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USE OF A PLASMA REACTOR WITH A THREE-JET MIXING CHAMBER FOR PROCESSING OF LIQUID TOXIC WASTE MATERIALS

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We present a brief review and show the outlook for processing of toxic waste materials by a plasma method. We carried out experimental investigations of the processing of liquid toxic organic and organochlorine waste materials in a plasma reactor with a three-jet mixing chamber.

One of the most serious ecological problems facing many industrially developed countries is pollution of the environment by communal and industrial waste materials that in the majority of cases have such undesirable properties as toxicity, carcinogenicity, mutability, corrosiveness, reactivity, and fire hazard. Radioactive and medical waste materials occupy a special place in this series. The accumulation of untreated hazardous waste materials on dumping and testing grounds, burial in the earth and at sea cannot be considered an appropriate means for neutralizing their harmful influence on the environment, since there is always a high risk of contamination of soil, ground and surface water, and air by hazardous substances. And this risk could persist for a long time. This presents a grave threat to the life of people, animals, vegetables, i.e., to the normal existence of the entire ecological system.

A very strong argument against the well-known and relatively cheap means of storing and placing waste materials is that in a number of cases, with a better understanding of the effect of chemical substances contained in waste on nature, it has been found that there is a greater danger from waste materials whose burial was not expected to cause ecological problems. This can be seen by the example of waste materials containing phenol-formaldehyde resins and pesticides.

Despite strict standards and rigorous requirements introduced in industrially developed countries on the siting and equipping of testing grounds, the burial and storage of hazardous waste materials, and their composition, preference is given to technological methods for neutralizing waste [1, 2], which include decontamination, reuse, and reduction of the volume of waste to be buried, despite the fact that technological methods for processing of waste materials require significant energy expenditures.

The technique most widely used for processing of liquid toxic waste materials is burning, pyrolysis, and thermal decomposition. Industrial furnaces and boilers are used only when the liquid waste materials have moderate or high calorific values and a minimal chlorine content. Low ecological indices and the very narrow range of organic waste materials that can be burnt in industrial furnaces made it necessary to develop special technologies for processing of toxic waste, some of which are already being applied, while others are at the stage of investigation. These include a combustion chamber with burners for liquid fuel injection, rotating roasting furnaces, electric infrared furnaces, fluidized-bed circulating furnaces, and combustion chambers with oxygen-enriched burners.

Unfortunately, all the above and other means for burning of liquid toxic waste have a substantial drawback. The thing is that in the burning of chlorine-containing organic substances at insufficiently high temperatures, in addition to nitrogen and carbon oxides, phosgene, dibenzofuran, dioxin, benzopyrene, and other ultratoxic products in amounts exceeding the maximum permissible concentrations (MPC) can be formed.

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An alternative approach to the existing and new technologies of low-temperature combustion of liquid toxic waste materials is their burning in a low-temperature plasma, i.e., high-temperature combustion. The use of electric-arc, high-frequency, and other means for producing plasma with mean mass temperatures of the order of 5000 K allows one to destroy organic and inorganic compounds at very high rates and with a high degree of conversion. Moreover, complex compounds can be destroyed very efficiently in a plasma in the absence of oxygen. It is also possible to effect such an important factor of thermal processing of waste as good mixing of the reacting components, resulting in an increase of the degree of conversion.

A considerable effort is currently devoted in many countries to the development of plasmochemical methods for processing of toxic waste, mainly organic compounds of chlorine and other halogens. Thus, in Russia investigations of the process of pyrolysis of organochlorine waste in a low-temperature electric-arc plasma were carried out with a view toward obtaining secondary raw material that can be reused in organochlorine synthesis [3, 4]. Hydrogen or methane was used as the plasma-forming gas. Subjected to processing were liquid, resin-like, and solid waste materials in the production of organochlorine substances. After purification, such products of pyrolysis as CO, C, C_2H_2, C_2H_4, CH_4, and HCl are again suitable for the synthesis of organochlorine compounds.

A plant for decontaminating chlorobenzene and dichloroethane in an electric-arc air plasma is described in [5]. It is noted that the presence of chlorine in waste gases seems to be due to excess air (oxygen), since the initial products contained sufficient hydrogen for chlorine bonding to obtain hydrogen chloride. Quenching and cooling were performed using an adiabatic flash tank and sprayed water. Gaseous chlorine was removed, while the weak solution of hydrochloric acid obtained from hydrogen chloride was neutralized by alkali.

One of the laboratories of the United States Environmental Protection Agency has developed a mobile plasma plant for processing of toxic waste materials [6]. The latter work cites test data on processing of carbon tetrachloride mixed with methyl ethyl ketone, ethanol, and water, as well as with methyl ethyl ketone and methanol. The results of investigations showed that in both cases the decomposition degree of CCl_4 attained 99.9999%. Analysis of the final products for toxic substances showed that the concentration of CO and NO_x was 0.01 vol.%. Tests for dioxins and furans revealed only traces. A similar plasma plant for processing of polychlorides of diphenyls was employed by the Westinghouse Corporation [7]. The results showed that the degree of diphenyl decomposition was 99.99%. The final products contained carbon monoxide, which was later burned out. No dangerous toxic substances (dioxins, dibenzofurans) were observed in the waste gases.

Another work, also conducted in the USA, [8] presents investigations of the decomposition of organic and organochlorine waste materials in a countercurrent plasma reactor. The power of an Ar-operated plasmatron was about 14 kW. Two types of raw material were used: 1) hydrocarbons: acetone, gasoline, methyl ethyl ketones (MEK), and special thinners. The final products were CO_2, H_2O, CO, H_2, and 0_2; 2) chlorinated hydrocarbons: chloroform, dichloromethane, carbon tetrachloride (CCl_4), and polychlorinated biphenyls (PCB). The final products were CL_2, C, CO, H_2O, H_2, HCl. The consumption of raw material varied, but for PCB it was equal to 5 ml/min; the conversion degree was more than 99%.

One other work on thermal processing of chemical waste by the plasma method was carried out by an English company EA Technology [9]. They used a plasma reactor with three electric-arc plasmatrons operating on three-phase alternating current with a frequency of 50 Hz. The total rated power on an arc was 50 kW. The reactor was steel, water-cooled, lined with alumina, and separated inside by partitions into several sections. The plasmatrons were installed in the first section of the reactor. The raw materials used were model chemical substances simulating harmful chemical waste, ethanediol, 1,1,1-trichloroethane, benzene-alcohol, 1,2-dichlorobenzene, oil refining waste, and polychlorinated biphenyls. Various technological regimes of the process were investigated, including steam supply to decrease soot formation. The raw material capacity of the plant was from 1.7 to 6.5 kg/h, energy expenditures ranged from 3.1 to 16.9 kW·h/kg, and the conversion degree was 99.9%. It is noted that the process of pyrolysis in the presence of steam is very efficient for the destruction of organochlorine compounds.

Concluding this survey of works, note should be made of the technological process PLASKON developed by the Australian company XIRO for processing of liquid toxic waste [10]. Unlike Westinghouse, which makes use of burners, PLASKON employs a plasmatron that operates on argon. The power of the plasmatron is 150 kW, and its efficiency attains 50%. The service life of the argon-operated plasmatron is fairly long, and the temperature of the argon–raw-material mixture attains 5000 K at the place of their mixing. A typical composition of waste in experimental investigations by the PLASKON technology is as follows (wt.%): chlorophenol 34.2, phenoxides 46.7, toluene 19.1.

Toluene is added to waste materials in order to decrease their viscosity and ensure their delivery through the atomizer. At the exit from the reaction channel, the mixture is rapidly cooled from 2000 K at a rate on the order of 10^6 K/sec to prevent reverse interaction of the decomposed initial raw material. For the most part, the mixture is of the following composition: CO, H, HCl, H_2O, and Ar, together with a small amount of finely dispersed carbon. There is a very small content of CO_2, indicating oxygen deficiency. Oxygen is added at the exit from the reactor to ensure the conversion of carbon into CO. The following products of pyrolysis and condensation of waste materials are obtained:

Elements of plasma	Condensation products	Final products
6 atoms of carbon	6CO – gas (effluent)	6 CO_2 – gas
4 atoms of hydrogen	2HCl – gas (scrubber)	2 NaCl + H_2O
2 atoms of chlorine	1H_2 – gas (effluent)	1H_2O
6 atoms of oxygen	carbon (scrubber)	carbon

At the exit from the plasma reactor the decomposition products are cooled by NaOH. The condensation products enter the scrubbers of the first and second stages and come in contact with the injected NaOH. The gas, which contains HCl, reacts with NaOH and forms a NaCl solution, which is then removed from the scrubber. The remaining gas, which contains CO, Ar, and H_2, is burned in the exiting flame after passage from the Venturi nozzle, and CO is converted to CO_2.

The data given indicate the advantages of the plasmochemical method for decontaminating of liquid toxic organochlorine waste materials compared to the technology of burnings in furnaces. The plasma method is more ecologically sound and economically efficient, at least for processing of highly chlorinated slightly combustible compounds, whose thermal destruction requires a large amount of additional fuel – natural gas.

The investigations dealing with the processing of liquid toxic waste described in the present work are characterized by the use of a highly turbulent plasma flow formed in a three-jet mixing chamber, which operates with three electric-arc plasmatrons. They ensured rather good mixing of the plasma flow with the raw material being processed. Two plasma plants were assembled: one at the Laboratory of Plasma Technology of the Heat and Mass Transfer Institute, Academy of Sciences of Belarus (Minsk), and the other at the Halle Wittenberg University (Merseburg, Germany). The latter plant is equipped with a system for automatic control and management of the parameters of its operation and with a modern system for controlling waste gases up to the determination of the quantity of ultratoxic compounds (dioxins and furans), which, according to German law, must not exceed 0.006–0.009 mg/m^3. Below, we will consider only the results for the plant at the Heat and Mass Transfer Institute of the Academy of Sciences of Belarus. A diagram of the plant is presented in Fig. 1. The main unit of the plant is a plasma reactor with a three-jet mixing chamber. The plant also includes a system for supplying raw material to the plasma reactor; it consists of a tank for liquid waste, gas and solution pipelines, and a pneumatic sprayer for supplying and dispersing waste material. At the exit from the reactor channel the final products of the process enter an expansion hopper and then successively a dry and a wet filter. To withdraw waste gases for analysis, a system was used that included a withdrawal pipe, a vacuum pump, and a set of evacuated flasks with a system of taps. Energy for the plant is provided by a system for electrical supply and ignition of the plasmatron, systems for gas and water supply to the reactor, as well as a system for controlling and managing the parameters of plant operation. The choice of the initial materials for investigations was made on the basis of a computer database on waste materials. This database was created by the state-owned Scientific-Industrial Company "Belvtorresursy" (Secondary Resource Materials of the Republic of Belarus.) It was found that, as a result of the work of more than a dozen of powerful enterprises, the city of Minsk alone accumulates a considerable amount of harmful waste

TABLE 1. Operational Parameters of Plasma Reactor

Number of experiment	Gas flow rate, g/sec	ΣN, kW	ΣN_1, kW	$T_{\mathrm{m.m}}$, K	T_{ex}, K	$\Sigma N/G_{\mathrm{m}}$, kW/kg	G_3	G_{d}, g/sec	Kind of raw material
1	6.47	84	68.55	5240	2350	6.48	–	0.52	Without raw material
2	6.25	104.4	102.60	5830	3320	8.05	–	0.16	AG
3	8.8	114.8	98.75	5290	2980	8.85	–	0.28	AG
4	8.8	114.8	98.75	5280	2780	8.85	6.95	0.28	AG
5	6.25	104.4	89.45	5710	3150	8.05	–	0.16	CM
6	6.25	104.4	89.57	5720	3110	8.05	6.95	0.16	AG
7	7.95	110.6	95.78	5350	2970	8,53	–	0.28	MC
8	7.95	110.6	96.42	5380	2990	8.53	–	0.28	MC
9	7.95	110.6	99.94	5670	2990	8.53	–	0.28	MC
10	5.75	93.6	76.26	5720	2860	7.22	–	0.27	MC + AG
11	5.75	93.6	76.26	5720	2860	7.22	6.95	0.27	MC + AG
12	5.75	100.8	83.66	5680	2900	7.77	–	0.27	MC

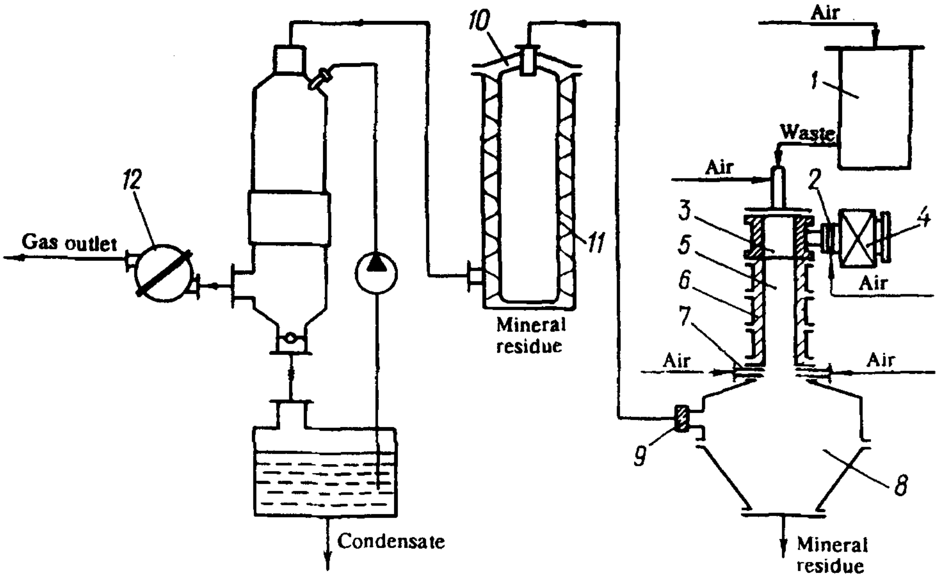

Fig. 1. Diagram of plasma installation: 1) tank for supplying and batching waste materials; 2) electric-arc plasmatron; 3) mixing chamber; 4) solenoid; 5) reaction zone; 6) reactor sections; 7) quenching ring; 8) separating hopper; 9) insulator; 10) filter; 11) scrubber; 12) fan.

materials (the total of tens of tons per year), including those that contain toxic organic substances and organochlorine materials. These include such substances as compounds with solvent residues, vat residues with methylene chloride MC, varnish and paint waste materials, waste materials of alcohol-gasoline (AG) mixtures with additions of gum rosin, vat residues with methyl chloroform, etc.

At the first stage, the objects of investigation were vat residues with methylene chloride and waste materials of an alcohol-gasoline mixture contaminated by gum rosin. Processing of other above-listed waste materials is hindered by the impossibility of their continuous supply into the plasma reactor. This will be a subject of further investigations.

TABLE 2. Relative Intensity of Ion Peaks (in % of Maximum Value)*

Sample	Mass units (m/u)												
	12 C	14 N	16 O	18 H_2O	28 N_2	29 C_2H_5+ CHO	30 NO	32 O_2	34 H_2S	36 HCl	40 C_3H_4	44 CO_2	46 NO_2
MAT-311 background				81	100			23				59	
Plasmatron background		12	2.5	8	100	5	3	55	0.5	0.6	10	19	
2 AG	4	36	12	4	100	13	14	48	0.4	0.3	31	43	
3 AG	2.5	33	6	5	100	10	8	46	0.1	0.05	22	43	
4 AG		5	3	26	100			43		0.2	7	33	
5 MC		15.5	7	4	100	5	7	48	0.5	0.25	15.5	21	0.35
6 AG		24	5	3	100	7	9	48	0.1		17	36	
7 MC		4	2.5	80	100		12	28			2	24	
8 MC		11	4.5	6.5	100	4.5	10	50	0.5		9.5	8.5	
9 MC		8	3.9	7.0	100	5.0	11	35	0.6		7.3	15	
10 MC+AG	1.72				100	8.6	8.6	34.5		7.2	10.3	24.1	
11 MC+AG	0.86				100	8.6	8.6	34.5		0.43	10.3	24	
12 MC	0.34				100	7.8	5.2	56.9	1.4	0.34	22.4	20.7	

*Mass-spectrometric investigations were carried out at the Institute of Molecular and Atomic Physics, Academy of Sciences of Belarus.

The results of experiments on decomposition of liquid toxic waste in the plasma reactor are presented in Table 1. The table contains operational and calculated parameters of the plasma reactor with three-jet mixing chamber. The power N of each of the plasmatrons was varied from 28 to 40 kW, the power at the reactor entrance N_1 ranged from 84 to 115 kW, the total discharge of the plasma-forming gas G_g varied from 6.25 to 8.8 g/sec, the mean mass temperature of the plasma-forming gas $T_{m.m}$ ranged from 5240 to 5830 K, and the temperature at the reactor exit T_{ex} ranged from 2350 to 3320 K. In view of the complexity of variation of the liquid waste flow rate G_m, it was kept constant and equal to 3.6 kg/h. In some of the experiments, we quenched the final products, i.e., supplied additional cold air to the transfer hopper at aflow rate G_3 of 6.95 g/sec. This aided, first, waste and burn-up, second, sudden sharp cooling from a temperature above 2000 K and prevented reverse reactions with the formation of dioxins/furans. The quantity of the dispersing gas supplied to the atomizer for spraying the raw material G_d was varied from 0.16 to 0.28 g/sec.

We investigated the gas phase of the final products of processing of toxic liquid waste by analytic (chemical) methods and by mass-spectrometric methods at the Institute of Molecular and Atomic Physics, Academy of Sciences of Belarus. We determined the content of nitrogen oxides analytically by the method of evacuated flasks and of chlorides by titrating them with silver nitrate with potassium chloride used as an indicator. Mass-spectrometric measurements were performed on a Varian MAT-311. The samples investigated were inserted into the mass spectrometer through the gas-supply system. The samples were subjected to electron impact in vacuum at a residual pressure of $10^{-5}-10^{-6}$ mm Hg. The ionizing radiation energy was 70 eV, the cathode emission current was equal to 300 μA, and the temperature of the ion source was 200°C. First, we recorded the mass spectra of the initial liquid waste materials: vat residues with ethylene chloride (sample No. 1) and an alcohol-gasoline mixture with additions of gum rosin (sample No. 2). In the mass spectrum of sample No. 1 we discovered chlorine as isotopes ^{35}Cl and ^{37}Cl. Sample No. 2 is an alkyl-substituted benzene with a mass of 274 m/u corresponding to $C_{14}H_{25}-C_{20}H_{34}$. The spectrum also displays ions with a mass of 77 m/u corresponding to phenyl, as well as fragments differing from one another by 14 m/u (CH_2-group) corresponding to saturated aliphatic hydrocarbons. The results of investigation of the gas phase of liquid waste materials are presented in Table 2, from which it follows that along with the peaks of the mass-spectrometer background ions 18 m/u (H_2O^+), 28 m/u (N_2^+), 32 m/u (O_2), and 44 m/u (CO_2^+) that are present in air, the gas contains ions with masses of 30, 40, and 46 m/u.

To determine the structure of the ions, we applied a high-resolution method. The "weighing" of an ion with a mass of 30 m/u made it possible to reference it to NO_1. Repeated "weighing" of an ion with a mass of 40 m/u gave contradictory results and did not allow us to determine precisely its structure in the following compounds: Ar^+, $C_3H_4^+$, $CH_2CN_2^+$, C_2O^+.

Since the intensity of the 46 m/u ion peak is small, it is not possible to record a high-resolution spectrum. However, the reddish black color of the gas allows us to assume that this ion corresponds to NO_2^+. The weak intensity of the NO_2^+ ion can be explained by the high reactivity of nitrogen dioxide. In reacting with the water vapor present in the air (the mass-spectrometer background), nitrogen peroxide forms nitric acid, whose mass spectrum is not registered. Comparison of the mass spectra of the gas phase after processing of raw material in the plasma reactor with the spectra of the initial waste materials makes it possible to assert that all the organic components of the waste materials are burned up, because the spectra differ very little from the spectra of the gas phase in the plasma reactor without these materials. The content of toxic compounds H_2S (34 m/u) and HCl (36 m/u) is insignificant, and they can be trapped by a scrubber. Chlorine in its pure form was not detected in the samples. In some gas phase samples, after processing of waste materials, we observed an increase in C^+ ions (12 m/u), which seems to be due to deficient oxygen for complete oxidation of the carbon to carbon dioxide.

Conclusion. The results of investigations on processing of liquid toxic organic and organochlorine waste materials agree rather well with the results of other works. The next task is optimization of the process to decrease specific energy expenditures and increase efficiency.

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