

# Plasma decomposition method of hazardous waste

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## 1. Introduction

Hazardous waste is defined as: "Any substance reactive in solid, liquid or gaseous form which has no foreseeable use and which by reasons of any physical, chemical, reactive, toxic, flammable, explosive, corrosive, radioactive or infectious characteristics causes danger or is likely to cause danger to health or environment, whether alone or when in contact with other wastes or environment, and should be considered as such when generated, handled, stored, transported, treated and disposed of" [1, 2].

This includes any product that releases hazardous substance at the end of its life, if indiscriminately disposed of.

The most frequent request for shipments of hazardous wastes for disposal are:

1. poly-Chlorinated Biphenil (PCB), such as transformers liquid-cooled electric motors, fluorescent light ballast, adhesives, hydraulic system and heat-transfer system;
2. persistent Organic Pollutants (POPs) such as Hexachlorobenzene (HSB), DDT, chlordane, toxaphene, dieldrin, aldrin, endrin, heptachlor, mirex and dioxins and furans;
3. other harmful pesticide substances are not mentioned above.

Pesticides are defined as:

"Any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during, or otherwise interfering with, the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies" [3].

Persistent Organic Pollutants (POPs) are chemical substances which are extremely stable, and are known to accumulate in biological tissue thereby posing a risk of adverse effects to human health and the environment [4].

One of the leading principles of waste management, hazardous or otherwise, is by source reduction, by which the generation of waste should be reduced to a minimum in terms of quantity and/or hazard potential. Thereafter wastes that are nevertheless generated should be reduced, recycled and only when none of the above is feasible final disposal options should be considered.

For hazardous wastes such as PCBs and other POPs it is not usually possible to reuse, recycle or recover and so they must be destroyed or neutralized in an environmentally sound manner. It is no longer considered environmentally sound practice to recover PCBs although this has been done in the past.

In addition to high temperature incineration there is a number of technologies available or being developed at present. However, communication with the Food Agricultural Organization (FAO) suggests that incineration is still the preferred mean of decomposition of pesticides for the moment by FAO, World Health Organisation (WHO) and the United Nations Environment Programme (UNEP).

The treatment of hazardous waste is: physical, physico-chemical, chemical methods, thermal processes, biological processes.

The best known decomposition technologies are: Gas Phase Chemical Reduction (GPCR), Electrochemical Oxidation, Molten Metal Pyrolysis, Molten Salt Oxidation, Solvated Electron Process, Supercritical Water Oxidation, Catalytic Hydrogenation, Based Catalysed Dechlorination (BCD), Plasma Arc [3].

In plasma arc treatment directing an electric current through a lowpressure gas stream a thermal plasma field is created. Plasma arc fields can reach 5000 to 15000°C.

Advantages of plasma decomposition technologies are:

1. the intense high temperature zone can be used to dissociate waste into its atomic elements by injecting the waste into the plasma, or by using the plasma arc as a heat source for combustion or pyrolysis [5];
2. the waste streams from plasma arc decomposition of wastes as "essentially the same as those from incineration..." such as combustion by-products as salts (described the National Research Council - 1993).

Various plasma reactors have been developed for thermal decomposition of hazardous waste. Environment Australia considered three available plasma systems of appropriate technologies for the decomposition of hazardous wastes. These are:

- PACT (Plasma Arc Centrifugal Treatment);
- PLASCON (In-Flight Plasma Arc System);
- STARTECH (Plasma-electric waste converter).

The PACT process, developed by Retech (USEPA, 1992 and Thomas, 1994), uses heat generated from a plasma torch to melt and vitrify solid feed material. Organic components are vaporized and destructed by the intense heat of the plasma and are ionized by the air used as the plasma gas, before passing to the off-gas treatment system metal-bearing solids are vitrified into a monolithic nonleachable mass.

The PACT mentioned above is a combination of Plasma Arc and Vitrification techniques [6].

In the PLASCON system a liquid or gaseous waste stream together with argon is injected directly into a plasma arc, which provides plasma/waste mixing temperatures in excess of 3000°C.

The STARTECH Plasma-electric Waste Con-

verter (PWC) was developed in the US by the Startech Environmental Corporation. The system was designed to treat wastes both hazardous and nonhazardous. Startech has an agreement with Zealmore Pty Ltd for the sale and installation of Startech Plasma Waste Converters in Australia (Schallhammer, 1997).

The Plasma Waste Converter forces gas through an electrical field to ionize the gas into a plasma. The plasma operates at temperature range from of 3000°C to 5000°C. The plasma chamber operates at normal atmospheric pressure.

The goal of this work was to develop a special experimental plasma thermo-reactor that decomposes materials at 4500°C, and to perform a safe decomposition of chosen hazardous waste (pesticides) in a plasma steam with the analysis pollutant of emissions. The basis was the environmental normative document "The Main Requirements for Burning of Waste LAND 19 - 99".

## 2. Materials and experimental procedure

Five different materials according to their influence and chemical composition were chosen for plasma decomposition:

- DNOK – banned in 1966. High acute toxicity.
- DDT – banned in 1975. Low degradability and dangerous for the environment.
- Caratan (Dinocap) – banned in 1990. Teratogenic effects at low doses.
- Fenturan – banned in 1990. Dangerous for the environment [7].
- Coal – in the form of graphite.

The pesticides were mixed with liquid glass, pressed into graphite capsules, and dried. This was done in order to avoid powder pesticides going out to environment during transfer to the plasma thermo-reactor, and to dose them easily. Weight of dried pesticides in one capsule was 60 g. A pure graphite capsule was decomposed separately, too.

After decomposition, the concentrations of emitted pollutants were recalculated under the normal conditions (0°C and 101.3 kPa) and standard oxygen concentration of 11% (LAND 19 - 99).

Statistical data processing were performed by using software "Statistica". For each test 5 specimen were used. Errors of the measurements did not exceed 8%.

The limits of emitted pollutants to the air are given in the standard "LAND 19 - 99" (Table 1).

Principal scheme of plasma decomposition system of pesticides is given in Fig. 1. The main parts of the system are a plasmatron and a chamber of plasma reactor (thermo-reactor). The thermo-reactor has an electric relation to the plasmatron and is the continuation of anodic part of the plasmatron. The thermo-reactor chamber is made of high temperature, electro-conductive and chemical-resistant material. The outer wall of this chamber is cooled. In the thermo-reactor, during decomposition, different gas can be used, and reduction environment can be created.

Plasma decomposition system for pesticides works as follows. Plasma torch generator unit 1 that is situated above the plasma reaction chamber 2, orients plasma stream along the reaction (burning) chamber. Atmosphere air is used as plasma creating gas (a gas feed unit

Table 1  
Limits of emitted pollutants (LAND 19 - 99)

No	The name of a pollutant or their group	Limits of pollutants mg/Nm <sup>3</sup> (LAND 19-99)
1	Coal monoxide	450
2	Nitrogen oxides	400
3	Sulphur dioxide	1100
4	Solid particles	50
5	Non-organic chlorine compositions	100
6	Non-organic fluorine compositions	8
7	Organic chlorine compositions	No data
8	Cd+Tl and their compositions	0.1
9	As+Pb+Sb+Cr+Cd+Cu+Mn+Ni+V+Sn	1.0
10	Metals in ashes, mg/kg: Cu+Cr+Ni+Pb+Cd+Mn+As+V	No data

10). The pesticides (P) in graphite capsules are transferred to the upper part of the reaction (burning) chamber with the help of a pesticides feed unit 3. A capsule with pesticides moves towards the centre of the chamber and is influenced by plasma stream. Material in the reaction chamber is decomposed to the atomic level, and comes during condensation into the solid form (A) in ashes cooler unit 4, and into the gaseous form (G) in the air tube that leads from the plasma reaction chamber to gas cooler 5. Gas in the cooler loses its high temperature and goes into gas analysis unit 6 with gas assessment measuring device and probes. The gas is pulled further from the gas analysis unit with the help of a fan at standard speed (5 m/s), until it

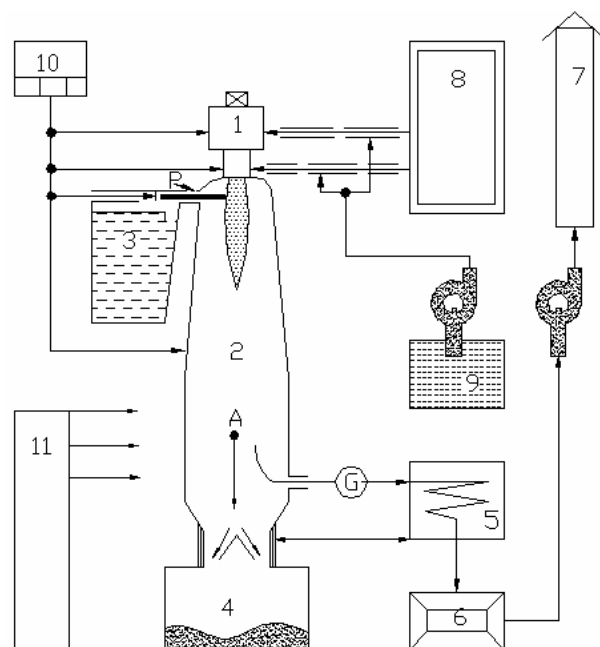


Fig. 1 Plasma decomposition system for pesticides: 1 – plasma torch generator unit; 2 – plasma reaction chamber; 3 – pesticides feed unit; 4 – ashes cooler unit; 5 – gas cooler; 6 – gas analysis unit; 7 – stack; 8 – electric power to plasma unit; 9 – water cooling pump; 10 – gas feed unit; 11 – process control system; P – pesticides; A – ashes; G – gas

comes into a stack 7. The plasma torch generator unit receives energy from an electric power unit 8, and it is cooled by water cooling pumps 9. Decomposition system of pesticides has equipment for temperature control, cooling of the reaction chamber, and the whole process control (process control system 11).

When plasmatron power is constant, temperature conditions of the thermo-reactor are controlled by choosing an appropriate cooling rate of the outer walls of the chamber, according to given regularity, found empirically (Fig. 2). The curve "heating" corresponds to the conditions when the plasmatron is on, the curve "cooling" – when the plasmatron is off (time is calculated from the beginning again). The outer wall of the thermo-reactor chamber during operation can not exceed 1000°C.

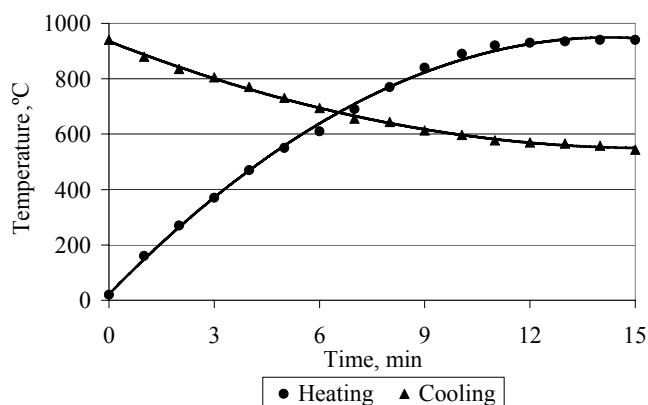


Fig. 2 Temperature conditions of the outer wall of the thermo-reactor chamber "heating – cooling"

The whole system is cleaned before decomposition of a new material.

Technical parameters of plasma decomposition system for pesticides are given in Table 2.

Table 2  
Technical parameters of plasma decomposition system for pesticides

No	Name	Parameter
1	Type of plasma torch generator unit	Special construction
2	Electric power unit	APR – 403
3	Plasma gas, discharge, m <sup>3</sup> /h	Atmosphere air = 2
4	Type of electric current	Direct
5	Power, kW	30
6	Cooling type of the system	Water, air
7	Dimensions of a pesticide capsule, mm	16x100
8	Capsule feeding rate, mm/min	12
9	Speed of moving gas in the air tube, m/s	5

### 3. Results and discussions

Before experiments with pesticides, the capability of the reaction chamber to reach high temperatures for material decomposition was checked. One of the chosen materials for plasma decomposition was aluminium hydroxide that passes many phase changes during heating, until it

becomes at about 1200°C an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> composition, so called corundum. When corundum is heated at higher temperatures, it does not change its phase composition, its melting temperature is 2050°C [8].

The experiment for decomposition of aluminium hydroxide in a plasma stream was done in by following method. Al(OH)<sub>3</sub> powder (fraction ≤ 100 μm) was fed into the plasma stream and decomposed. The decomposed material in the reaction chamber passes a certain distance down and is condensed in a certain geometric shape, in an extra and intensely cooled "casting" mould (Zone A, Fig. 1). The cast detail is monolithic, with a good filling of the mould, and it shows a high degree of material overheating during its condensation.

On the other hand, the material is condensed in the casting mould at high cooling rate. Roentgen diffraction analysis (Fig. 3) shows differences between gauge corundum according to "Staford" standard (curve 1) and corundum that was received during Al(OH)<sub>3</sub> decomposition in plasma at the controlled temperature of 4500°C, at high cooling rate in condensation (curve 2).

In the second case, according to XRD (Fig. 3), the height of corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) spikes is relatively low, and rather large quantity of an amorphous part in corundum is seen. And so, the plasma reaction chamber guarantees effective decomposition of hard-fusible materials and extremely rapid cooling of the decomposed material at the same time. For example, it is possible to cover with glass the ashes of destructed pesticides.

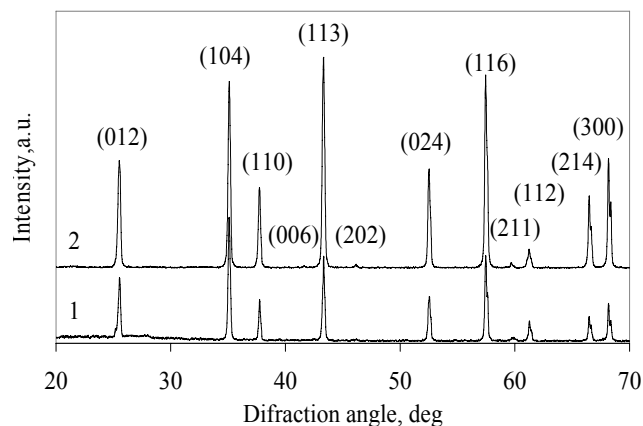


Fig. 3 XRD patterns of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>: 1 – Alumina (Aldrich Chemical Co., 99.7%) Standard; 2 – corundum, received during Al(OH)<sub>3</sub> decomposition in plasma at 4500°C

The later experiments were done for decomposition of chosen pesticides.

The analysis of pollutants emission in gas during decomposition showed that organic compositions were destructed fully in all cases.

1. Concentration of coal monoxide is in all cases lower than the limit: in DNOK – for about 2 times, in Fenturan – for about 13 times (Fig. 4).

2. Concentration of nitrogen oxides (NO<sub>x</sub>) exceeds the limit in all cases not less than 10 times, even in the case when an empty graphite capsule is destructed.

3. Concentration of sulphur dioxide in Fenturan decomposition is lower than the limit 11 times. SO<sub>2</sub> was not found in the decomposition of other pesticides.

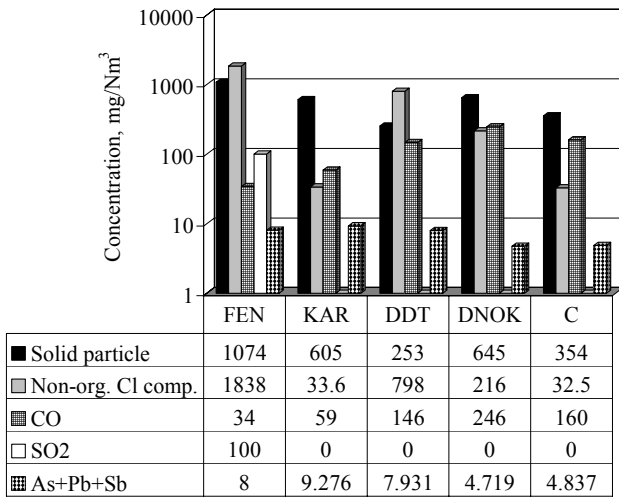


Fig. 4 Emission of pollutants in gas

4. Concentration of solid particles in gas is in all cases higher than the limit, even in that case when an empty graphite capsule is destructed, in DNOK – for about 13 times, in Fenturan – for about 21 times.

5. Nonorganic chlorine compositions exceed the limit in Fenturan for about 18 times, and the concentration is lower than the limit for about 3 times in Caratan decomposition.

6. Nonorganic fluorine compositions were not found in any case.

7. Organic chlorine compositions are destructed fully in all cases.

8. Cd + Tl and their compositions were only in DDT decomposition but their concentration was lower than the limit for about 100 times. They were not found in decomposition of other pesticides.

9. Metals: As+Pb+Sb+Cr+Cd+Cu+Mn+Ni+V+Sn and their compositions in gaseous form exceed the total limit for about 10 times (Fig. 4).

Copper is in all cases a dominant element by weight, comparing to other elements (Fig. 5) (the result of copper electrode erosion in plasma torch generator unit, and a component of a pesticide).

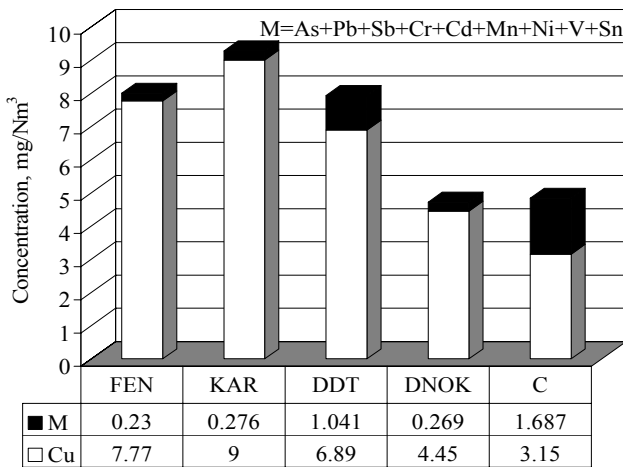


Fig. 5 Metals As+Pb+Sb+Cr+Cd+Cu+Mn+Ni+V+Sn and their compositions – emission in gas

Emission of metals and their compositions (except for Cu) in gas is a little bit greater in DDT (Pb, As) and graphite capsule (Cr, Ni, Pb) decomposition (Fig. 6).

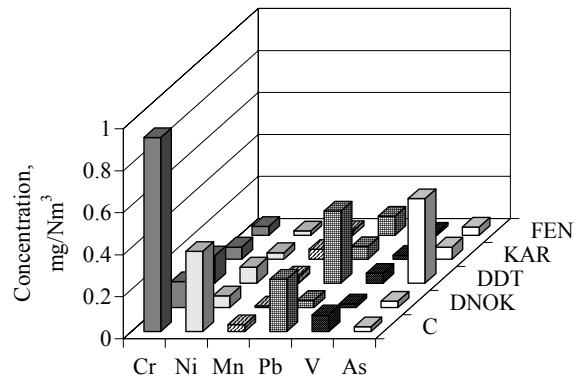


Fig. 6 Emission of metals (except for Cu) in gas

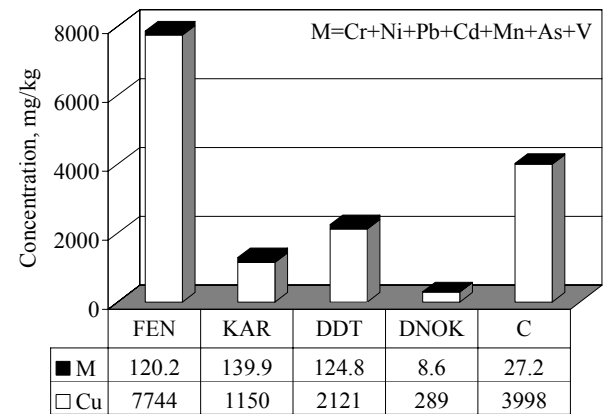
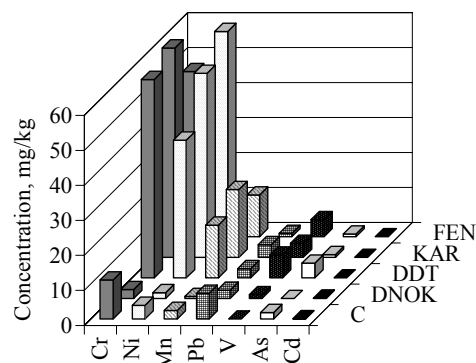


Fig. 7 Emission of metals in ashes



	FEN	KAR	DDT	DNOK	C
■ Cr	47.2	59.9	56.8	2.61	11.2
□ Ni	58.7	52.6	39.4	1.7	4
▨ Mn	11.9	19.4	15.1	0.63	2.52
▩ Pb	1	3.64	2.63	2.4	7.4
■ V	4.89	4.02	6.61	1.1	0
□ As	0.73	0.76	4.19	0	1.9
■ Cd	0.01	0.03	0.03	0.11	0.15

Fig. 8 Emission of metals (except for Cu) in ashes

Emission of metals Cu+Cr+Ni+Pb+Cd+Mn+As+V and their compositions is different in ashes after decomposition of different materials. The limits are not defined. It is obvious that the weight of copper in all cases is relatively much greater than total weight of the rest chemical elements (Fig. 7).

The highest emission of metals (except for Cu) in ashes is for Fenturan, Caratan, and DNOK. Relatively large quantities of Cr, Ni, and Mn are found here (Fig. 8) (chemical composition by elements in pesticides).

Decomposition experiment of pesticides and coal was done without any means for collecting and filtering of pollutants in the gaseous form, in order to get "clean" results. Only 5 materials were destructed, and only once, and the emission of pollutants was assessed according to LAND 19 - 99. Consequently, no parameters of plasma reaction chamber were changed. Atmosphere air was used as plasma gas because of the low cost of the process.

Under such conditions of the process, it is possible to explain why emission of pollutants exceeds the limits in some cases.

Considerable formation of nitrogen oxides ( $\text{NO}_x$ ) in noticeable concentrations starts from 1200°C.

A necessary condition for nitrogen in air to oxidize is the atomic oxygen in the torch. Then, the following reactions take place:



3 factors have the main influence for formation of nitrogen oxides ( $\text{NO}_x$ ):

- concentration of oxygen atoms in the reaction (burning) chamber;
- temperature in the decomposition zone;
- exposure time of decomposition products to high temperatures.

The following means for reduction of "thermal" nitrogen oxides can be used:

- reduction of an air surplus ratio;
- reduction of exposure time of burning products to high temperatures;
- recirculation of burning products;
- multistage burning.

It can be achieved by the change of parameters of plasma reaction chamber.

Nitrogen oxides, solid particles, nonorganic chlorine compositions, metals and their compositions can be collected in the solutions, too, using chemical methods of collection [9].

#### 4. Conclusions

1. A plasma thermo-reactor was developed for decomposition of materials at 4500°C. Organic compositions are destructed fully.

2. The limits of pollutants according to LAND 19 - 99 are not exceeded: for coal monoxide, sulphur dioxide, organic chlorine compositions, nonorganic fluorine compositions, Cd + Tl and their compositions.

3. Too high emission in gas of nitrogen oxides, solid particles, nonorganic chlorine compositions and met-

als: As+Pb+Sb+Cr+Cd+Cu+ Mn+N+V+Sn, as well as their compositions, could be avoided by complex use of a classical system of filters, cyclones, and scrubbers. Additionally, it is necessary to use chemical methods, to recirculate burning products, to decrease temperature of the decomposition process, to change the composition of plasma gas, and to use catalysts.

4. As far as plasma thermo-reactor guarantees decomposition of any materials and partial fuse of particles during condensation, it would be possible to use sand, that could do the function of protective covering with glass for ash particles. It is probable that after an extra check, these partially fused materials could be either preserved or used as a filling medium for construction and road repairing.

5. This method could be used for decomposition or synthesis of other materials with different chemical compositions from ionized steam, as well for casting of hard-fusible ceramics with a certain geometric shape.

6. A separate application could be decomposition of hazardous industrial, pharmaceutical waste and narcotic materials.

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Measurement of emissions of pollutants was done in co-operation with the United Research Centre.

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## PLAZMINIS PAVOJINGŲ ATLIEKŲ SKAIDYMO BŪDAS

### Резюме

Straipsnyje aprašomas cheminių atliekų (senų pesticidų) skaidymas, panaudojant oro plazmos srautą, kai plazminio termoreaktoriaus darbo zonoje pasiekama temperatūra viršijanti 4500°C. Pateikti pesticidų (karatano, fentiurano, DNOK ir DDT) dozavimo, jų skaidymo plazmos sraute bei teršalų surinkimo techniniai sprendimai. Aprašyti vykdyto technologinio proceso testai „in situ“, pateikti analizės pelenuose (po skaidymo) rezultatai ir į aplinkos orą išmetamų teršalų ribinės vertės, reglamentuojamos aplinkos apsaugos normatyviniu dokumentu „Pagrindiniai atliekų deginimo reikalavimai LAND 19-99“.

Remiantis tyrimų duomenimis galima teigti, jog net tuo atveju, kai eksperimentas atliekamas „švariai“ ir nenaudojamos jokios filtravimo sistemos, anglies monoksido koncentracija yra mažesnė už leistiną nuo 2 iki 13 kartų, sieros dioksido apie 11 kartų, o chloro organiniai junginiai suskaidomi visiškai.

Išvadose pateikiama pasiūlymų dėl suskaidytų medžiagų panaudojimo galimybių, skaidomų medžiagų asortimento išplėtimo. Ši plazminė sistema galėtų būti pritaikyta ir naujų sunkiai lydomų medžiagų sintezei.

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## PLASMA DECOMPOSITION METHOD OF HAZARDOUS WASTE

### Summary

The article presents a decomposition method of chemical waste (old pesticides) with the help of an air plasma stream, when temperature in plasma thermo-reactor zone reaches more than 4500°C. Technical solutions for dosage of pesticides (Caratan, Fenturan, DNOK, and

DDT), their decomposition in plasma stream and collection of pollutants are given. The tests of a performed technological process “in situ” are described, ashes analysis after decomposition is made, and the limits of emitted pollutants to the air are found according to the environmental normative document “The Main Requirements for Burning of Waste LAND 19-99”.

The research shows that, even in the case of a “clean” experiment without any filtering system, the concentration of carbon monoxide is lower than the limit for 2 to 13 times, sulphur dioxide – for about 11 times, and chlorine combinations are destructed completely.

Conclusions show the application fields of destructed materials, indicate the other decomposable materials. This plasma system could be adapted for the synthesis of new nonfusible materials, too.

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## ПЛАЗМЕННЫЙ МЕТОД РАЗЛОЖЕНИЯ ОПАСНЫХ ОТХОДОВ

### Резюме

В статье представлен способ разложения химических опасных отходов (старых пестицидов) в потоке воздушной плазмы. Температура в рабочей зоне плазменного термореактора превышает до 4500°C. Представлены технические решения для разложения пестицидов (каратана, фентиурана, ДНОК, ДДТ), их дозирования, обработки в плазменном потоке и сбора в виде отходов. Определены данные „in situ“ завершеного технологического процесса, представлены результаты анализа после разложения в пепле и выбросов в воздушную среду, предельные критические значения, регламентируемые нормативным документом для окружающей среды „Основные требования для сжигания LAND 19 – 99“.

На основе выполненных исследований можно утверждать, что даже в том случае, когда эксперимент выполняется „чисто“ и не используются системы фильтрации, концентрация монооксида углерода меньше допустимого значения от 2 до 13 раз, диоксида серы примерно в 11 раз, а органические соединения хлора разлагаются полностью.

В выводах представлены предложения по возможности использования разложенных материалов, для расширения ассортимента разлагаемых материалов. Данная система может быть использована и для синтеза новых тугоплавких соединений.

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