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ANALYSIS OF POLLUTION CHARACTERISTICS OF ORGANIC AIR POLLUTANTS IN NEW DRY PROCESS CEMENT PRODUCING

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ABSTRACT

Cement industry is a large coal-burning, but also to produce coal-based VOCs is one of the sources. VOCs are one of the important precursors for the formation of fine particles of PM2.5. In order to obtain the pollution characteristics of organic air pollutants in the production of cement industry, in order to ensure the validity of the data. This article select the nearest cement plant in Hebei LuQuanDingXin(A plant) 1 line rotary kiln (clinker production line of 2500 t / d) and 2-wire rotary kiln line 1 (3000 t / d) and GaoCheng cement (B plant) NSP Rotary Kiln (4000 t / d) as the research object.

The organic pollutants emitted from the cement production were detected and the particulate matter in the flue gas was sampled. The organic pollutants in the particulate matter were detected and the characteristics of the organic pollutants in the cement industry were analysed.

1. INTRODUCTION

The air pollutants produced by dry-process cement plants mainly include gaseous pollutants and VOCs in particulate pollution. Table 1 shows the main sources of pollution and the main categories of dry-process cement plants.

Table 1: Main pollution sources and types of cement plants

Classification	Pollutant pollution factor	Source Classification	position
Organic gaseous pollutants	VOCs	Point source	Kiln flue exit
particulates	TSP	Point source	Kiln flue exit
	PM2.5	Surface source	Production plant

In this study, the main items of the study of organic air pollutants are as follows [1]:

(1) Kiln tail emission characteristics of particulate matter. Collection of cement kiln tail chimney of the particulate matter concentration and analysis of particulate matter VOCs; collection of non-organized around the cement plant emissions of fine particles and analysis of fine particulate matter VOCs;

(2) The characteristics of flue gas emissions. The flue gas of cement kiln tail chimney was collected by Suma tank and the VOCs were analysed by GC-MS.

2. Sampling Plan for Organic Air Pollutants

2.1 Sampling point location

Sampling and testing of organic air pollutants and particulate matter should be selected strictly in accordance with the national standard "Emission Standard for Air Pollutants in Cement Industry" (GB 4915-2004).

Combined with the actual scene, select a representative sample points.
(1) Flue gas discharge port
In the kiln chimney monitoring mouth to collect smoke and smoke.

(2) The surrounding environment monitoring
In the source downwind (2 to 50 meters range) concentration of the highest point (down to the maximum concentration of the landing area to capture the maximum pollution characteristics of the principle) set up a monitoring point, collecting fine particulate matter.

2.2 Sampling time

Instantaneous collection of 24h particulate pollutants from each flue gas port through the Soma tank. Atmospheric fine particulate matter in the surrounding area of the factory was 3, and the effective number of each sample was 3.

2.3 Experimental apparatus and materials

Table 2: Experimental apparatus and materials

Project	Sampling equipment	Sampling material
Smoke and dust	Wuhan Tianhong dust particles sampler	Quartz filter cartridge
Smoke	Intech Soma tank system	
Atmospheric fine particles	Wuhan Tianhong flow of atmospheric particulate matter sampler	Switzerland MUNKTELL quartz filter

2.2 Test methods

At the same time, in the three different cement kiln flue gas, dust non-organized around the plant, and VOCs were measured by collecting the PM2.5 of three typical new dry cement plants (A plant, B plant). Table 3 shows the analysis items, the monitoring methods and the instruments used [2].

Table 3: Analysis items, monitoring methods and instruments

Analyse the project	Monitoring methods	Analytical Instruments
Mass of particulate matter	HJ656-2013 "ambient air particulate matter (PM2.5) manual monitoring method (gravimetric method) technical specifications"	METTLER TOLEDO
VOCs	HJ 759-2015 "Determination of volatile organic compounds in the ambient air - Gas chromatographic-mass spectrometry"	Shimadzu, GCMS-QP 2010 Plus

(1) Method for the determination of VOCs in flue gas from chimneys of cement kilns

Refer to "Ambient Air Volatile Organic Compounds Determination Tank Sampling / Gas Chromatography-Mass Spectrometry" HJ 759-2015. The flue gas samples were collected by sulmer tank with inner wall energization. The samples were condensed by cold trap and analysed by thermal analysis. The samples were separated by gas chromatography and detected by mass spectrometer [3]. Quantitative analysis was performed by qualitative and quantitative internal standard method comparing with reference material mass spectrometry and retention time.

Using the method of instantaneous sampling, after cleaning and pumping into a vacuum 3.2L Soma tank to the sampling point. After installation of the filter, through the 2-meter-long wall of the inertia of the copper pipe into the chimney depth sampling (with absorbent cotton to block the sampling port to prevent air interference), open the sampling tank valve to start sampling. After the pressure in the tank is the same as the atmospheric pressure at the sampling point, close the valve and seal with the sealing cap. Record the sampling time, location, temperature, humidity, atmospheric pressure.

The prepared sample was connected to a gas cold trap concentrator. Take 400mL sample concentration analysis, while adding 50.0mL standard internal standard gas, according to the following instrument conditions were determined. After the sample collection, to ensure that the valve is completely closed, and sealed with a sealing cap sampling port sampling, isolated from the outside gas.

Cold trap concentration instrument conditions:
Temperature: 100 ℃; baking temperature: 150 ℃; baking time: 15min; temperature:

Time: 5 min; analysis temperature: 180 ℃; analysis time: 3.5 min; baking temperature: 190 ℃; baking time: 10 min / min; 15min;

Three-stage focusing: focusing temperature: -160 ℃; analysis time: 2.5min; baking temperature: 200 ℃; baking time: 5min.
Transmission line temperature: 120 ° C.

Gas Chromatography-Mass Spectrometry conditions include gas chromatographic conditions and mass spectrometric conditions.

Gas chromatography analysis conditions:

Capillary column: Agilent VF-624MS, 60m x 0.25mm, 1.4um film thickness (6% cyanopropylphenyl-94% dimethyl polysiloxane fixative);

The temperature was raised at the initial temperature of 35 ℃ for 5min and then raised to 150 ℃ at 5 ℃ / min. After 7min, the temperature was raised to 200 ℃ at 10 ℃ / min and maintained for 4min.

Inlet temperature: 140 ° C. Solvent delay time: 5.6 min. Carrier gas flow rate: 1.0 mL / min.

Mass spectrometric analysis conditions:

Interface temperature: 250 ℃. Ion source temperature: 230 & lt; 0 & gt; C. Scanning method: standard sample using EI (full scan), the selected sample selected ion scan (SIM). Scanning range: 35 amu ~ 300amu.

Standard curve plotting:

(TO15) of 10 nmol / mol, and 50.0 mL of an internal standard standard gas of 100 nmol / mol (internal standard gas component was used as the internal standard gas) were separately extracted at 50.0 mL, 100 mL, 200 mL, 400 mL, 600 mL and 800 mL Mol / mol, 2.5nmol / mol, 5.0nmol / mol, 10.0nmol / mol, respectively) were prepared by the same method as follows: Nmol / mol, 15.0 nmol / mol, and 20.0 nmol / mol, with an internal standard concentration of 12.5 nmol / mol. The measurement was carried out successively from the low concentration to the high concentration according to the above instrument conditions. Laboratory analysis of each standard curve of VOCs good linear correlation coefficient in 0.9990 ~ 1 between [4].

Quality Assurance and Quality Control:

Blank: transport blank, the concentration of the target in the laboratory blank are lower than the method determination limit.

Determination of parallel samples: A parallel sample was analysed for each batch. The relative deviation of the target in the parallel sample is less than 30%.

Internal standard: The retention time of the internal standard in the sample is not more than 20s, and the range of the quantitative ion peak is between 60% and 140% for the continuous calibration or the calibration curve of the latest calibration curve.

Each clean 20 cans to take a can of high purity nitrogen analysis, to determine whether the cleaning process is clean.

(2) Determination of PM2.5 Concentration and VOCs in Non - tissue Emissions around the Plant

The PM2.5 was collected from the surrounding area of the plant, and the VOCs were quantitatively and quantitatively analysed by GC-MS to study the emission concentration of particulate matter and emission characteristics of the cement kiln.

PM2.5 samples were taken from the Wuhan Tianhong PM-50C sampler using a quartz filter. The mass concentration of the sample was obtained by differential method. The sampling time, location, temperature and atmospheric pressure were recorded.

In the sample collection, the first quartz filter, the filter tube placed in a muffle furnace bake 500 ℃ 2h, to remove impurities on the quartz filter. The quartz filters were then equilibrated in a constant temperature and humidity chamber at constant temperature (20.0 ± 0.4) ° C and constant humidity (38.5% ± 4.6% RH) for 48 hours to make them constant weight. Using a METTLER T / Weigh the weight of the quartz filter before and after sampling, and then calculate the PM2.5 mass concentration of the non-tissue emissions around the plant area according to the collected mass and the actual sampling volume [5].

The extract was centrifuged in a 250 mL Soxhlet extractor and extracted with 60 mL of dichloromethane for 12 h. The extract was concentrated on a rotary concentrator under reduced pressure to about 2 mL, and 20 mL of n-hexane the alkanes were concentrated to about 2 mL. The concentrated extract was then transferred to the column top of the prepared silica gel column. The column was eluted with 30 mL of n-hexane and 100 mL of n-hexane / methylene chloride in a volume ratio of 1: 1. The eluate was collected and transferred to the rotary evaporator to continue vacuum distillation concentrated to about 2mL, and then gently with high purity nitrogen gas to 1mL volume reserve.

The VOCs were quantitatively and quantitatively analysed by GC-MS. The gas chromatographic-mass spectrometer (Shimadzu, GCMS-QP 2010 Plus) was used to characterize and quantify the VOCs in PM2.5 samples collected from quartz membrane samples.

Standard curve drawing:

The concentrations of PAHs were 0.4, 1.0, 2.0, 4.0, 8.0 and 10.0 mg / L, respectively. The concentration of acenaphthylene (Ace) and phenanthrene (Phe) in PAHs were lower than that of quantitative detection lines. (BbF) and benzo (k) fluoranthene (BkF) were combined in the GC / MS reconstructed ion current diagram with the majority of the overlapping BbF and BkF, Together for quantitative analysis. In this study, the following 13 PAHs were studied: naphthalene (Nap), acenaphthene (Acy), fluorine (Flor), anthracene (Ant), fluoranthene (Pyr), benzo (a) anthracene Benzo (b, k), benzo (a), pyrene (BaP), benzo (g, h, i) pyrene (BghiP)) Anthracene (DahA), indeno (1,2,3-c, d) pyrene (Ind). Laboratory analysis of each standard curve of PAHs linear good correlation coefficient were between 0.9990 ~ 1.

Laboratory analysis of each C_{10}-C_{25} alkane standard curve of a good linear correlation coefficient ≥ 0.9990.

The quantitative SIMS of VOCs (PAHs, C_{10}-C_{25} alkane) was obtained by quantitative qualitative chromatogram and characteristic fragment ion, combined with NIST standard organic mass spectrometry library. According to the quantitative ion peak area, the external standard Legal quantity.

Quality Assurance and Quality Control:

Blank: transport blank, laboratory blank, solvent blank concentration of the target are lower than the method determination limit.

Determination of parallel samples: A parallel sample was analysed for each batch. The relative deviation of the target in the parallel sample is less than 30%.

(3) Determination of Dust Concentration and VOCs in Chimney of Cement Plant

Through the dust parallel sampler TH-880F, the pre-treated quartz filter cartridges were used to collect the soot at the same speed. The analysis method was the same with the above-mentioned non-organized PM2.5 concentration and the VOCs analysis method.

3. Results and discussion

3.1 VOCs in Flue Gas from the Chimney of Cement Plant

In order to ensure that the data of this study is representative, during the testing period, the production equipment of Dingxin Cement Plant and Gaocheng Cement Plant are in normal operation and the working conditions are stable. The concentrations of VOCs emitted from the flue gas after kiln dust removal are shown in Table 4 below.

Table 4. Emission concentration of VOCs in flue gas after dedusting of cement kiln (ng / m3)

NO	Target compound	A kiln plant 1 line	A kiln plant 2 line	B kiln plant 1 line
1	Dichloromethane	-	21.88	-
2	Hexane	-	10.18	-
3	Tetrahydrofuran	-	9.38	-
4	Cyclohexane	-	3.06	-
5	Carbon tetrachloride	-	-	214.15
6	Benzene	3.48	27.68	-
7	Dioxane	165.00	-	-
8	Dichloropropene	-	-	251.12
9	Methyl isobutyl	5.76	13.86	-
10	Methanone	-	4.83	1.91
11	Dichloropropene	4.33	-	-
12	Trichloroethane	69.11	65.79	-
13	2-Hexanone	-	-	-
14	Dibromochloromethane	25.00	-	-
15	Chlorobenzene	32.50	-	64.72
16	Ethylbenzene	192.9	-	503.90
17	Xylene	7.00	-	1.00
18	Styrene	55.71	-	-
19	Tetrachloroethane	192.68	-	-
20	Ethyl toluene	-	-	64.01
21	Trimethylbenzene	-	-	69.35
22	Trimethylbenzene	100.78	-	77.35
23	1,2-Dichlorobenzene	625.71	-	81.59
24	1,4-Dichlorobenzene	175.98	-	-
25	Benzyl chloride	251.88	-	-
26	Trichlorobenzene	32.14	-	128.02
	Total VOCs	933.04	156.83	1456.12

The monitoring results in Table 4 show that 26 VOCs were detected in 67 of the environmental standards HJ 759-2015, and the total emissions of VOCs in the 1st kiln line of the A plant was the highest (1933.04 ng / m3), with the largest concentration of dichlorobenzene , Which accounted for 32.37% of the total VOCs. Secondly, the total emissions of VOCs in the first kiln of B plant was 1456.12ng / m3, of which the largest was 2-hexanone, accounting for 41.95% of the total VOCs. The total emissions of VOCs in the second kiln of A plant is the lowest, 156.83ng / m3, of which the xylene content is the highest, accounting for 34.61% of the total VOCs. Benzene, dichlorobenzene, benzyl chloride, carbon tetrachloride, dichloropropene, trichlorobenzene, of which two of the VOCs emitted by the sampling points are dioxane, xylene, tetrachloroethane, trimethyl, Toluene and toluene are the key active components in VOCs.

Different kinds of VOCs play their respective roles in the migration and change of air pollution and the contribution rate of ozone generation potential. By comparing the types of VOCs in the new dry cement plant, the contribution rate of atmospheric pollution sources to the atmosphere in Shijiazhuang cement industry Such as providing theoretical and scientific basis. The concentration of VOCs in the gaseous pollutants in the cement plant and the concentration of each component are shown in Table 5. The comparison of the VOCs and the average volume fraction of the components in the cement plant gaseous pollutants is shown in Figure 1.

Table 5: Comparison of VOCs and Concentration of Components in Gaseous Pollutants of Cement Plant (ng / m3)

Sampling location	VOCs	Alkanes and derivatives	Olefins and derivatives	Benzene series	Ketones
A plant 1 line	1933.04	362.01	-	1496.16	74.87
A plant 2 lines	156.83	44.48	4.83	27.86	79.65
B plant 1 line	1456.12	214.15	253.02	988.95	0.00

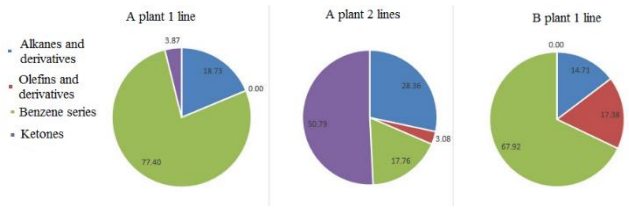

Figure 1: Comparison of VOCs and the average volume fraction (%) of gaseous pollutants in cement plant

From Table 5 and Figure 1 shows that the new dry cement plant gaseous pollutants in the VOCs can be divided into alkanes and derivatives, olefins and derivatives, benzene and ketones. Among them, chlorinated paraffins were the main constituents in alkanes and their derivatives. Chlorinated paraffins in the three sampling sites accounted for 10.19%, 13.95% and

14.71% of all VOCs. On the whole, the benzene series, alkanes and their derivatives accounted for the main components, while the A plant 2 lines have 50.79% ketones, B plant 1 line ketone below the detection line is not detected, A plant 1 line alkene low In the detection line, not detected. There is a certain difference between the volatile organic compounds at the end of the cement plant. The reason may be that the content of VOCs in the cement plant is low, and the collection efficiency of the existing detection method is not high, which needs to be improved.

3.2 Concentration around the plant fugitive emissions of PM2.5

Table 6: The cement kiln sampling point of PM2.5 concentration

Business	Sampling point location	Mass concentration (ug/m^3)
A plant	1 line	24.8996
A plant	2 line	63.7097
B plant	1 line	83.4671

Filtration sampling, VOCs below the detection line, not detected.

4. Conclusion

After the experiment, the conclusions are as follows:

(1) 26 kinds of 67 kinds of environmental standard HJ 759-2015 were detected in the flue gas at the chimney of the cement plant. The VOCs in line 1 were mainly dichlorobenzene, accounting for 32.37% of the total VOCs. The main components of VOCs in B line were the 2-hexanone, accounting for 41.95% of the total VOCs. The xylene content of the VOCs in line 2 of the A plant is the highest, accounting for 34.61% of the total VOCs.

(2) New dry process cement plant VOCs are mainly alkanes and derivatives, alkenes and derivatives, benzene and ketones, of which alkanes and their derivatives are mainly chlorinated alkanes.

Through comparison and analysis, we can see that the emissions of organic air pollutants in cement plant flue gas and particulate matter are lower than inorganic air pollutants, and the typical characteristic of air pollutants emitted from flue gas is NOx.

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