cd output is equal to the daily input.

Pb input from different raw materials (1760 kg·day^{-1} of CP #1; 263 kg·day^{-1} of CP #2; 36 kg·day^{-1} of CP #3) and coal (10.8 kg·day^{-1} of CP #1; 9.5 kg·day^{-1} of CP #2; 5.6 kg·day^{-1} of CP #3) almost all ended up in the clinker (1729 kg·day^{-1} of CP #1; 209 kg·day^{-1} of CP #2; 42 kg·day^{-1} of CP #3), and it further entered to cement products (2839 kg·day^{-1} of CP #1; 208 kg·day^{-1} of CP #2; 76 kg·day^{-1} of CP #3) (Figure 5). In other words, the Pb flow mainly followed the sequence of from raw materials to raw meal, then to clinker, and finally to cement products.

Similarly, most of the Cd input (30.8 kg·day^{-1} of CP #1; 1.8 kg·day^{-1} of CP #2; 1.3 kg·day^{-1} of CP #3) were also entered into the clinker first (29.2 kg·day^{-1} of CP #1; 1.6 kg·day^{-1} of CP #2; 1.7 kg·day^{-1} of CP #3) and then to cement products in three CPs (37.4 kg·day^{-1} of CP #1; 1.7 kg·day^{-1} of CP #2; 2.2 kg·day^{-1} of CP #3) (Figure 6). These phenomena were much different to that of Hg and Tl, which have hardly been found in the clinkers.[7,46]

In addition, the results of this study were also different to previous speculations that Pb and Cd been volatilized at high temperature and concentrated in kiln tail dust.[12,13] This might be controlled by many factors that would restrict the volatilization of these elements during the clinker sintering process (clinkerization) in preheater, precalciner, and rotary kiln. According to previous studies, the main form of Pb in the clinker sintering process could be lead sulfate and lead chloride,[47,48] and it was eventually dissolved in the clinker

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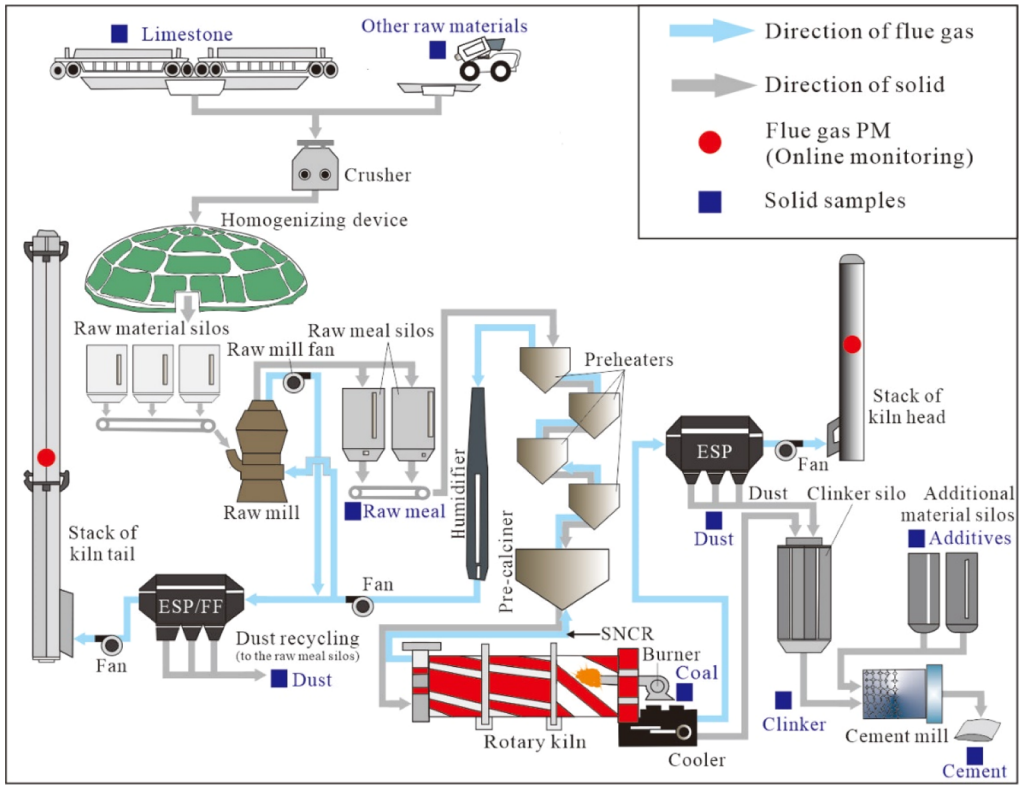

Figure 7. Schematic diagram of the preheater/precalciner cement manufacturing facility and sampling points.

with sulfate. Cd was dominated by cadmium oxide/hydroxide and cadmium chloride in that process.[47,49] These compounds have high stability than others at high temperatures; Cd could also form the solid solution of Cd sulfate salts in the clinker,[50] thus, they were easier to be consolidated into the clinker. In addition, sulfur in raw meal could lower the surface tension and the viscosity of the melt (above 1338 °C)[51] and promotes the solidification of Pb and Cd,[52,53] while chlorine would reduce the solidification ability of clinker over Pb and Cd by decreasing the interstitial phases during the clinkerization.[54] Moreover, due to the reaction of SiO_2 with heavy metal oxides and chlorides, which are shown in eqs 1−3, silicate of heavy metals might be formed eventually during the clinkerization process, which might be the main way for Pb and Cd to exist in the clinker production process.[55] Therefore, the extremely high content (>20%) of SiO_2 during the cement production process could also have a great inhibition effect on the volatilization of Pb and Cd. Under the combined action of the above reasons, the volatilization of Pb and Cd was greatly inhibited during the clinkerization.

$$MO + SiO_2 \rightarrow MO{\cdot}SiO_2 \quad (1)$$

$$2xMCl_2 + ySiO_2 + xO_2 \rightarrow 2xMO{\cdot}ySiO_2 + 2xCl_2\uparrow \quad (2)$$

$$xMCl_2 + ySiO_2 + xH_2\vec{O}xMO{\cdot}ySiO_2 + 2xHCl\uparrow \quad (3)$$

where M stand for heavy metals; x and y are stoichiometric number.

A small part of Pb and Cd might be volatilized in the rotary kiln at 1450 °C, while, as the hot flue gas goes to the five-stage preheaters and precalciner where the temperature drops dramatically (from 1450 to 300 °C), Pb and Cd would condense and adhere to the raw meal powder and re-entered the rotary kiln; thus, this will reduce the atmospheric emissions of Pb and Cd, and the cycling of Pb and Cd should be constrained between the rotary kiln and the preheater; the formation of silicate of Pb or Cd will lead to the discharge of these metals out of the kilns in the form of clinker. Therefore, it was difficult for Pb and Cd to pass through the preheater and precalciner and return to the raw meal soils, and almost all Pb and Cd end up in the clinker during clinkerization. In addition, the modern APCDs, especially PM removers, can remove almost all (>99.9%) PM that contains Pb and Cd, thus leading to a negligible atmospheric of these two elements, which is different to Hg, with the latter which may exist in gaseous form (elemental or oxidized) and penetrate the dust collector.

3. CONCLUSIONS

Based on the field investigations of three precalciner CPs, it was found that the semi-volatile elements Pb and Cd do not enrich inside the clinker production system, especially in raw meal and kiln tail dust, as that found for Hg and Tl; this resulted in a dynamic equilibrium with almost all daily Pb and Cd input from different raw materials and fuels ended up in the clinker, and very little portions (<0.006%) of Pb and Cd were atmospheric-lost. The mechanism was the formation of specific stable metal compounds of Cd and Pb during the clinkerization process, such as Pb/Cd silicate or sulfate, which were easier to be consolidated into the clinker. Limestone used in some plant may contain high levels of Pb (e.g., 319 ± 243 mg·kg^{-1}) and Cd (5.5 ± 0.2 mg·kg^{-1}), which lead to high Pb and Cd in the clinker and the final products of cement. However, raw materials with high Pb and Cd concentration did not lead to a much increase in atmospheric emissions from stack gas. The total emission of cement industrial in Guizhou was estimated to be 145.3 kg·yr^{-1} for Pb and 1.77 kg·yr^{-1} for Cd in 2018, and the total national

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atmospheric emission from this industry was estimated to be 2.58 tonnes·yr^{-1} for Pb and 31 kg·yr^{-1} for Cd. The results of the estimation of atmospheric emissions in this study indicated that atmospheric emissions of Pb and Cd from the cement industry had been effectively controlled, but some cement products containing high metals needed to be monitored and to be evaluated for their long-term environmental impacts.

4. EXPERIMENTAL SECTION

4.1. Description of CPs. Three precalciner CPs in Guizhou Province were selected to study the fate of Pb and Cd during the cement production, with CP #1 located in the east of the province, #2 in the central, and #3 in the west of the province. In these three CPs, limestone and other raw materials were produced locally. Coal used in CP #1 was produced from Henan and Shaanxi Provinces, which are located in central China. However, the coal used in CP #2 and CP #3 was produced from the central and western areas of Guizhou Province, respectively; both of the above areas are the main coal-producing areas in Guizhou, and coal is either bituminous or anthracitic and formed in the late Permian.

APCDs used in kiln tail were different in the three CPs studied (Table S1). The devices used at kiln tail consisted of a selective non-catalytic reduction (SNCR) unit combined with an ESP in CP #1 for NOx and PM controls, respectively; an SNCR plus ESP-FF for CP #2, and an SNCR plus FF for CP #3, while the same ESP was used at kiln head.

4.2. Sample Preparation and Determination. Solid samples, including different raw materials (limestone, clay, sandstone, etc.), coal, intermediate products (raw meal and kiln dust from APCDs), clinker, additives, and cement products were collected simultaneously (about 1 kg per sample) for 3−6 times over a 2−3 day sampling period for each CP, and the specific sampling locations are shown in Figure 7. The stack flue gas and contained PM were not measured in this study, but the PM concentration in flue gas as well as other material input and output information were provided by these CP companies. Since the temperature in the stack gas (70−100 °C) was lower than any elemental or ionic Pb/Cd vapor, it is therefore assumed that all Pb/Cd in the stack gas was in particulate form and their atmospheric emissions were calculated based on the Pb/Cd content in particles (kiln dust) and the particle content in the stack flue gas. Simultaneously, information about various input and output material quantities and flue gas flow was gathered from the CP companies, which is shown in Table S2 of Supporting Information.

All solid samples were air-dried and ground to sizes smaller than 0.15 mm. The sample digestion method used was developed by Liang and Grégoire in 2000[56] with the following procedures, 50 mg powders were weighed into Teflon digestion bottles, and 1 mL HF and 1 mL HNO_3 were added to the samples and then placed in an oven pre-heated at 190 °C for 24 h. After cooling, samples were heated on a hot plate at 120 °C to evaporate the solution to incipient dryness. Subsequently, 0.5 mL of HNO_3 was added to the Teflon bottles and continuously heated on a hot plate until dry. Then, 200 ng of Rh as an internal standard, 2 mL of HNO_3, and 2 mL of deionized water were added sequentially and placed in an oven pre-heated to 150 °C for 5 h. Finally, 0.4 mL of the digestion solution was transferred into a 15 mL centrifuge tube, and deionized water was added to obtain a volume of 10 mL. The Pb and Cd in this solution was measured by inductively coupled plasma mass spectrometry (Analytik Jena, Germany). The data of solid samples were reported based on their air-dried masses.

4.3. Quality Assurance and Quality Control. All Teflon bottles used for digestion were washed with 20% nitric acid (HNO_3) and rinsed with deionized water. HF and HNO_3 were distilled twice to remove impurities. Quality assurance and quality control were checked using blanks, duplicate samples, and certified reference materials. Certified reference materials of limestone (JLS-1; JDO-1), coal (NIST 1632d), fly ash (NIST 1633c), and soil (GSS-5) were also digested and analyzed along with solid samples from the CPs. The resulting recovery of Pb was in the range of 96−99% and Cd was in 95−116%.

4.4. Calculations of Enrichment Factors and Atmospheric EMFs. *4.4.1. Enrichment Factors.* To assess the degree of enrichment of Pb and Cd in the clinker production system, the enrichment factor is calculated according to a method for Hg,[7,57] which is to divide the total amount (gram or kilogram) of the target trace element in the clinker production system by the daily input (gram or kilogram) from different raw materials and fuels, as follows

$$\begin{aligned}&\text{enrichment factor}\\&= \frac{\text{total Pb or Cd accumulated inside the clinker production system}}{\text{daily input of Pb or Cd into the clinker production system}}\\&= \frac{[\text{total Pb or Cd in the raw meal}}{\text{daily input of Pb or Cd from different raw materials and coal}}\end{aligned} \quad (4)$$

when the enrichment factor is approximately equal to 1, it means there is no enrichment of Pb or Cd that occurred in the clinker production system; if the enrichment factor is greater than 1, it represents that Pb or Cd has been enriched or retained during the process, and a higher value means a higher enrichment of Pb or Cd inside the system.

4.4.2. Atmospheric EMFs. To quantify the atmospheric emissions of Pb and Cd from these three CPs, EMFs of Pb and Cd from precalcined CPs are estimated from the emissions from the kiln tail and head. Atmospheric EMF from a CP is either based on the clinker production (EMF_1 in eq 5 in the unit of mg·tonne^{-1} clinker) or the cement production (EMF_2 in eq 6 using unit of mg·tonne^{-1} cement), as follows

$$EMF_1 = \frac{M_{\text{Pb or Cd}} \times 1000}{M_{\text{clinker}}} \quad (5)$$

$$EMF_2 = \frac{M_{\text{Pb or Cd}} \times 1000}{M_{\text{cement}}} \quad (6)$$

where $M_{\text{Pb or Cd}}$ is the amount of Pb or Cd emitted into the atmosphere per day (g·day^{-1}), which is calculated by the total amount of PM emissions and the Pb or Cd concentration in kiln head/tail dust; M_{clinker} is the daily output of clinkers (tonne·day^{-1}), and M_{cement} is the daily output of cement products (tonne·day^{-1}).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01329.

Basic information of the studied CPs; more detailed information of daily input and output quantities of different materials in the three CPs; and atmospheric EMFs of Pb and Cd for the three studied CPs (PDF)

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Author Contributions

Z.L. involved in the conception of the study. Z.L., L.Y., and G.H. performed the field investigation. X.L., G.S., Y.H., G.W., L.Y., and G.H. were involved in the experimental analysis. Y.H. wrote the main manuscript. J.L. and Z.L. edited and revised the manuscript. All authors have read and approved the final manuscript.

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Notes

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