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Research and Application of Detoxification and Harm Reduction Technology for Fly Ash from Refuse Incineration

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Abstract: *Municipal solid waste incineration fly ash (MSWIFA) is rich in chlorine salt, carbon component, heavy metal and dioxin (PCDD/Fs) with high concentration. It has been listed in the national hazardous waste list. It must be safely and innocuous treated before its resource utilization and landfill. There are few studies on the pollution characteristics and treatment of msi fly ash in Macao. The pollution characteristics of toxic and harmful substances such as heavy metals and dioxins in msi fly ash were introduced in this paper. The research status of many fly ash detoxification and harm reduction technologies such as chemical agent stabilization method, cement solidification technology, heat treatment technology, flotation technology and microwave pyrolysis technology were analyzed. The research progress and existing problems in the treatment of heavy metals and dioxins in msi fly ash by the latter three technologies were elaborated emphatically, and their application prospects were prospected.*

Keywords: *MSWIFA, Heavy metals, Dioxins, Detoxification and harm reduction*

1. Introduction

In recent years, with the rapid development of national economy, urbanization process intensified, the quality of life of the people continues to improve, the output of urban solid waste (MSW) is also increasing, many large and medium-sized cities in China are facing the crisis of "garbage siege". The incineration can make the garbage sterilized at high temperature to achieve innocuity and volume reduction, and the waste heat from the incineration can supply heat and generate electricity, thereby achieving the purpose of resource utilization. According to the latest "Statistical Yearbook of Urban and Rural Construction in 2021" and "Statistical Yearbook of Urban Construction in 2021" released by the Ministry of Housing and Construction, by the end of 2021, domestic waste removal and transportation volume in the country was about 250 million tons, up 5.9% year-on-year. There are currently 583 domestic waste incineration plants, with the domestic waste incineration capacity reaching 720,000 tons/day, with the incineration capacity accounting for 68.1%. Fly ash will be produced after garbage incineration, accounting for about 2%–5% of the mass of the original garbage. Fly ash is usually rich in high concentrations of unintentionally released persistent organic pollutants (UP-POPs) such as dioxins and toxic components such as heavy metals, which is listed in the National Catalogue of Hazardous Wastes (HW18) by many countries, including China, and it is stipulated that fly ash must be harmless before it can be safely landfilled or recycled.

In this paper, combined with the production of MSWI fly ash and its pollution characteristics rich in chlorine, carbon, heavy metals and dioxins, a variety of MSWI fly ash detoxification and harm reduction treatment technologies were introduced, and their environmental and economic benefits in mswi fly ash detoxification and harm reduction treatment were evaluated.

2. Generation and pollution characteristic of MSWI fly ash

2.1. Generation of Mswi Fly Ash-A Case Study of Macau

Macau produces about 500,000 tons of municipal waste every year, and the amount of fly ash produced is 20,000 to 30,000 tons/year [1] by incineration at the refuse incineration center located in Taipa Beian Industrial Zone in Macao, figure 1 below shows the Macao waste incineration plant incineration process. That is, municipal vehicles carrying garbage must be weighed and automatically recorded by a computer, the garbage is discharged and stored in a garbage pit, the garbage is twisted, cut and crushed, and then put into a feeding funnel by an arm-gathering crane, and an incinerator is a mitsubishi martin reverse-pushing mechanical grate furnace; The flue gas generated in the incineration process is injected with lime slurry in a neutralization reactor to neutralize acid gas in the flue gas, and activated carbon is sprayed at the same time to adsorb heavy metals and dioxins in the flue gas; and finally, the flue gas passes through a bag filter to remove dust particles in the flue gas and then is discharged through a chimney, and the discharged tail gas meets European union standards.

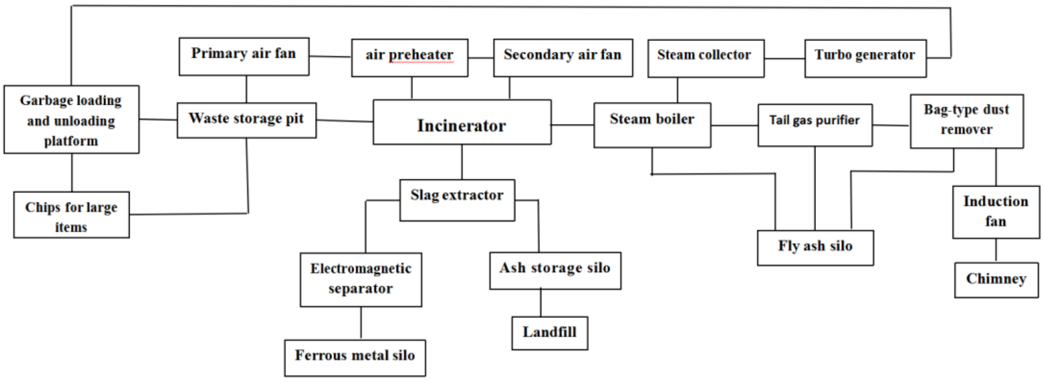

Figure 1: Process flow of Macao Refuse Incineration Plant

However, the terminal process described above for controlling dioxin emissions may be accompanied by the production of significant amounts of MSWI fly ash that is considered hazardous waste (China Classification Code: 772–002-18). The mass balance of dioxins generated throughout the MSWI system indicates that approximately 69.9%-91.5% of the total dioxins can be efficiently enriched into the MSWI fly ash. In addition, it has been reported that the annual dioxin emissions from municipal solid waste fly ash are almost 425 times the flue gas emissions even if the landfill disposal criteria are fully met (GB16889-2008 3.0μg I-TEQ/kg).

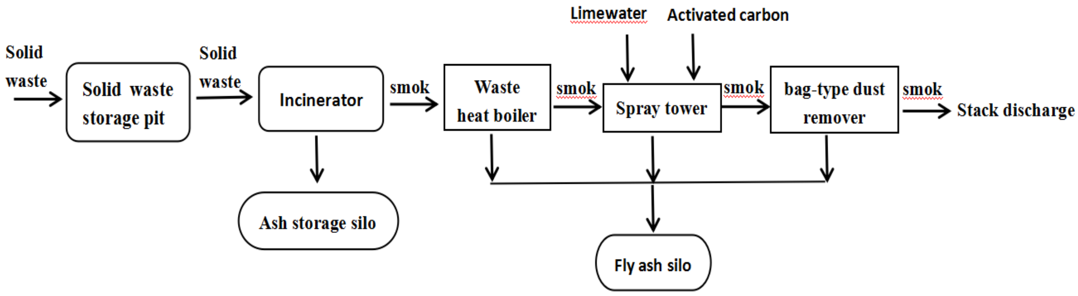

Figure 2: Fly ash production process of refuse incineration plant

The collection method of fly ash from garbage incineration plant is: the fly ash generated from the three links of the mixing waste heat boiler, spray tower and dust collector is collected together, as shown in Fig. 2 In the spray tower link, the acid gas, heavy metal, organic poison and other pollutants in the fly ash are effectively removed by adding lime water and activated carbon. However, the fly ash additionally contains reactants that react with the acid gas in the flue gas (such as CaCl2 and CaSO4), and some alkali that is added in an excessive amount and does not react, such as Ca(OH)2. The cyclone dust collector is positioned closest to the garbage incinerator, and the particle size of the collected granular material is larger than that of the granular material collected by the bag type dust collector and the electrostatic dust collector due to the limitation of collection efficiency; Generally, the granular materials collected here are fine powders with the water content usually less than 1%, mainly composed of inorganic substances and heavy metals after combustion. The bag-type dust remover usually has high collection efficiency and can remove the ultra-fine particles not removed in the first two links[2] .

2.2. Characteristics of Mswi Fly Ash Pollution

2.2.1. Basic Chemical Composition of Mswi Fly Ash

The main chemical components in MSWI fly ash are shown in Table 1[3-7] below. It can be seen from the table that the components of fly ash from municipal solid waste incineration in different cities are similar, with the main components being calcium compounds, silicon compounds and aluminum compounds, followed by potassium, sodium, sulfur and other compounds. However, the content of each component in fly ash from different cities varies greatly, with the content of calcium compound ranging from 18.61% to 58.42%, with the maximum value being three times the minimum value; The silicon compound content is 3.75-38.26 percent, with a difference of 10 times; The content of other compounds also has a difference of several times or even more than ten times, for example, the content of magnesium compound in fly ash from Hangzhou is 13 times that in fly ash from Shenzhen. On the whole, the content of each component in mswi fly ash is in a relatively low value, and the calcium content is relatively high, which is due to the excessive amount of CaO injected by mswi power plant to better neutralize the acid gas in the flue gas during the mswi process. the high concentration of CaO can maintain a high pH value of the fly ash, which is conducive to stabilizing the heavy metals contained therein. Secondly, in order to efficiently remove dioxins, PCBs and other toxic organic substances in the flue gas, a large amount of activated carbon (PAC) needs to be sprayed, resulting in a large amount of carbon component in the MSWI fly ash.

Table 1: Composition of Fly Ash from Different Cities (%)

	CaO	Al2O3	K2O	MgO	Na2O	SO3	Fe2O3	P2O5	SiO2
Macao	58.42	1.65	4.11	1.72	3.51	6.58	2.44	0.77	3.75
Guangzhou	30.57	5.74	4.18	2.09	4.49	6.91	2.26	1.18	15.92
Shanghai	33.37	7.42	-	2.72	-	12.03	4.01	-	24.5
Hangzhou	18.61	14.09	2.21	4.85	4.12	-	5.59	-	38.26
East China	23.62	8.52	5.99	-	2.29	14.6	5.27	2.64	25.11
Shenzhen	18.79	1.34	16.89	0.37	6.31	14.13	0.89	0.58	4.12

Note:-indicates not detected

2.2.2. Heavy metal pollution in fly ash

During the incineration process of municipal solid waste, a large number of heavy metals volatilize into the flue gas due to high temperature and are finally enriched

In fly ash, most of the heavy metals are distributed in fly ash accounting for 3%–5% of the total incineration waste. The contents of heavy metals Pb, Zn, Cd and Cu in fly ash are too high or have leaching toxicity, which may enter the soil due to improper disposal. Heavy metals in the soil cannot be degraded by microorganisms and will be enriched, or even converted into more toxic organometallic compounds (such as methylmercury). Once ingested by organisms, they can be amplified by the food chain and finally endanger human beings. When heavy metals are caught in the rain and snow, they will migrate to pollute the groundwater and thus bring more serious harm[2]. The main hazards of several heavy metals are listed in Table 2[8-10].

Table 2: hazards of heavy metals in fly ash

Heavy metal	Harm
Lead	It affects the nervous system of the human body, thereby damaging nerve endings, and simultaneously hinders brain development and hematopoietic function.
Zinc (Zn)	Higher content will lead to poor development, metabolic disorders and other adverse symptoms.
Mercury	Mercury poisoning mainly damages the nerves of people. High mercury content in the body may lead to the occurrence of mental illness.
Nickel	Causing central circulation and respiratory disorders and inducing leukemia, etc.
Arsenic	Accumulation in human body can cause cardiovascular toxicity and nervous system toxicity such as peripheral neuritis.
Cadmium (Cd)	Damage to the human kidney and liver function, can form cadmium protein with protein, inhibit many enzyme system, cause anemia, etc.

①Formation mechanism of heavy metals in fly ash

Metal and their compounds are evaporate into that flue gas during the refuse incineration process, and the flue gas is cooled from a high temperature(800 deg c-1000 deg c) furnace enters a flue with lower temperature (400 deg c-500 deg c), and rapid cooling leads heavy metals to be condensed from the flue gas to form discrete metal particle aerosol or adsorb on the surface of fly ash particles to obtain concentration. The main behaviors of heavy metals in this process include homogenization of fine flue gas particles and heterogeneous deposition on the fly ash surface[11] .

②Sources of heavy metals in fly ash

The heavy metals in fly ash are derived from the combustion and evaporation of heavy metals and their compounds contained in domestic waste during incineration. The heavy metal content of municipal solid waste is the main factor that determines the heavy metal content in fly ash. Municipal solid waste contains a variety of artificial and natural substances, and almost all of these components contain a certain amount of heavy metals, such as Cu, Zn, Pb, Cd, Cr, Hg, Ni, etc. The main sources and existing forms of heavy metals in waste incineration fly ash are shown in Table 3 [12]below.

Table 3: sources and existing forms of heavy metals in fly ash

Heavy metal	Existing form	Source
Cu	CuO、Cu(OH)2、CuCl2	Metal products, glass and ceramic waste
Zn	ZnSO4 ·7H2O、ZnO、ZnCl2	Waste such as batteries, coatings, and preservatives
Pb	PbCO3、PbO、PbCl2	Battery, pesticide, coating and other waste
Cd	CdO、CdCl2、Cd(OH)2	Battery, metal, PVC, coating, plastic and other waste
Cr	Cr2O3、CrCl2	Waste such as paint, leather, metal surfactant, etc
Hg	HgCl2	Fluorescent lamp, mercury-containing batteries, electrical supplies, paint, plastic, waste paper

③Migration and transformation of heavy metals in fly ash

Due to the properties of heavy metals (such as boiling point), garbage components (chlorine, alkali metal content, etc.), the furnace operation environment (temperature, time, atmosphere) and other factors, heavy metals migration and transformation, distribution in the flue gas, fly ash and bottom ash. The chemical forms of heavy metals in MSWI fly ash are determined by the behavioral characteristics of heavy metals. The species and speciation of heavy metals in MSWI fly ash are variable, which depends on factors such as the type of incinerator, temperature, operating conditions and the components of municipal solid waste. The metal content in fly ash is related to the incineration temperature and the boiling point of various heavy metal substances. Heavy metal substances with the boiling point lower than the incineration temperature can be volatilized completely and enter the flue gas. Under the high-temperature incineration condition, chlorine can promote the conversion of most heavy metal oxides to chloride, thus affecting the migration and conversion of heavy metals. This is because the chlorides such as CdCl2, ZnCl2, PbCl2 and CuCl2 have lower boiling points and are more easily gasified. The results of main migration and transformation paths of heavy metals during incineration are shown in Table 4 [13]. The lower the boiling point of heavy metals, the more easily they condense and the higher the content of fly ash.

Table 4: Main migration and transformation paths of heavy metals during incineration

Heavy metal	Main existing form	Boiling point/℃	Transformation process
Cu	Cu	2573	Cu→CuCl2→CuCl；Cu→CuCl
	CuCl2	993	
	CuCl	1366	
Zn	Zn	907	ZnO→ZnCl2
	ZnO	1800	
	ZnCl2	732	
Pb	Pb	1740	PbO→PbCl2
	PbO	1470	
	PbCl2	950	
Cd	Cd	765	CdO→CdCl2
	CdO	1385	
	CdCl2	960	
Cr	Cr	2670	Cr→CrCl3
	CrCl3	1300	

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The speciation of heavy metal chloride results in the occurrence of heavy metal elements in fly ash in exchangeable state (such as chloride salt) and carbonate combined state (such as carbonate and hydroxide). This result is consistent with the speciation distribution results of heavy metals in MSWI fly ash, as shown in Fig.3 The exchangeable state and carbonate binding state of heavy metals Cd, Cu and Pb are relatively high, followed by Zn and Cr. The contents and leaching concentrations of heavy metals in MSWI fly ash are shown in table 5. The heavy metal contents and leaching concentrations are in the order of Zn > Pb > Cu> Cd/Cr > Ni > As > Hg. among them, the leaching concentrations of Cd, Zn, and Pb exceed the limits of gb5085. 3–2007 "identification of leaching toxicity in identification standards for hazardous wastes" and become the heavy metals that need to be focused on in fly ash treatment and disposal.

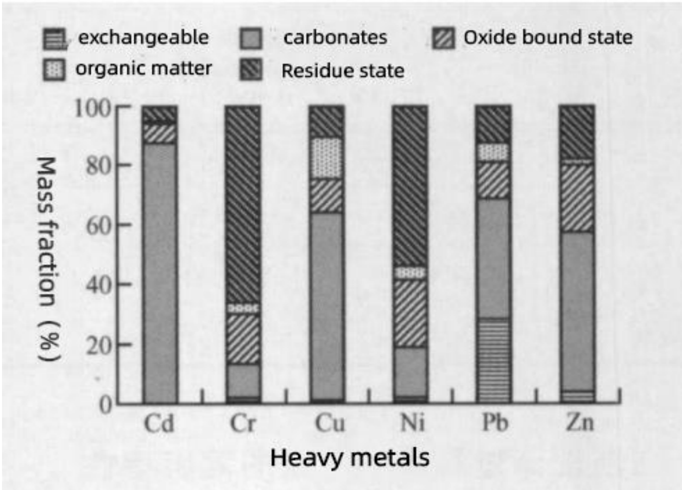

Figure 3: Morphological distribution of heavy metals in mswi fly ash [14]

Table 5: Heavy Metal Content and Leaching Concentration in Fly Ash from MSWI (Based on HJ/T 300-2007)

Heavy metal	Cu	Zn	Pb	Cd	Cr	Ni	Hg	As	reference
Total content /(mg/kg)	842.80	7126.5	2130.23	194.33	291.65	15.78	25.52	/	[2]
Leaching concentration/ (mg/l)	16.46	135.70	18.15	9.62	0.81	0.01	0.096	/	
Total content/ (mg/kg)	757.0	7640	1830	191.0	229.0	44.1	/	46.0	[15]
Leaching concentration /(mg/l)	0.902	9.057	0.423	0.813	0.0355	0.0974	/	0.0041	
Total content /(mg/kg)	One point six	14208	139	190	265	20.2	0.8	6.9	[1]
Leaching concentration /(mg/l)	0.46	21.57	0.63	4.62	0.034	0.19	0.012	<0.1	
Identification standard of leaching toxicity /(mg/l)	100	100	Five	One	15	Five	0.1	Five	

Note: GB 5085.3-2007 is the leaching toxicity identification of hazardous waste identification standard; /:not detected.

2.2.3. Fly Ash Dioxin

The commonly mentioned dioxins refer to the general names of dioxin-like substances, i.e., chlorine-containing organic compounds containing two or one oxygen bond connecting two benzene rings, including polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). There are 75 PCDD isomers and 135 PCDF isomers because there are 1 to 4 substitutable chlorine atoms

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per benzene ring. The molecular structures of PCDDs and PCDFs are shown in figure 4.

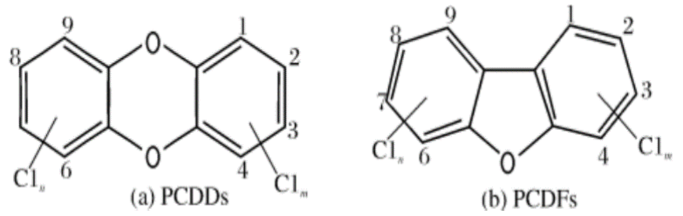

Figure 4: Molecular Structure of PCDD/FS

① **Physicochemical properties and toxicity of dioxins**

Dioxins are high melting point, high boiling point compounds, colorless crystals at room temperature; Chemically stable, symmetrical in both horizontal and vertical directions; Insoluble in acid and alkali, extremely soluble in water, soluble in most organic solvents; The thermal stability is good, and decomposition doe not begin until that temperature is more than 700 DEG C; Extremely lipophilic, easy to accumulate in organisms; It is difficult to degrade naturally, and microorganisms, hydrolysis and photolysis in nature have little effect on the molecular structure of dioxin. Longer half-life.

Dioxins are highly toxic, with teratogenicity, carcinogenicity and mutagenicity, strong biological toxicity, difficult to degrade, and remain in the environment for a long time. If accumulated for a long time in the human body, they will cause cancer and damage the nervous system and other organs. After entering the human body, they are difficult to be discharged. They are listed as Class I carcinogens by the International Cancer Center. The Stockholm Convention also lists dioxins among the first batch of persistent organic pollutants that must be controlled preferentially. The toxicity of dioxin varies with the number of chlorine atoms contained and the substitution position of chlorine atoms on the benzene ring. It is generally considered that the isomer substituted by 1–3 chlorine atoms is not significantly toxic, while the compound containing 4–8 chlorine atoms is toxic. Among them, the toxicity of 17 isomers substituted by 2378- chlorine is more significant. Particularly, 2378-TCDD is the most toxic, known as "the most toxic compound on earth", and its acute toxicity is 1000 times that of potassium cyanide and 900 times that of arsenic. The toxicity of the other 2378- chloro-substituted homologues decreased with the increase in the number of chlorine atoms.

Since dioxins in the environment are usually present as mixtures, the toxic amount of dioxins is usually evaluated by converting the toxic amount of dioxins from the different isomeric components into the toxic amount of 2,3,7,8-TCDD, which is the most toxic of dioxins, known as the toxic equivalent (i-TEQ). The factor derived from the ratio of the toxicity of the other dioxin isomers to the toxicity of 2,3,7,8-TCDD is defined as the international toxicity equivalent factor (I-TEF). The TEQ calculation method for dioxin toxic equivalent of samples is shown in the following formula, i.e., the sum of the mass concentration of each dioxin and the product of its international toxic equivalent factor I-TEF represents the dioxin toxic equivalent of samples.

$$\mathrm{TEQ}_{(\mathrm{PCDD}/Fs)} = \sum_{i=1}^{n=17} \left[C_i \times (I - TE\mathrm{F})_i \right] \tag{1-1}$$

Where: Ci— concentration of toxic dioxin, class I, ng/g or ng/L;

(I-TEQ)i— International TEF for the Class I toxic dioxin.

②**Formation mechanism of dioxin**

The micro-mechanism of dioxin formation during refuse incineration is complex. Different types and treatment capacity of incinerators, incineration temperature, diversity of refuse and tail gas purification equipment will all affect the concentration of dioxin. Different incineration technologies (such as different temperatures, residence times and oxygen volumes) lead to different thermodynamic processes, and these complex and variable factors increase the difficulty in studying the specific formation mechanism of dioxins in incineration systems. The basic mechanisms of dioxin generated from the incineration source and flue gas cooling process mainly include the following three ways, shown in table 6.

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Table 6: Formation of PCDD/Fs in Fly Ash from Municipal Solid Waste Incineration

Dioxin sources		Incinerator reaction zone	Temperature	Formation mechanism
Inherent in waste		Firebox	/	Existing in waste that is not destroyed or decomposed during high-temperature incineration
High temperature homogeneous reaction		Firebox	500～800℃	Coupling reaction of cyclization and substituted chlorination of precursors
Heterogeneous catalytic reaction at low temperature	Precursor catalyzed reaction	Afterburning zone	300～400℃	Transition metal catalytic chlorination precursor
	Ab initio synthetic reaction	Afterburning zone	200～400℃	Metal compounds catalyze the reaction of residual carbon with hydrogen, oxygen and chlorine

③Characteristic of fly ash dioxin fingerprint

The dioxin concentration level and fingerprint characteristics in MSWI fly ash are of great importance for the detoxification, harm reduction, treatment and disposal of MSWI fly ash. The distribution and proportions of PCDD and PCDF homologues in fly ash from different incinerators are shown in Fig.5. The toxic equivalent of dioxin in fly ash from fluidized bed furnace is 2.1074ng/g, and Figure 5(a) shows that the toxic equivalent of dioxin is mainly PCDF, with the contribution rate of 80.2%. Among them, the most important is 23478PeCDF、234678HxCDF、123678HxCDF、123478HxCDF。 The dioxin toxicity of fly ash from grate stokers was only 0.7349 ng/g. Figure 5(b) shows that PCDF is predominant with a contribution rate of 79.1% and the predominant species is 23478-PeCDF. The other two fly ash TEQs were below the level of 3.0 ng/g (calculated as I-TEQ) in the sanitary landfill pollution control standard. However, for both leaching toxicity of heavy metals and dioxin toxicity, the toxicity of fly ash from fluidized-bed furnace used in the experiment was higher than that of fly ash from grate furnace. In addition, we should also pay attention to the change of PCDFs content in the research on dioxin detoxification and harm reduction treatment of fly ash from MSWI.

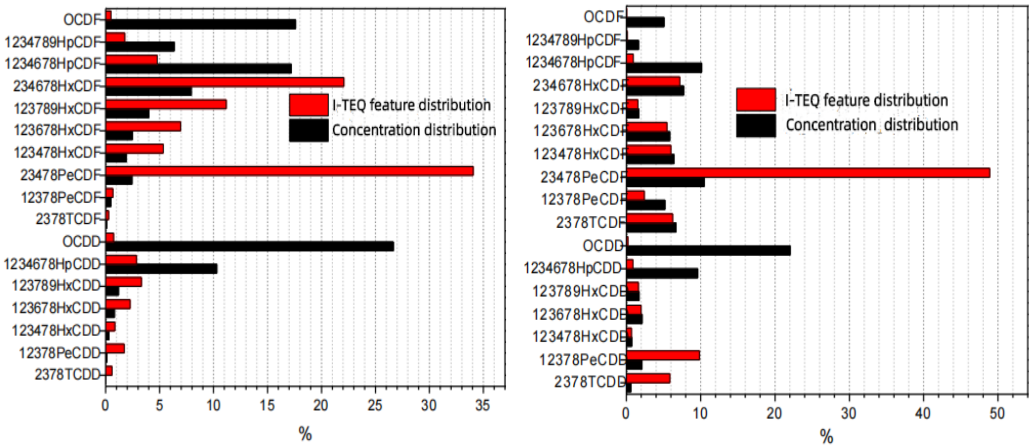

Figure 5: Fingerprint distribution of dioxins in (a) fluidized bed furnace fly ash and (b) grate furnace fly ash [15]

3. Detoxification and harm reduction treatment technology for MSWI fly ash

3.1. Curing Stabilization Technique

Solidification and stabilization technology refers to the use of additives or binders to chemically or physically fix harmful components in waste. For solidification treatment, binders such as cement are usually used to wrap the waste and convert the fly ash into non-flowable solids or form compact solids to achieve pollutant fixation and reduce leaching. For stabilization, the heavy metals in fly ash are mainly

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converted into low-toxicity, low-migration and insoluble substances. At present, the researches on curing/stability in China and abroad can be divided into four categories: ① single chemical stability; ② combination of chemical stability and adhesive cure; ③ adhesive curing, in the majority with cement curing, including other cheap alternative adhesive to replace part of the cement; ④ other methods such as hydrothermal method and soil polymer curing. Here we introduce some potential hydrothermal methods.

The hydrothermal method is the most common one for zeolite synthesis. Water is used as the medium for zeolite crystallization. Silicon source, aluminum source and alkali (such as NaOH and NaHCO3) are used to prepare zeolite molecular sieve and other minerals after crystallization under certain temperature and pressure. The main purpose of using hydrothermal method to treat fly ash is to stabilize heavy metals in the mineral system synthesized after hydrothermal treatment and realize the degradation of dioxin at the same time. A number of institutions have carried out relevant research in China, with Zhejiang University and the Center for Ecological Environment of Chinese Academy of Sciences as typical representatives. Ma Xiaojun [16] Experimental and theoretical studies on the hydrothermal stabilization of heavy metals in fluidized bed fly ash and the degradation of dioxins have been systematically carried out on the basis of previous studies. The results show that the leaching concentrations of heavy metals in fly ash from all hydrothermal treatments are lower than the landfill standards in China; Under the optimal conditions (reaction temperature: 150℃, NaOH: concentration 0.5 mol/L, liquid-solid ratio: 4:1 mL/g, reaction time: 12 h), the concentration of heavy metals in the residual liquid reached the national wastewater discharge standard, and the stabilization efficiency of heavy metals exceeded 95%. The degradation rate of dioxin decreases with the increase of temperature, and the formation of free radicals under oxygen atmosphere significantly accelerates the degradation of dioxin. As that hydrothermal method is beneficial to the stabilization of heavy metal in the fly ash and the degradation of dioxin, and the zeolite synthesized in the treatment process can be used as an adsorbent and an acid neutralizing agent, the method has significant ecological benefit. Therefore, it is a potential fly ash treatment method.

3.2. Heat Treatment

Heat treatment technology is to degrade organic pollutants (such as dioxins and furans) in fly ash by using heat at high temperature (above 1000°C) and firmly stabilize heavy metals in dense structures. According to the different temperature, generally including sintering, melting and glass curing two categories. The chemical property of the product after the heat treatment is stable, the environmental pollution caused by pollutants can be effectively prevented, the volume of the treated product is smaller, and the treatment is easier. The solidified product can be used as building material for building industry such as subgrade and foundation. Because the method needs high temperature treatment, has high energy consumption and high investment on equipment, and simultaneously exists volatile heavy metal elements such as Pb, Cd, Zn and the like in the fly ash in the melting process, the concentration of secondary pollutants in the flue gas needs to be strictly monitored.

Wang Xuetao[17], etc The effects of different factors such as temperature and additives on the melting were studied. The results showed that the temperature in the melting process had a significant effect on the heavy metals. The addition of silicon dioxide promoted the solid solubility of heavy metals and the leaching rates of heavy metals in fly ash after melting treatment were low. Sakai et al.[18] The migration characteristic of heavy metals in municipal solid waste incineration fly ash and bottom slag dure melting were studied. that results show that heavy metal in fly ash will redistribute due to different volatilization temperatures after melting. low volatile metals such as al, Ca, Zn, Ni, Mn will be transferred to the slag, while high volatile metals such as Cd and Pb will be transferred to the waste gas of melting furnace.

In 1987, Hagenmaier et al. first proposed that "anoxic condition, heating temperature of 250–400 C, and residence time of 1 hour" and other key parameters could realize the effective degradation of fly ash dioxin (abbreviated as Hagenmaier reaction). Subsequently, the field of low temperature heat treatment pyrolysis of dioxins has become a hot research topic. Foreign researchers earlier

A study was initiated on the low temperature heat treatment technology for dioxins in fly ash from the refuse incineration process, Ishida et al[19]Under the above conditions, the domestic waste incineration fly ash was treated at 350 C, and the degradation rate of dioxin toxic equivalent was as high as 99.6%, and the high-chlorine dioxin homologues in the fly ash showed the basic characteristics of gradual conversion to low-chlorine. Many scholars in China and abroad have conducted some experiments to find the optimal conditions for dioxins in low-temperature heat-treated fly ash, as shown in Table 7.

Table 7: Literature Review on Optimal Conditions of Low Temperature Heat Treatment for Dioxins

Author	Treatment conditions	Treatment result
Vogg et al[16]	It is considered that under aerobic condition (air), heating to 400 ~ 600℃	Pcdd/fs degrades effectively
Jan stach, et al[17]	Treat at 340°C. For 6 hours unde a nitrogen atmosphere	Optimal treatment conditions
Lisal., stellan m.[18]	Heating at 500°C for 60min	The removal rates for total pcdd/fs and total teq were ninety-seven percent and 99%, respectively
Yan jianhua[19]	The temperature was 400°C. And that retention time was 1nitrogen atmosphere	Optimal treatment conditions
Peng zheng[20]	450°Ctreatment under static air condition for 1h	Optimal treatment conditions
Ji sasha[21]	45min at 400°C. In an inert atmosphere	The fly ash has the highest dioxin removal rate

It could be seen that there were contradictions between the results of these studies. The differences between the fly ash itself inevitably caused the differences between the experimental results. However, it is undeniable that temperature, reaction atmosphere, reaction time and other factors can affect the degradation efficiency of PCDD/Fs.

In addition, the dioxin regeneration reaction during the low temperature heat treatment is also closely related to the chlorine content in the fly ash. The low-temperature heat treatment technology has the advantages of simple operation, low energy consumption, high dioxin degradation efficiency, and the like, which determines that the technology has a good popularization and application prospect in the aspects of fly ash dioxin detoxification and harm reduction. However, the technology cannot stabilize the heavy metals in MWSI fly ash, and the applicability to the pollution characteristics of high chlorine, high carbon and the like needs to be further explored and optimized.

3.3. Microwave Pyrolysis Technology

In order to avoid the disadvantages of low heating efficiency, uneven temperature, high processing cost and other shortcomings in the traditional medium and low temperature heat treatment, microwave pyrolysis technology was introduced into the medium and low temperature pyrolysis PCDD/Fs as a new technology with high efficiency, energy saving and environmental protection.

Microwave heating belongs to body heating. In conventional heating, the external heat source transfers heat from the outside to the inside by conduction and convection, which is not only inefficient, but also leads to uneven temperature distribution (high outside and low inside). Compared with the conventional heating mode, the microwave heating has the advantages of uniform heating, high heating speed, selective heating, energy saving, even improvement of material performance and the like; In addition, microwave energy belongs to clean energy, which is also one of its great advantages for improving the labor environment and production conditions.

In order to improve the microwave absorption ability of fly ash, relevant scholars (Zuo W et al.[18] and Kishima T et al.[19]) on microwave sensitizers such as graphite, residual coke, activated carbon, and silicon carbide, and they found that when 48% activated carbon was used as the microwave sensitizer under the operating temperature of 900℃, reaction time of 30s, and microwave power of 600W, the microwave treatment technology could effectively degrade hcb in fly ash. In contrast, when no activated carbon was present and other treatment conditions were the same, the temperature of the fly ash sample could only be heated to about 300 C. WeiG.X et al[20] Treatment of fly ash by flotation can enhance its absorption of microwave energy, but its foaming process may cause secondary pollution.

Yongming Ju et al. [21] HMs was stabilized by washing pretreatment with phosphorus-containing anions, and its main influencing factors and thermodynamics were studied. In addition, single-mode microwave (MW) energy was used to further irradiate the wet fly ash adsorbed with phosphorus anions. The results showed that the combination of washing pretreatment with phosphorus (P)-containing anions and microwave pyrolysis could change the morphological distribution of HMs and effectively stabilize the residual phases of heavy metals such as Cd, Zn, Cr, Cu, and Pb in diagenetic minerals. At the same time, MSWI fly ash could be used as a good adsorbent to remove phosphorus. Under the optimal conditions of mass ratio of SIC to wet fly ash of 10:2, temperature of about 480℃, and nitrogen

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atmosphere, the total degradation rate of PCDD/Fs is about 99.1%; The presence of thiourea (TU) also shortens the MW irradiation time by 27.8%–61.5% as compared with that in the absence of TU, and promotes the generation of hot spots.

The microwave pyrolysis technology has enriched the research on the detoxification and harm reduction of dioxins in fly ash. It has a broad development prospect. At the same time, it has the advantages of high heating efficiency, low energy consumption, good degradation efficiency, environmental protection and clean, and deserves more attention.

3.4. Flotation Technology

Flotation is a physicochemical separation technique that is widely used in ore processing to separate minerals and is also used to separate residual carbon components from MSWI fly ash. The natural hydrophobicity of PAC and the foam flotation technology can be used to separate the residual PAC and adsorbed dioxin and other pollutants in fly ash, to separate the main components of fly ash and reduce the residual dioxin concentration in MSWI fly ash. Liu et al. used flotation column to remove carbon component in fly ash from medical waste incineration. Under the optimal operating conditions of slurry concentration of 0. 05 kg/L, kerosene dosage of 12 kg/t, foaming agent dosage of 3 kg/t, and air flow rate of 0. 06m3/ h, 92. 7% carbon component was removed, and residual slurry with < 5% carbon content and refined ash with high carbon content were obtained. Among them, the toxic equivalent concentration of dioxin in the residual slurry was only 1. 47 ng I-TEQ/g, which was lower than the limit (3 ng I-TEQ/g) stipulated in GB 16889—2008 Pollution Control Standard for Domestic Waste Landfill Sites. The combined use of microwave and fine ash can also effectively degrade the dioxin in the fine ash, the degradation rate is as high as 99. 6%, and the toxic equivalent concentration is reduced to 0. 08 ng i-teq/g. The flotation technology can effectively separate carbon components, dioxins and heavy metals in MSWI fly ash, which is one of the most potential technologies for the harmless and resource utilization of fly ash.

In summary, Table 8 gives a comprehensive comparison of MSWI fly ash detoxification and harm reduction treatment technologies.

Table 8: Comprehensive Comparison of Fly Ash Detoxification and Harm Reduction Technologies by MSWI

Processing technic	Applicability	Heavy metal treatment effect	Dioxin degradation effect	Superiority	Defect	Environmental effect	Evaluate
Chemical reagent stabilization technology	No requirement	Stable	All-or-none	The expansion effect is not obvious	High cost and non-degradable dioxin	Less impact	High cost
Cement curing technology	High carbon and high chlorine have hinder effect	Stable	All-or-none	Simple operation and less investment	Risk re-release heavy metals and non-degraded dioxins	Significant expansion effect	High environmental risk
Hydrothermal technology	No requirement	Stabilization or separation	Significant effect	Low equipment requirement and low energy consumption	Risk of corrosion of reaction equipment	Less impact	Engineering application is difficult
Melting technique	High carbon is only suitable for reference carbon type melting furnace	Partially stable	Significant effect	Molten heavy metal, high removal efficiency of dioxin	High equipment requirement and high energy consumption	Can cause secondary pollution of heavy metal chloride	High energy consumption and easy generation of secondary pollution
Low temperature heat treatment technology	No requirement	All-or-none	Significant effect	Simple operation and low energy consumption	No effect on heavy metals	Less impact	Long heating time
Microwave pyrolysis technology	No requirement	Partially stable	Significant effect	High heating efficiency and high dioxin removal efficiency	High equipment requirements and need to add microwave sensitizer	Less impact	Low energy consumption and large potential
Flotation technology	High carbon application	Remove	Remove	Low cost and low energy consumption	Application engineering has not yet started	Less impact	Use in combination with other techniques

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4. Conclusions

The characteristics and concentration of MSWI fly ash have affected the research on fly ash detoxification and harm reduction and resource utilization technology. The analysis of pollution characteristics showed that MSWI fly ash contained high chlorine, high carbon components, heavy metals and dioxins (PCDD/Fs) and other toxic substances. The pollution characteristics of high chlorine and high carbon limit the application of cement curing technology; High temperature heat treatment (melting and sintering) technology can simultaneously treat heavy metals and dioxins in MSWI fly ash, but has the problems of high energy consumption and secondary pollution; The low-temperature heat treatment technology has the advantages of high efficiency and low energy consumption in the detoxification and harm reduction of dioxin in MSWI fly ash, but compared with microwave heating, the heating time is long and has no effect on heavy metals. Hydrothermal treatment can stabilize heavy metals and degrade dioxins at the same time with low energy consumption and environmental and economic benefits. However, the engineering application is difficult and the flotation technology is used to separate the main components, which helps to promote the harmless and resource-based utilization of MSWI fly ash. On this basis, we can achieve the technical, economic and environmental advantages of fly ash detoxification and harm reduction treatment by means of technical combination, and put forward the combination process of water washing flotation pretreatment and microwave pyrolysis. Water washing can remove most of the chlorine salt and part of the heavy metals, flotation can separate the residual carbon components and adsorption of dioxin and other pollution

And obtaining a fine ash layer with high carbon content, and simultaneously reducing the possibility of dioxin re-synthesis in the microwave pyrolysis process, and finally degrading UP-POPs such as dioxin in the fine ash layer by microwaves.

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