

Organic-Waste Disposal in High-Temperature Metallurgical Systems

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Abstract—Globally, organic waste is the largest component of hazardous waste. Chlorine-bearing organic waste is a particular environmental hazard. The main disposal method for organic waste is high-temperature combustion in special incinerators and in rotary cement furnaces. However, combustion is associated with the risk that secondary supertoxics such as dioxins and furans may be formed. Comparison of dioxin formation for waste combustion in incinerators, cement furnaces, and high-temperature metallurgical systems (oxygen converters) shows that oxygen converters are preferable, thanks to the high temperatures, intense heat and mass transfer, active oxidizing atmosphere, the presence of highly active basic slag, rapid cooling, and complete combustion of the waste gases. Data on the content of 17 dioxin and furan isomers in the dust transported by exhaust gas from converters containing paper and plastic waste at OAO EVRAZ ZSMK show that the total concentration is considerably below European standards for waste gases from stationary sources. No significant difference is observed in the concentrations and isomer profile of dioxins and furans in the experimental and standard melts.

Keywords: hazardous organic waste, dioxins, combustion, incinerator, cement furnace, oxygen converter

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Globally, organic waste is the largest component of hazardous waste. Examples include petroleum-bearing waste (spent oil, oil sludge, oil-contaminated soil, waste from the cleaning of petrochemical equipment, spent vehicle filters), wastes from the chemical and coke industry, biological and medical waste, and spent charcoal and fabric filters from gas-purification systems.

Chlorine-bearing organic waste is a particular environmental hazard. The following are some examples:

—organochlorine polymers (PVC, chloroprene rubber, chloride polyesters, polystyrene, polyamides) from discarded components;

—spent organochlorine solvents;

—dielectrics;

—superseded organochlorine pesticides;

—unusable light fractions, distillation residues, and tars from plants producing organochlorine compounds;

—wastewater formed in the production and utilization of organochlorine products.

The production and use of twelve organochlorine materials that are a particular hazard to humans—persistent organic pollutants—was prohibited by the Stockholm Convention. These are known as the dirty dozen: polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), aldrin, dieldrin, dichlorophenyl-trichloroethane (DDT), endrin, chlordane, hexachlo-

robenzene, mirex, toxaphene, and heptachlor [1]. Organochlorine compounds are found in solid domestic waste—for example, in some plastics—and in medical waste disinfected by chlorine-based solutions. Persistent organic pollutants are highly toxic to all living organisms, and they accumulate in living tissue. They are carcinogens, mutagens, and also embryo-, neuro-, and immunotoxins; they impair the hormonal and reproductive systems; and they produce anemia and liver and kidney diseases. They do not undergo biodegradation in the atmosphere and therefore, according to the Stockholm Convention, which was ratified by Russia in 2011, their long-term storage is forbidden [2]. Wastes of persistent organic pollutants must be collected for subsequent processing.

The main disposal method for organic waste is high-temperature combustion [3–6]. Combustion may be used for organic waste of any kind, since it converts the main elements in most organic compounds—carbon, hydrogen, and oxygen—to the environmentally safe compounds CO₂ and H₂O and, in the presence of chlorine, to hydrogen chloride, which is used in wet gas purification [3]. However, to ensure complete decomposition of the hazardous organic compounds, the following conditions must be met:

—combustion temperatures no lower than 1200°C;

—at least 2-s residence of the combustion products in the chamber (the two-second rule);

- excess oxygen in the combustion zone;
- fast cooling of the waste gas below 200°C, so as to prevent secondary dioxin formation.

If these conditions are not satisfied, polycyclic aromatic hydrocarbons, many of which are carcinogens (for example, benzopyrene), and highly toxic polychlorinated dibenzodioxins and dibenzofurans may be formed on combustion.

Waste-combustion technology has progressed from open combustion and simple garbage incinerators, which are strong environmental polluters, to highly efficient incinerators equipped with complex systems for waste-gas purification, whose atmospheric emissions are minimal.

In Russia today, several types of incinerators are produced for the combustion of solid and liquid organic waste, including chemical, medical, and biological wastes, petroleum sludge, and chlorinated waste categorized as persistent organic pollutants (for example, PCB oils, pesticides, and herbicides). An incinerator consists of a brick-lined chamber with a burner supplied with diesel fuel or natural gas. In incinerators, as a rule, two-stage waste destruction is employed: combustion at 850–900°C; and final combustion of the gases formed at 1100–1200°C, with subsequent mechanical and chemical purification.

Outside Russia, rotary cement furnaces are widely used to process hazardous organic waste. In 2003, an expert UN panel recommended rotary cement furnaces for the disposal of PCDD and PCDF [7]. Cement furnaces satisfy the conditions guaranteeing complete decomposition of the organic compounds (including organochlorine compounds) in the waste.

An international document presenting data on the PCDD and PCDF emissions in different processes was published within the framework of the UN environmental program [8]. According to that document, “PCDD and PCDF may be sent for combustion with toxic waste, may be formed during combustion, or may be formed at the end of combustion as the exhaust gases cool.” Accordingly, the following primary means of optimizing the process in the cement furnace so as to minimize PCDD and PCDF formation were cited in [7]:

- continuous supply of fuel and waste, with recording of the content of heavy metals, chlorine, and sulfur;
- monitoring of the materials charged in the furnace;
- preliminary treatment (drying, crushing, mixing, grinding) of the waste so as to ensure uniform charging and hence maximize the efficiency of combustion in the most stable conditions;
- charging of the waste in the primary or secondary furnace chamber with preliminary roasting or heating (above 900°C);

- charging of the waste separately from the raw mixture if it contains organic materials;
- stabilization of the technological parameters (constant fuel properties, constant dosing, excess oxygen, monitoring of carbon monoxide content);
- no charging of waste during furnace startup and shutdown;
- fast cooling of the exhaust gas below 200°C.

By this means, PCDD concentrations in the exhaust gas lower than 0.1 ng/m³ may be obtained in existing equipment; this is consistent with European standards. If these primary measures do not shift the PCDD concentrations in the exhaust gas below 0.1 ng/m³, improvement of the methods of dust removal from the exhaust gas was recommended in [7]—for example, by means of activated-charcoal filters or selective catalytic reduction.

However, complete decomposition of organic waste cannot be guaranteed in rotary cement furnaces. The furnaces include several temperature zones, which bleed into one another: the heating zone (500–600°C); the calcination zone (900–1200°C); the sintering zone (1450°C); and the cooling zone (1000–1200°C). Only one of those zones prevents PCDD and PCDF formation, and prolonged residence is required. However, prolonged residence cannot be ensured, since furnace gases pass successively through all the temperature zones. The residence time in each zone may hardly be precisely guaranteed, since all the zones are continuous. According to EC standards, the geometry of the furnace’s hot zone must ensure gas residence at temperatures no lower than 850°C for no less than 2 s (the two-second rule), with an oxygen concentration no less than 6%. It is difficult to meet this very stringent requirement. Increase in the emissions is observed when the furnace begins operation. Therefore, the EC standards call for the onset of trash pyrolysis or combustion only after heating to 850°C [7].

Compared to incinerators or cement furnaces, high-temperature metallurgical systems (such as the blast furnace or oxygen converter) permit safer combustion of the fuel components of organic waste. Metallurgical systems provide excellent conditions for the safe disposal of toxic wastes: temperatures above 2000°; an active oxidative or reducing atmosphere; intense heat and mass transfer; and the presence of highly active basic slag, which binds the residue from waste combustion for vitrification. In such conditions, dioxin formation is practically impossible. In addition, powerful metallurgical systems are equipped with systems for gas capture and purification (including wet gas purification) and also with a closed water-supply system.

In UN documents, the PCDD and PCDF emissions from various technological processes are tabulated (Table 1) [5].

High-temperature metallurgical systems ensure minimal atmospheric emissions of dioxins and furans:

Table 1. PCDD and PCDF emissions from various sources

Source	Emissions, $\mu\text{g TE/t}$ of product			
	in air	in product	in waste	
			ash	slag
Combustion of solid domestic waste at a trash-incineration plant with a complex gas-purification system	0.50	N	15	1.5
Combustion of medical waste in incinerators with a complex gas-purification system	1.00	N	150	—
Rotary cement furnace	0.15–5.00	ND	0.003–1.0	—
Blast furnace	0.01	N	—	N
Oxygen converter	0.06	N	—	1.5

The following notation is adopted here: TE, international toxic equivalent; N, none; ND, no data.

1–2 orders of magnitude less than the state-of-the-art systems used globally for the combustion of hazardous organic waste. In addition, the combustion of organic waste in metallurgical systems provides additional heat and reduces the consumption of traditional fuels such as coke, coal, fuel oil, and natural gas. From a technological perspective, blast furnaces may process liquid and solid organic waste with piece sizes less than 100 mm, while oxygen converters are suitable for solid organic waste of piece size 5–10 mm.

We now consider the potential for processing hazardous organic waste in the oxygen converters at OAO EVRAZ ZSMK. The following temperatures are employed:

- above 1000°C during scrap heating;
- above 1380°C during the charging of hot metal;
- from 1440 to 2000°C and more during injection.

During waste combustion, the atmosphere in the converter is industrial-grade oxygen (at least 99.5% O₂), which ensures intense heat and mass transfer and hence complete combustion of all the organic components present and destruction of the structure of the complex organic compounds, including dioxins.

The wastes are present in the converter during the entire melt. Complete combustion occurs during scrap heating and subsequent injection. From the initial introduction of the waste in the converter, it is in close contact with the fluxes; lime is the main flux. On injection, lime ensures the formation of basic calcium-bearing slag. The presence of considerable lime in the converter accelerates the decomposition and oxidation of the complex organic compounds and the destruction of dioxins. The residues from waste combustion pass to the molten slag, which absorbs all the combustion products. On subsequent cooling, the residues are vitrified and pose no risk to the environment.

Converters are equipped with gas-exhaust channels in which the gases cooled, purified, and burned. The exhaust gases pass through a cooling system, where their temperature is reduced to 850°C, and then sent for the first stage of purification, by means of water

sprays. At this stage, the gas is cooled further to 250–300°C, some impurities are removed, and the humidity is raised to complete saturation. The saturated gases then pass through stages I and II of the rectangular Venturi tubes, in which most of the purification occurs. After droplet capture, the dried gas is sent for final combustion. Wet purification of the exhaust gas ensures up to 99.5% dust capture. The circulating water in the wet purification system is characterized by pH 11–12; this indicates a high content of lime. High alkalinity of the circulating water improves the efficiency with which chlorine-bearing gases (hydrogen chloride, gaseous chlorine) are removed from the gas leaving the converter. Thus, existing gas-purification systems provide favorable conditions for the capture of chlorine-bearing impurities from the exhaust gases when they are formed—for example, when the wastes contain PVC components or residues of chlorine disinfectants.

Table 2 compares the dioxin formation in different waste-combustion processes: an incinerator, a rotary cement furnace, and an oxygen converter.

In the converter, the conditions for dioxin-free waste processing are present:

- high-temperature combustion (above 1250°C);
- intense heat and mass transfer;
- active oxidative atmosphere, with an excess of industrial-grade oxygen;
- active liquid slag that absorbs compounds containing sulfur and halogens and solidifies to vitrified slag;
- rapid cooling of exhaust gas to 40–60°C in the wet gas-purification system;
- gas combustion in the burner at 1500°C.

Repeated dioxin synthesis is prevented by three-stage wet purification of the exhaust gas ensuring 99.5% dust capture and rapid gas cooling to 40–60°C and exhaust-gas combustion.

Thus, high-temperature metallurgical systems (in particular, oxygen converters) are the safest known

Table 2. Comparison of dioxin formation in different waste-combustion processes

Characteristic	Conditions of dioxin formation	Waste-combustion system		
		incinerator	rotary cement furnace	oxygen converter
Waste-charging method	Large batches	Large batches	Preliminary waste treatment for uniform small-batch charging	Small-batch loading (0.1–2.0 kg/t of steel) and intense oxygen injection, ensuring good heat and mass transfer on combustion
Combustion temperature, °C	<900	850–900	From 500 to 1450 (in several temperature zones)	From 1440 to 2000 or more (high-temperature combustion)
O ₂ content, %	Insufficient oxidant	21	21	99.5 (excess oxygen, oxygen blast)
Purification of exhaust gas	Dust traps operating above 200°C	Dry purification (in some cases, wet purification and a scrubber with 93% dust removal)	Electrofilters	Three-stage wet purification with 99.5% dust capture and rapid gas cooling to 40–60°C
Combustion of exhaust gas	No combustion	Burner (flame) combustion at 1500°C	No combustion	Burner (flame) combustion at 1500°C
Ash/slag formation		Ash	Ash	Highly active liquid slag with >50% CaO, creating good conditions for sulfur and halogen absorption; solidification to vitrified slag

means of burning hazardous organic waste, including organic chlorine waste.

At OAO EVRAZ ZSMK, converter trials are conducted with specially prepared batches containing solid domestic waste: compressed paper, card, and polyethylene waste; and polystyrene electronic-instrument housings crushed to <20 mm pieces.

The trials are conducted in converter shop 2, on 350-t converter 4. The existing technological instructions are employed for injection in the trial and comparison melts. The consumption of solid domestic waste is 1.0–8.8 kg/t of steel. The characteristics of the trial and comparison melts are basically the same. In the melts with solid domestic waste, practically no carbon fuels are employed; the steel temperature at discharge is higher than in the comparison melts. Calculations of the material and thermal balance indicate that, on introducing solid domestic waste in amounts of 7.2 kg/t, 8338.1 kJ of additional thermal energy is introduced in the converter; that amounts to 4.21% of the total heat supply.

In the experimental melts, bales of compressed paper and polyethylene and sacks of crushed polystyrene are supplied to the converter together with the scrap and fluxes (lime). After charging, the batch is heated by combustion of the waste in a current of industrial-grade oxygen for 5–6 min. Then hot metal is introduced, and conventional smelting with oxygen injection into the melt continues for 17–18 min, with the addition of fluxes.

The results of the industrial trials were described in detail in [9]. There is little difference between the basic parameters in the trial and comparison melts. The

steel temperature at tipping is higher in the trial melts (1706 and 1655°C) than in the comparison melts (1619–1661°C and 1629°C). That indicates higher bath temperatures in smelting on account of the high heat of combustion of the waste. The mean dust content of the exhaust gas after purification is 117 mg/m³.

The accreditation laboratory at Bashkir regional environmental center (Ufa) has analyzed the dust in the gas emissions for its dioxin content, in the trial and comparison melts; the United States EPA-1613 method is used, with adaptations for Russian conditions. In this method, the dioxins are extracted by means of solvents from the object of interest, dioxins are deposited from the matrix, and impurities present are removed on sorbents. A high-resolution chromatograph and mass spectrometer is used for quantitative analysis by isotopic dilution. The internal standards employed are the 17 isomers of dioxins and furans, labeled with the carbon isotope C¹³. Five isomers of tetrachlorodioxins are investigated: 1,3,6,8-TCDD, 1,2,3,4-TCDD, 1,2,3,7-TCDD, 2,3,7,8-TCDD, and 1,2,3,9-TCDD. Table 3 presents the results of quantitative isomer-specific analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans.

No significant difference is seen in the concentrations and isomer profile of dioxins and furans in the experimental and standard melts. There is also little difference in the toxic equivalents (TEQ).

The experimental data on the PCDD and PCDF content in the ash samples may be used to assess the pollution by the exhaust gas. If we assume that the samples analyzed consist of dust emitted to the atmosphere from the smokestack with furnace gases, the quantity of

Table 3. Isomer concentrations and toxic equivalents (TEQ-WHO) of the isomers (calculated for the toxicity of 2,3,7,8-TCDD) in accordance with the toxic equivalency factors (TEF) for the dust captured in the trial and comparison melts

Isomers	Trial melt		Comparison melt	
	concentration, pg/g of dust	TEQ-WHO, pg/g of dust	concentration, pg/g of dust	TEQ-WHO, pg/g of dust
2,3,7,8 – TCDD	5.36	5.36	5.78	5.78
1,2,3,7,8 – PnCDD	4.90	4.90	6.99	6.99
1,2,3,4,7,8 – HxCDD	2.89	0.29	1.78	0.18
1,2,3,6,7,8 – HxCDD	4.49	0.45	3.54	0.35
1,2,3,7,8,9 – HxCDD	0.86	0.09	0.06	0.01
1,2,3,6,7,8 – HpCDD	8.95	0.09	11.18	0.11
OCDD	18.71	0.00	18.47	0.00
2,3,7,8 – TCDF	898.51	89.85	651.86	65.19
1,2,3,7,8 – PnCDF	262.34	13.12	247.41	12.37
2,3,4,7,8 – PnCDF	269.53	134.77	342.77	171.39
1,2,3,4,7,8 – HxCDF	86.53	8.65	96.35	9.64
1,2,3,6,7,8 – HxCDF	99.76	9.98	123.17	12.32
1,2,3,7,8,9 – HxCDF	6.61	0.66	8.46	0.85
2,3,4,6,7,8 – HxCDF	43.69	4.37	64.36	6.44
1,2,3,4,6,7,8 – HpCDF	54.50	0.55	50.58	0.51
1,2,3,4,7,8,9 – HpCDF	15.44	0.15	13.71	0.14
OCDF	18.80	0.00	16.35	0.00
Total PCDD, pg/g of dust	46.16	11.18	47.8	13.42
Total PCDF, pg/g of dust	1755.71	262.09	1615.02	278.82
Total PCDD + PCDF, pg/g of dust	1801.87	273.27	1662.82	292.24

emitted dioxins associated with dust particles will depend on the concentration of suspended particulates in the exhaust gas. Thus, if the concentration of suspended particulates in the exhaust gas is 117 mg/m³, the total content of dioxins and furans in the exhaust gas is 31.94 pg/m³ for the trial melt and 34.40 pg/m³ for the comparison melt. Note that the European standard for the exhaust gases of stationary sources is 0.1 ng/m³.

CONCLUSIONS

By analysis of the high-temperature processes in metallurgical systems and the available research data, we find that today high-temperature metallurgical systems are the safest known means of burning hazardous organic waste. That is particularly true of waste containing supertoxics such as dioxins and furans and also carcinogenic hydrocarbons, which are formed in considerable quantities in the combustion of some types of wastes, even at incineration plants and especially in disorganized waste combustion. The use of metallurgical smelters to process solid domestic waste may be a valuable approach to the processing of hazardous organic waste.

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