DOI 10.34660/INF.2022.73.57.173

从二恶英中净化气体的方法

METHODS OF GASES PURIFICATION FROM DIOXINS

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抽象的。 介绍了有关二恶英的特性、毒性和结构的信息。 介绍了世界上发达国家二恶英类物质销毁的基本原理和技术。
关键词：二恶英，销毁方法。
Abstract. *Information on the properties, toxicity and structure of dioxins is presented. The basic principles of the destruction of dioxins and technologies adopted in the highly developed countries of the world are described.*
Keywords: *dioxins, destruction methods.*

Properties of dioxins

The term dioxins is commonly used to refer to a family of compounds whose structure is based on Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Each compound contains two benzene rings linked by oxygen atoms. In the case of PCDD, the rings are connected by two oxygen bridges; in the case of PCDF, the rings are connected by a C-C bond and an oxygen bridge. Figure 1 shows the structural formulas of PCDD and PCDF indicating the position of hydrogen atoms that can be replaced by a Cl or other halogen atom.

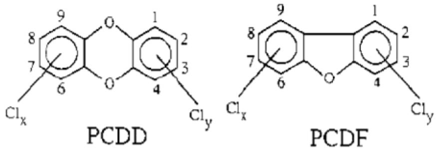

Figure 1. *Structure of PCDD and PCDF. [1]*

Dioxins are by-products of the production of chlorophenols, their formation also accompanies the combustion of compounds containing C, H, O and Cl (or Br) atoms. Dioxins and furans (PCDDs and PCDFs) form in the temperature range of 250-450 ºC. There is also evidence of the formation of such compounds in the range from 150 to 240 ºC. Dioxins and phenols are formed more easily, so the temperature in the smoke filters is kept below 200 ºC.

The content of dioxins in waste gases, waste water or solid residues is highly dependent on the choice of technology and equipment. The literature distinguishes between primary and secondary sources of dioxins. According to this classification, sources of dioxins that are released into the environment and/or in places other than the place of waste processing are classified as secondary sources. For example, anthropogenic dioxins that are prevented from entering gaseous emissions by purification systems may remain in adsorbents and yet enter the food chain and increase human consumption. The average half-life of dioxins in the soil is 10-12 years, and in the human body 6-8 years. Dioxins are sparingly soluble in water, are not destroyed by acids, are resistant to alkalis, and strongly bind to solid carriers. [1]

Much is known **about the toxicity** of dioxins. Let's note that out of the known 75 dioxins and 135 furans, the toxicity of only a small number of compounds of this class has been seriously studied. The action of 2,3,7,8-tetrachlorodibenzodioxin has been most intensively studied. Very low doses of 2,3,7,8 TCDD cause weight loss, reduced immunity, decreased testosterone, skin and liver disease. [11] The average lethal dose for humans, obtained by calculation, is 0.05-0.07 ppm for a single oral intake. [2].

The MAC criterion for dioxins is completely unacceptable. This follows from the well-established fact that there is no dose of dioxin so low that it would be safe. The allowable daily dose established in Russia is 10 pg/kg of body weight/day, the American norm is 6 femtograms (10^{-15} g) per kilogram of body weight per day. These norms are set out of impotence, since the already existing dioxin pollution in Western countries is so high that these norms are easily exceeded. [2] In Europe in 2012, the norm for the concentration of dioxins is 0.1 ng/m^3. The norm of dioxin content in sediments is 1-2 ng/kg (Europe). [1]. Table 1.

Table 1.

MAC or SRLI for polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs).*

An object	Dioxins DE (PCDD+PCDF)	Σ PCB	Regulatory document (for dioxins)
Atmospheric air	0.5 pg/m^3	1 μg/m^3	GN 2.1.6.014-94
Air emissions	0.1 ng/m^3		European norm
Drinking water, ground and surface water, withdrawal points	20 pg/l 1 pg/l	1 μg/l	Order of the Ministry of Health of the USSR No. 142-9/105 dated 05.05.1991 ------ GN 2.1.5.2280-07

The soil	0.33 ng/kg	60 ng/kg	Order of the Ministry of Health of the USSR dated 08.09.86 No. 697 DSP

* Estimated safe exposure level

Ways of formation of dioxins have not yet been fully identified. It is believed that in the process of MSW processing, they are formed at temperatures of 700-1000 ºC. The volume of their formation depends on the conditions of the process and the feedstock, and, above all, the presence of Cl- and Br-containing components in it. Factors that increase the formation of dioxins are temperatures above 150 ºC, alkaline reaction medium, the presence of carbon, CO, chlorides and copper compounds as catalysts.

Destruction of PCDD and PCDF.

Numerous methods have been developed for soil disinfection and disposal of waste from dioxinogenic technologies, based on various principles - physical, chemical, biological, and more often combined. Efficient and economical methods for disinfecting soils and chemical industry waste from dioxins have been developed in the USA, as well as in Germany, Italy, and France.

"Burnout" of PCDDs and PCDFs is the most accepted method for their destruction. According to the standards of the European Union, the geometry of the hot zone of the burner must ensure that gases stay in the zone with a temperature of at least 850 °C for at least 2 s (two seconds rule) at an oxygen concentration of at least 6%. This is a very strict requirement and it is not easy to withstand it. It is especially difficult to achieve a high oxygen content in the combustion zone. These incinerators are equipped with additional heaters to maintain this temperature at all times. The fuel in them is oil, and usually only some of its fractions are active. Most modern incinerators use factory filters (often with Teflon membranes) that allow submicroparticles to be collected and thus can trap dioxins from the solid phase [4].

Compliance with the rule of two seconds means the complete destruction of dioxins when this requirement is met, which is completely untrue. The requirement of two seconds means that under these conditions the concentration of dioxins in the exhaust gases will be acceptable for their purification to the required 0.1 ng/m^3 (at 11% oxygen in the gases). This implies that the degree of purification will not be lower than "six nines", that is, 99.9999 96; [5-7].

The method of "burnout" dioxins is criticized. The notion that "everything will burn" at high temperatures is a mistake. This does not take into account the special property of dioxins - the ability to new synthesis in the cold zone (there is a so-called "de novo synthesis" - the synthesis of complex molecules from simple ones). A lot of evidence indicates the inefficiency of this method for reducing the concentration of products of incomplete combustion (PIC). PIC also includes dioxins. It is reported in [4] that when examining waste incinerators, it was shown that dioxins are formed during the combustion process, and that their formation occurs in the cooling zone, therefore, an increase in temperature during combustion does not lead to the destruction of dioxins. Hot electrostatic filters, which are so common in all cleaning schemes, generate dioxins themselves. Thus, during the examination of the incinerator in Florida on one incinerator, the following results were obtained: at a temperature of 242n°C on an electrostatic filter of 242 °C, dioxin emissions amounted to 893 ng/nm^3, at a temperature of 282°C - 2100, and at 347 °C - 8533. [8-10]

It is shown that the emissions of 15 toxic substances (PIC) from various types of combustion furnaces do not improve with a change in temperature from 700 to 1500 °C, with a change in the residence time of gases in the furnace from 2 to 6 s and a change in oxygen concentration from 2 to 15%. In addition, high tem- peratures lead to an increase in the volatility of the components, resulting in an increase in emissions, including hazardous metals. [9]

It is a common notion that quenching the off-gases ("quenching") will reduce the formation of dioxins. True quenching involves lowering the temperature many hundreds of degrees in a fraction of a second to freeze the thermodynamic equilibrium position at high temperature. This is difficult to achieve in real conditions of the WIP. But even if it were possible to freeze the hot mixture of gases, they would not achieve a decrease in concentration, since "new" dioxins are formed not in vapors, but on the surface of fly ash particles.

A typical "quenching" scheme: flue gases with a temperature of more than 850 °C enter either the water injection chamber or the waste heat boiler, where they are cooled to approximately 320 °C. [9]. These are precisely the temperature conditions under which secondary dioxins are formed. Thus, the waste heat boiler in the scheme under consideration is an ideal reactor for the formation of secondary dioxins. It is believed that reducing the oxygen content of the off-gases (European Union regulations require at least 6% in the gases during combustion) could

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improve the performance of this reactor in terms of secondary dioxin production.

Other dioxin removal methods are known and are detailed in the Annex. Let's take a quick look at some of the most effective ones.

Disinfection of waste **using infrared heating**. The process involves two processing. Decontamination efficiency 99.9999 %. Destruction of organic components of highly toxic waste, achieved instead of oxidation by electric **pyrolysis**. The temperature in the heat treatment zone is maintained at the level of 2200-2500 ºC, the processing time is milliseconds. The gases after pyrolysis undergo additional purification in a cyclone and in an adsorber with activated carbon. Stationary and mobile installation options have been developed. The main products formed during the treatment of soils contaminated with dioxins are hydrogen, chlorine and

HCl. Only materials that are homogeneous in phase (not sludge) can be processed in the plant. Dioxin disinfection efficiency ->99.999%.

The method of destruction of organic substances by melts, mainly sodium and potassium carbonates, with simultaneous air blowing has been known since 1969 and was originally used for coal gasification. Hydrocarbons are oxidized to carbon dioxide and water. Chlorine atoms of organochlorine substances are absorbed by the melt. The advantage of the process is a relatively low temperature (about 800-1000 ºC) and the absence of nitrogen oxides in emissions. Both solid and liquid wastes with low water and ash content can be processed. Destruction efficiency has been demonstrated on poisonous substances and herbicides. Impurities of highly toxic dioxin I are destroyed by 99.96-99.98%.

A dechlorination process was developed in an inert gas atmosphere at 600-800 ºC using calcium oxide fixed on silica gel. The process takes place in an electrically stirred reactor. Dioxins and furans are destroyed by more than 99.99%.

Several effective technologies have been created for the disinfection of highly toxic liquid wastes by high-temperature **pyrolysis in pyroplasm**. The processed waste is introduced directly into the plasma arc (> 5000 ºC). In this case, complex organic molecules decompose into atoms, which later recombine into the simplest molecules - H , N , CO, CO , HCl, ethylene, acetylene, etc. With this technology, not only liquid wastes are treated, but also suspensions of solids.

Several chemical methods of disinfection from dioxins and related compounds have been proposed and implemented. These include **dechlorination, oxidation and ozonolysis, reduction, chlorolysis**, etc. Some of them have not received industrial implementation, such as the destruction of dioxins with the help of quaternary ammonium base chlorides, as well as chlorolysis and oxidation with the help of ruthenium tetroxide. The treatment of dioxin-containing waste with alkaline reagents is considered, for example, in the USA to be particularly effective.

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Oxidation of dioxins by atmospheric oxygen under **non-catalytic conditions** is effective only at temperatures above 500 ºC. A number of methods have been developed that make it possible to oxidize dioxins and related compounds of various kinds with powerful oxidizing agents. In addition, catalysts are being developed that allow the oxidation of dioxins at temperatures below 100°C. The possibility of disinfection of dioxin-containing waters using **ozonation**, **RuO** , an aqueous solution of **hydrogen peroxide**, and a number of other technologies has been shown.

Photoexposure is one of the most effective methods for the destruction of dioxins. Successful photodegradation of dioxins must be preceded and/or accompanied by the use of any other methods - extraction, oxidation, dechlorination, etc. A number of combined disinfection methods have been developed. The most effective, however, is the destruction of dioxins by catalytic oxidation and photodegradation after their preliminary extraction from soils by solvents or sublimation into solutions at 500-600 °C.

A number of technologies combine the energy of **UV radiation and the action of oxidizers - ozone or hydrogen peroxide**. The process is carried out in water and is suitable for the destruction of halogenated solvents, pesticides, etc.

An effective means of **decomposing dioxin I is the photolysis** of its aqueous suspensions. The method of heterogeneous photochemical destruction of chlorine-aromatic compounds, including dioxins, under catalytic conditions is based on their irradiation in the presence of aqueous suspensions of semiconductors (TiO is most effective). In these systems, dioxins are rapidly destroyed and substances aremineralized with the formation of HCl, $CO_2$and other non-toxic products.

Methods are being developed for the **catalytic destruction** of dioxins and furans, which make it possible to drastically reduce the temperature, energy intensity, and cost of the process. It turned out, for example, that copper effectively catalyzes dechlorination and hydrogenation. The degree of destruction is 99.9999%. The method was used to neutralize liquid laboratory waste containing dioxins and furans. It is believed that low-temperature catalytic decontamination of these substances can become an alternative to high-temperature thermal decomposition.

Institute of Catalysis SB RAS (IC SB RAS), Novosibirsk is engaged in the development of technology for the neutralization of PCDD and PCDF and other highly toxic organochlorine compounds in exhaust gases based on **new generation glass fiber catalysts** with the Research Triangle Park (RTP), North Carolina, USA. The authors of the project believe that, compared with traditional catalytic processes, a significant increase in the efficiency of dioxin conversion can be expected, first of all, the elimination of the formation of secondary dioxins and other highly toxic products (phosgene, elemental chlorine), as well as a reduction in capital and operating costs due to a decrease in the cost of the catalyst and increase its service life. The method assumes high selectivity for the oxidation of organochlorine compounds into safe products (CO , H O, HCl), as well as the virtual absence of toxic by-products and secondary waste

Dioxin extraction technologies are based on sorption, extraction, coagulation and flocculation. A 93-98% reduction in dioxin emissions from solid waste is achieved by using sorbalite. Efficiency is improved by the addition of activated carbon. In Germany, a technology has been developed for the sorption of PCDD and PCDF from flue and flue gases using lignite coke filters. In this case, it is possible to reduce the concentration of dioxins in the purified gas by at least 2 orders of magnitude, bringing it up to acceptable standards. Zeolite-like natural montmorillonite chemically modified with aluminum hydroxide, natural smectite treated with copper salts, etc. were tested [1,2].

For the effective extraction of trace amounts of highly toxic PCDD and PCDF from industrial wastewater and liquid waste, their **sorption** using effective sorbents has been proposed. The method for removing trace amounts of PCDD and PCDF from sewage ponds and wells is based on **coagulation and flocculation with aluminum salts. Coagulants and polymeric substances introduced into wastewater from pulp and paper industries** contribute to the release of their lignin, tannin and dioxins. To do this, the effluent is passed through a suspended sediment - flocculated lignin and tannin. A pilot plant of continuous operation ensures the release of wastewater from dioxins and other substances by 90-95%.

The sorption properties of PCDD and PCDF are also used in modern waste incineration plants (WIP).

The level of emissions into the atmosphere depends on the specific combustion technology and gas cleaning system, but there are general principles for solving this problem. Usually the first step is dust cleaning with an electrostatic dust collector. This is followed by chemical, adsorption and/or catalytic treatment using appropriate equipment.

Only some of the listed technologies are able to meet the standard adopted in civilized countries. Specifically, in the United States, 40 CFR 264.343, established by the EPA, must ensure the destruction and disposal of 99.99% of all major hazardous components, and for the most hazardous organic components of toxic waste, such as PCDD, PCDF and PCBs, destruction and annihilation of 99,9999% [2,3]. It is obvious that the development of new and improvement of the presented technologies is necessary and is on the agenda.

References

1. Dioxin emission to air from MSW combustion- Data from some IEA member countries (Lars Sørum, Febr.2004)

2. L.A. Fedorov. Dioxins as an Environmental Hazard: A Retrospective and Perspective ed. V.V. Onoprienko. Moscow VO "Nauka" 1993

http://www.seu.ru/cci/lib/books/dioksiny/4/05.htm

3. (U.S. EPA Health Assessment Document for 2,3,7,8-Tetrchlorodibenzo-p-Dioxin (TCDD) and Related Compounds. EPA/600/BP-92/001c, August 1994).

4. Have, H. and Henriksen, K. S. An Energy-Efficient Combustion System for High-Moisture Organic Wastes and Biomasses. //Water and Environment Journal, (1998), V.12. pp. 224–232. doi: 10.1111/j.1747-6593.1998.tb00177.x

5. Commoner B. ,Shapiro K., Webster T. The origin and health risks of PCDD and PCDF. //Waste Management and Research .1987.V.5. pp.327-346.

6. Trenholm A. and Thurnau R. Proceedings of the Thirteen Annual Rasearch Simposium. Cincinnati: U.S. EPA Hazardous Waste Engineering Research Laboratory, EPA/600/9-87/015, July 1987

7. Yufit S.S. Typical mistakes of the authors of waste incineration plants projects. M.: IOC RAS, Ecoline Methodical Center, 1998.
8.”An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the U.S. for the Years 1987, 1995, and 2000 “.EPA. November 2006. http://cfpub.epa.gov/ncea/CFM/recordisplay.cfm?deid=159286
3. Hagenmaier H., Lindig C., She J. Correlation of environmental occurance of polychlorinated dibenzo-p-dioxines and dibenzofurans with possible souces. // Chemosphere. 1994.v.29. V.9-11. pp.2163-2174.
4. Jan G.P., Born. K.N. //Organochlorine Comp.(Dioxin’96) 1996, v. 27, p.46-49 .