

# CO-PROCESSING AGED REFUSE IN A BENCH-SCALE SIMULATED CEMENT KILN DEVICE

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## Introduction

Aged refuse that is bio-stabilized through years in the landfill can also be called stabilized waste or mineralized waste. Substances such as kitchen waste, plants, and paper in the original municipal solid waste (MSW) are basically decomposed into soil after long-term landfill, so the nature of the aged refuse is basically stable. Aged refuse can be divided into two categories according to the size of the particle: fine-grained (<15mm) and coarse-grained (>15mm). The main combustible components of coarse-grained aged refuse are substances that can be recycled and utilized such as plastics, textiles, and woods<sup>[1,2]</sup>. According to statistics, the total aged refuse in the world reached 2 billion tons, of which at least 200 million tons of aged refuse exist in China<sup>[3]</sup>. The landfill capacity of the existing domestic landfills tends to be saturated, and the combustible components of aged refuse (CCAR) have a higher calorific value than the MSW. Mining aged refuse from landfills and disposing of it properly can make room for landfilling more domestic waste. The key is how to achieve energy efficiently and clean utilization of CCAR.

According to the research results, cement kiln co-processing solid waste technology requires a long residence time and high combustion temperature. Flue gas disturbance is beneficial to the complete incineration and decomposition of waste. An alkaline environment can inhibit formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs). The cement kiln firing system and the exhaust gas treatment system have high adsorption<sup>[4]</sup>, sedimentation, and dust collection characteristics, and the PCDD/Fs can be solidified in the clinker without causing re-diffusion of PCDD/Fs.

With regard to the co-processing of CCAR in cement kilns, the pollution profiles and mechanisms, especially with respect to PCDD/Fs, have not yet been studied, although many field investigations of flue gas emission levels and profiles of PCDD/Fs in cement kilns have been done. It is important to study these issues to ensure sustainable development of CCAR co-processing in cement kilns.

## Materials and methods

**Materials** The aged refuse was sampled at the landfill of Tianziling Waste Treatment Plant in Hangzhou, Zhejiang Province, China. The designed use period of this landfill was 13 years, and it holds more than 9 million tons of solid waste from Hangzhou and surrounding municipal areas. After screening of aged refuse, samples of fine-grained refuse (grains smaller than 15 mm) and samples of coarse-grained refuse (grains larger than 15 mm) were obtained. We studied mainly the combustible components (plastics, textiles, and woods) in coarse-grained aged refuse. The landfill time is about 11 (S1), 15 (S2), and 19 years (S3), respectively. The fractions of the three combustible components are shown in **Fig. 1**:

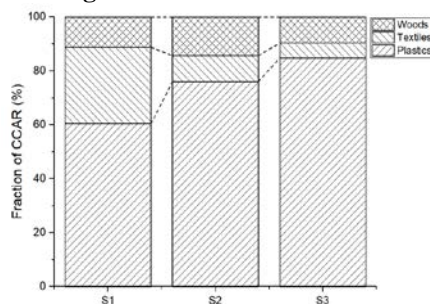


Fig. 1. Fraction of combustibles in the CCAR samples

**The bench-scale simulated cement kiln device** In the new dry-process cement production system, the cement clinker is produced in three main stages: (1) the high temperature incineration stage, (2) the precalciner burner and cyclone preheater stage (850-250°C), and (3) the post-preheater stage. On the one hand, a lot of scholars have verified that the second stage is the main area for pollutant formation. On the other hand, the main components of CCAR are plastics, textiles, and woods, the content of heavy metals and chlorine are relatively

high, and co-processing of CCAR may affect the normal operation of the cement kiln and increase PCDD/F emissions. So, a bench-scale simulated cement kiln device (**Fig. 2**) was designed and manufactured to simulate the precalciner burner and cyclone preheater stages, and to study the formation of pollutants such as PCDD/Fs in the flue gas. The overall height of the device is about 1.8 m, the height of the precalciner burner is about 0.7 m, and the total height of the five-stage cyclone preheater is 0.7 m. It is equipped with a temperature controller to control the temperature in the precalciner burner and keep it above 850°C. There are two automatic screw feeders that can achieve continuous feed, which will be used to study the effects of adding CCAR from different locations on the formation of pollutants such as PCDD/Fs. The device has a total of 6 sampling holes for collecting flue gas from each stage of the cyclone and the precalciner burners. A raw meal bucket and an ash bucket are used to collect raw meal and ash.

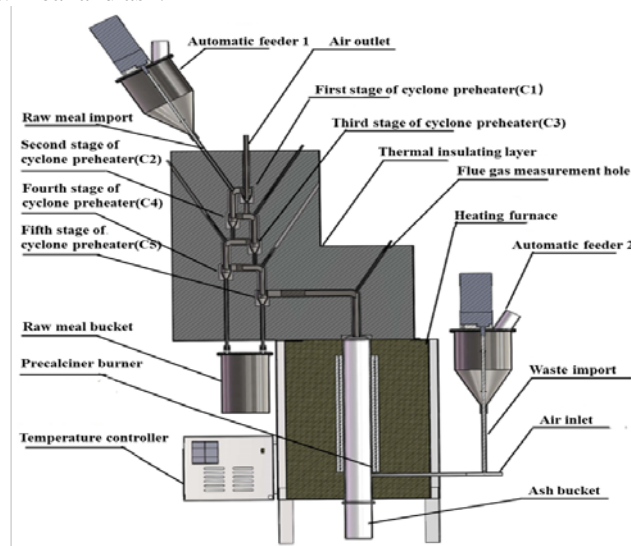


Fig. 2. Simulated cement kiln device

*Experimental design* The experimental conditions are presented in **Table 1**. Each group is carried out twice to ensure the accuracy and stability of the experimental results. The temperature of the precalciner burner was controlled at 850°C and of the first stage of the cyclone separator (C1) was about 320°C measured by a thermocouple during the experiment.

Experiments in groups A, B, C, D and E were conducted to learn the possible factors that influence pollutant formation from different CCAR and different adding positions. Experiments in group A can be regarded as controls. First, the pollution formation from a mixture of 5% sample 1 (S1) and raw meal was tested in test B to investigate the role of different CCAR in pollution formation. Then a similar test was conducted on a mixture of 5% sample 2 (S2) and raw meal in test C. Finally, a mixture of 5% of sample 3 (S3) and raw meal was tested in test D. Test groups C and E are conducted to determine the influence of adding CCAR in different positions (automatic feeder 1 and 2) on pollution formation.

Heavy metals in the flue gas were absorbed by a solution of 5% nitric acid and 10% hydrogen peroxide and HCl was absorbed by a 0.1 mol/L sodium hydroxide solution. PCDD/Fs were collected by an XAD-II resin and toluene solution, and the toluene solution was placed in an ice bath. The total device inlet flow rate was 20 L/min.

Table 1 Experimental conditions

Group	Reactants	Feeders	Quantity	Flue gas	Time
A	Raw meal	Automatic feeder 1	20g/10min	1L/min	30min
B	5% S1+Raw meal	Automatic feeder 1	20g/10min	1L/min	30min
C	5% S2+Raw meal	Automatic feeder 1	20g/10min	1L/min	30min
D	5% S3+Raw meal	Automatic feeder 1	20g/10min	1L/min	30min
E	Raw meal/S2	Automatic feeder 1/2	19g/10min/1g/10min	1L/min	30min

PCDD/Fs analysis

The cleanup procedure of PCDD/Fs samples was conducted according to the USEPA 1613 method. A DB-5ms (60 m × 0.25 mm I.D., 0.25 μm film thickness) capillary column was used for separation of the different PCDD/Fs congeners. All tests were conducted in duplicate; the arithmetic average of the results was further used in our analysis of suppression. Target compounds were the 17 toxic 2,3,7,8-substituted PCDD/Fs congeners.

## Results and discussion

### *The analysis of heavy metals and HCl in C1 flue gas*

It can be seen from **Table 2** that the content of the volatile heavy metal Hg and the semi-volatile heavy metals As, Pb, and Cd in C1 flue gas is low. Except for group B, the two types of heavy metal concentrations before and after co-processing of CCAR is in the same range. The concentrations of low-volatility heavy metals such as Cr, Cu, and Sn were high. The concentrations of such heavy metals increased (from 1.62 mg/m<sup>3</sup> to 1.99, 5.76 and 6.42 mg/m<sup>3</sup>, respectively) significantly after co-processing of CCAR, because the concentrations of these heavy metals CCAR are high, especially Cr and Cu, which is consistent with the results reported by researchers who investigated cement kiln co-processing of waste tires. In addition, most of the low-volatility heavy metals, such as Cr and Cu, will be solidified in the cement clinker, and the change in concentration of these heavy metals will affect the cement compressive strength. HCl is mainly derived from the combustion of PVC substances and inorganic chlorides present in CCAR. In the case of full combustion, the chlorine in the PVC can be completely converted into HCl. The release of HCl is increased in the presence of moisture and sulfur, and about 50-60% of NaCl is converted to HCl.

Except for Group A and Group E, the emissions of HCl by other groups are higher than the limit of 10 mg/m<sup>3</sup> specified in the national standard of China (GB 30485-2013). Because the main CCAR components are plastics, textiles, and woods, the content of Cl is high, and the flue gas at the C1 has not passed through the air pollution control device. In addition, the existence of a large number of Cl will cause much harm. First of all, the existence of HCl, O<sub>2</sub>, and precursors, at an appropriate temperature (250-600°C), will lead to synthesis of PCDD/Fs. Second, chloride, sulfate, and their compounds are responsible for the formation of low-temperature melt and crusts, which can cause different degrees of blockage in the kiln. Finally, the excessive presence of Cl in cement will cause freezing and thawing of concrete and the corrosion of steel bars in concrete, affecting the service life and safety of concrete buildings.

Table 2 Concentrations of heavy metals and HCl in C1 flue gas (mg/m<sup>3</sup>)

No.	As+Pb+Cd	Cr+Cu+Sn+Mn+Ni+Be	Hg	HCl
A	0.17	1.62	0.010	6.81
B	0.38	1.99	0.040	11.31
C	0.15	5.76	0.009	11.10
D	0.17	6.42	0.016	12.58
E	0.19	3.21	0.007	7.36

### *The formation characteristics of PCDD/Fs in C1 flue gas*

The PCDD/F formation increased as CCAR was added (results are shown in **Table 3**). The concentration of PCDD/Fs increased in groups B, C, and D compared with group A, from 5.16 ng/m<sup>3</sup> to 5.82, 7.91, and 7.44 ng/m<sup>3</sup>, respectively, and the corresponding TEQ value increased from 0.33 ng I-TEQ/m<sup>3</sup> to 0.56, 0.69, and 0.72 ng I-TEQ/m<sup>3</sup>, respectively. The results show that the co-processing of CCAR does promote the formation of PCDD/Fs, which is consistent with the results reported by other research. The toxic equivalents are much higher than the limits (<0.1 ng I-TEQ/m<sup>3</sup>), because no air pollution control system was used in this simulated device.. Meanwhile, the weight average level of chlorination (Cl-PCDD/Fs) decreased slightly, indicating that the chlorination of PCDD/Fs was inhibited and lower chlorinated PCDD/Fs are synthesized; this is maintained at around 6.5 basically.

In terms of raw meal, the ratio of PCDFs/PCDDs is 1.7, and it is indicated that de novo synthesis was the dominant PCDD/F formation pathway for the cement kiln. The ratio of PCDFs/PCDDs increased from 1.7(Group A) to 1.98 (Group B), 3.83 (Group C), and 3.45 (Group D) after co-processing of CCAR, indicating that co-processing of CCAR in a cement kiln further promotes the de novo synthesis of PCDD/Fs. It is well known that CuCl<sub>2</sub> is an important metal catalyst for de novo synthesis. S1 (11 years), S2 (15 years), and S3 (19 years) have different compositions of combustible components due to different landfill age, and the heavy metal concentration (especially Cu and Fe) and chlorine content are also different, which is the main reason for the difference in PCDD/Fs produced in Group B, Group C, and Group D. The overall trend is that CCAR with more chlorine and Cu is likely to generate more PCDD/Fs when co-processing.

Comparing the data of Groups C and E, it can be seen that CCAR has different impacts on the formation of PCDD/Fs when input from different feed inlets. The addition of CCAR at the raw meal preparation system produces more PCDD/Fs than addition at the precalciner burner. The PCDD/F concentrations are 7.91 and 7.41 ng/m<sup>3</sup>, respectively, corresponding TEQ values of 0.69 and 0.55 ng I-TEQ/m<sup>3</sup>, respectively. The reason may be that the temperature at the precalciner burner is 850-900°C, the CCAR is more likely to be burned completely, and less PCDD/Fs are formed. It is also confirmed that the main formation area of PCDD/Fs in the cement kiln is the cyclone preheater at the temperature range 250-500°C, which verifies previous work of other researchers who believe that this area is the major area for PCDD/F formation<sup>[5,6]</sup>.

Table 3 Concentration and distribution of 17 2,3,7,8-substituted-PCDD/Fs in groups

	A	B	C	D	E	Unit
PCDDs	1.91	1.95	1.64	1.67	3.59	ng/m <sup>3</sup>
PCDFs	3.25	3.87	6.27	5.77	3.82	ng/m <sup>3</sup>
PCDD/Fs	5.16	5.82	7.91	7.44	7.41	ng/m <sup>3</sup>
PCDF/PCDD	1.70	1.98	3.83	3.45	1.07	/
Cl-PCDD	7.39	6.72	6.34	6.47	7.53	/
Cl-PCDF	6.71	6.34	6.43	6.41	6.38	/
Cl-PCDD/Fs	6.97	6.47	6.41	6.42	6.94	/
I-TEQ	0.33	0.56	0.69	0.72	0.55	ng I-TEQ/m <sup>3</sup>

#### Principle component analysis

Principal component analysis (PCA) was used to learn the similarities and differences of congener distributions among various samples (Fig. 3). The matrix is used to statistically investigate the signatures representing 10 PCDD/F homologue groups of all 5 samples. Before statistical analysis, no data transformation was performed. Factor 1 and factor 2 separate all samples into two clusters (A and B), which separately explains 65.5 and 22.1% of the total variance. PCA shows that homologue profiles of group E are closer to those of group A, and homologue profiles of groups B, C, and D are similar. In general, results of clustering obtained from PCA are in accordance with the former discussion. This further verified that the CCAR is completely burned at the precalciner burner, which has little effect on the distribution of congeners (E is compared with A), but is added at the raw meal preparation system, which significantly influences the distribution (B, C, and D is compared with A).

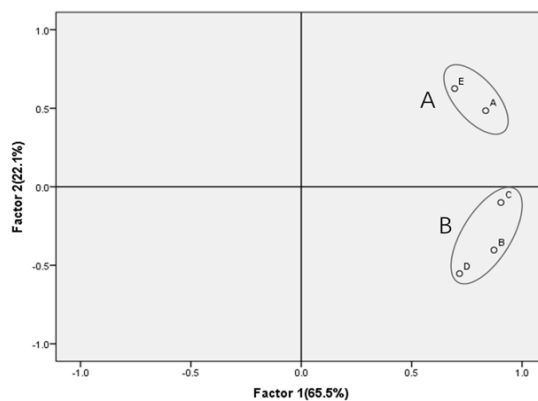


Fig. 3. Principle component analysis of homologue profiles

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