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# PLASMA-THERMAL PROCESSING OF TOXIC HALOGEN-CONTAINING ORGANIC WASTE

**A. N. Knak, V. A. Kalitko,**
**A. L. Mossé, and S. A. Fyodorov**

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*Results of experimental plasma-thermal processing of halogen-containing organic waste at temperatures of 4000–5000 K are reported. Analyses of exhaust gases of waste processing by chemicoanalytical and mass-spectrometric methods show complete thermal decomposition of the waste.*

**1. Introduction.** The most widely employed method of processing of toxic organic waste is burning, provided that the waste possesses is moderate to high calorific power and has a minimum amount of halogens.

Unfortunately all traditional methods of burning of such waste are characterized by a significant drawback: at comparatively moderate combustion temperatures, in addition to nitrogen and carbon oxide, phosgenes, dibenzofurans, dioxins, benzopyrenes, and other ultratoxic products can be formed in amounts which considerably exceed permissible concentrations [1].

An alternative to the existing technologies of low-temperature burning of toxic waste is processing in thermal plasma, i.e., high-temperature combustion. The use of electric-arc, SF, and other types of plasma with mean-mass temperatures of about 5000 K makes it possible to implement destruction of organic and inorganic compounds at very high rates and with a high degree of conversion [2]. Moreover, destruction of complex compounds in plasma proceeds rather efficiently in the absence of oxygen. Such an important factor of thermal processing of waste as thorough mixing of reacting components in a multijet plasma reactor can be also achieved [3].

In the first stage of investigation we processed liquid toxic waste in a plasma unit with a straight-through reactor. Use was made of one 5-17 kW electric-arc plasma generator with a flow rate of the plasma-forming gas (air) of 0.7–1.6 $m^3/h$ or of steam of 1.5–2.0 kg/h. The mean-mass temperature at the reactor inlet was 3000–5000 K. The mass flow rate of the waste processed was varied from 0.2 to 1.8 kg/h. As raw waste we employed model mixtures containing cyclohexane. Samples were analyzed by a mass-spectrograph and a gas chromatograph. Results of the investigations published in [4] have shown that the content of chlorine-containing compounds in exhaust gases does not exceed 0.5 $ng/m^3$. This parameter can be improved by providing good mixing of the plasma with the processed waste. For this, in the second stage of investigations a highly turbulized plasma flow was formed in a three-jet mixing chamber, for which three electric-arc plasma generators were operated. In this case, the plasma flow was sufficiently well mixed with the processed raw waste. For these purposes two plasma installations were fabricated: one in the plasma technology laboratory of the Heat and Mass Transfer Institute (HMTI) of the Academy of Sciences of Belarus (Minsk, Belarus) and another at the Halle-Wittenberg University (Merseburg, Germany). We shall dwell on results obtained on the plasma unit designed in the Republic of Belarus.

**2. Experimental Installation.** To carry out experimental investigations concerned with processing of chlorine-containing waste, we used the plasma technological installation depicted in Fig. 1. The main unit of the installation is a plasma reactor based on a three-jet mixing chamber with three electric-arc plasma generators, model PFS-3, designed and fabricated at the HMTI (Minsk, Belarus). The installation includes a system for raw-waste material feeding to the plasma reactor consisting of a reservoir for the solution, gas and solution

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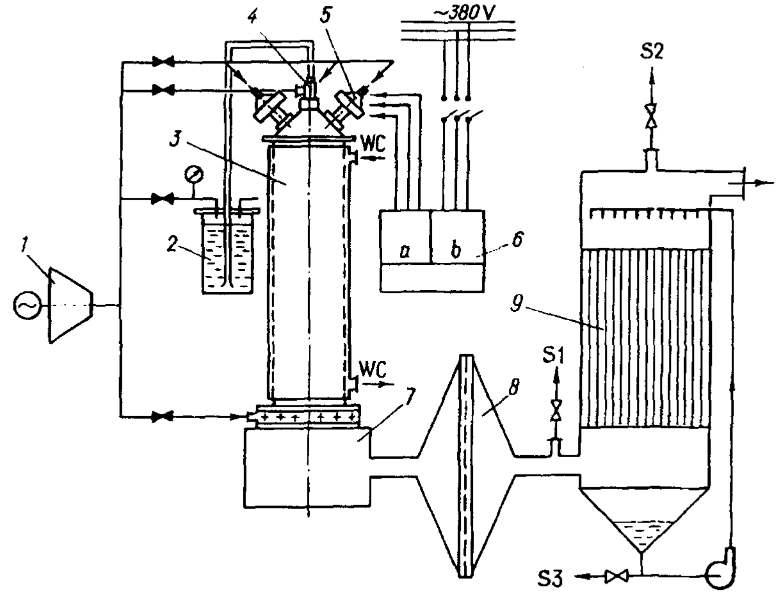

Fig. 1. Schematic of the experimental setup for plasma-thermal processing of toxic waste: 1) compressed-air feeding system; 2) liquid-waste feeding system; 3) reactor; 4) atomizer; 5) plasma generators; 6) electric power sources of the plasma generators (a - direct current, b - alternating current); 7) intermediate bunker; 8) filter; 9) water-alkali scrubber; WC - water cooling of the experimental setup; S1...3 – sampling for analysis.

pipelines, and an atomizer for raw-waste feeding to the reactor. To sample waste gases for analysis, use was made of a system consisting of intake pipes, a vacuum pump, and evacuated flasks with a set of cocks.

The operational principle of the installation is as follows. Plasma jets entering the mixing chamber interact with each other and with the waste supplied and form a heterophase flow, which provides a reaction zone along the entire reactor, where physicochemical processes of thermal decomposition of the waste take place. Separation of the products of thermal decomposition proceeds in a bunker. The gas flow arrives in the filter to separate a finely divided fraction. Exhaust gases passing through a water-alkali scrubber are ejected by a fan to the atmosphere.

For processing we used, as liquid waste, industrial vat residues containing methylene chloride and alcohol-benzene mixture waste contaminated with colophony, an initial analysis of which was not conducted.

**3. Processing of Chlorine-Containing Waste. Analyses and Results.** Destruction of liquid toxic oxides in the plasma reactor with the three-jet mixing chamber proceeded at the following conditions. A power of each plasma generator varied from 28 to 40 kW, the total power of the reactor was from 84 to 115 kW, the total flow rate of the plasma-forming gas was within the limits of 6.25–8.8 g/sec, the mean-mass temperature of the plasma-forming gas ranged from 5240 to 5835 K, and the temperature at the reactor outlet varied from 2350 to 3320 K. A flow rate of the liquid wastes was maintained constant due to difficulties encountered in its control and equal to 3.6 kg/h. In some experiments, the final products were subjected to quenching, i.e., to abrupt cooling by mixing with cold air in an intermediate bunker immediately after leaving the reactor, which favored, firstly, reburning of the waste and, secondly, its abrupt cooling from a temperature higher than 2000 K thus preventing reverse reactions to form dioxins/furans.

An analysis of the gaseous phase of the final products of waste processing was made by analytical (chemical) and mass-spectrometric methods. The analytical methods were employed to determine the content of nitrogen oxides (the method of evacuated flasks) and of chlorides (by silver nitrate titration of chlorides in the presence of potassium chromate as a tracer).

Mass-spectrometric analysis were made by a "Varian" MAT-311 device, which is widely used to investigate the composition of organic compounds in solid, liquid, and gaseous states and is recognized presently as one of the most informative, high-speed, sensitive, and reliable mass-spectrometers.

TABLE 1. Operating Conditions for Processing of Bromine-Containing Waste (Aqueous Solution)

| n | $N$, kW | $G_{p.g}$, g/sec | $G_{c.g}$, g/sec | $T_{ch}$, K | $T_r$, K | $T_{out}$, K | $G_{r.w}$, g/sec | $G_{r.w}/G_{p.g}$, kg/kg | $N/G_{r.w}$, kWh/kg |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 94.0 | 4.7 | 5.1 | 4580 | 3740 | 620 | 3.6 | 0.77 | 7.25 |
| 2 | 119.8 | 4.7 | – | 5630 | 4200 | 600 | 9.3 | 1.98 | 3.58 |
| 3 | 119.8 | 4.7 | – | 5680 | 4200 | 600 | 15.5 | 3.30 | 2.15 |

TABLE 2. Results of Analyses of Exhaust Gases (Aqueous Solution)

| n | HBr, g/liter | |
|---|---|---|
| | before entering the scrubber | after leaving the scrubber |
| 1 | 0.076 | 0.031 |
| 2 | 0.20 | 0.102 |
| 3 | 0.337 | 0.143 |

TABLE 3. Operating Conditions for Processing of Bromine-Containing Waste (Organic Solvent)

| n | $N$, kW | $G_{p.g}$, g/sec | $G_{c.g}$, g/sec | $T_{ch}$, K | $T_r$, K | $T_{out}$, K | $G_{r.w}$, g/sec | $G_{r.w}/G_{p.g}$, kg/kg | $N/G_{r.w}$, kWh/kg |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 81.7 | 6.0 | – | 3800 | 1850 | 410 | 5.6 | 0.93 | 4.05 |
| 2 | 108.0 | 6.0 | – | 4100 | 2700 | 580 | 7.2 | 1.20 | 4.17 |
| 3 | 108.8 | 6.0 | – | 4140 | 2710 | 580 | 12.5 | 2.08 | 2.42 |

TABLE 4. Results of Analyses of Exhaust Gases (Organic Solvent)

| n | HBr, g/liter | |
|---|---|---|
| | before entering the scrubber | after leaving the scrubber |
| 1 | 0.014 | 0.006 |
| 2 | 0.018 | 0.009 |
| 3 | 0.031 | 0.015 |

A comparison of mass-spectra of the gaseous phase after raw waste processing in the plasma reactor with spectra of the initial waste allows us to assert that all organic components of the waste burn out, since these spectra differ insignificantly from those of the gaseous phase in the plasma reactor without input of waste. The content of toxic $H_2S$ and HCl compounds is insignificant, and they can be captured by a scrubber. Chlorine in pure form is not detected in the samples. After processing in some samples of the gaseous phase an increase in the number of C ions is observed, which is likely to be attributed to a lack of oxygen for complete carbon oxidation to carbon dioxide.

4. **Processing of Bromine-Containing Waste. Analyses and Results.** In the investigations we used loose solid waste which had bromine-containing phenols in different amounts.

Prior to the experiments, the waste was subjected to elemental analysis by different methods. Thus, using an electronic scanning microscope with a microspectrum analyzer, model "Nanolab-7," we established that the waste sample did not contain potassium, sodium, calcium, and other metals. The content of carbon in the sample was detected by an AN-7529 analyzer to equal to 29.6%, while that of sulphur determined by an A5-7932 analyzer amounted to 0.08%.

The results obtained were checked by chemical analysis. As a result, the average concentrations produced by all methods of elemental analysis were as follows: C = 30.03%; $H_2$ = 4.31%; $Br_2$ = 50.32%; $N_2$ = 0.51%; S = 0.08%; $O_2$ = 14.75%.

Prior to processing we carried out thermal analysis of the bromine-phenol containing waste to determine minerals and other admixtures. Thermal analysis of the samples in air was made by the derivatographic method using a Hungarian (the firm "Neom") OD-103 unit. The amount was 100 mg, the rate of temperature rise was 55 deg/m, and the weight scale was 100 mg. At temperatures of 318–368 the sample lost 25% of its mass at a maximum rate at 368 K, which can be attributed to loss of water by the sample. At 468 K the endothermal process of melting was observed.

Decomposition of the sample proceeded in two main stages. The first stage started at 513 K, reached its maximum rate at 609 K, and ceased at 623 K. The decomposition proceeded rapidly without the participation of atmospheric oxygen and with absorption of heat. In this stage, 40% of the mass of the initial sample was observed, which can be interpreted as splitting out of bromine and/or HBr.

The second stage occurred in the temperature range 623–873 K and proceeded with heat release and the participation of atmospheric oxygen. The inflections in the graphoanalytical curves near 733 K give grounds to think that decomposition in the second stage involves two substages: at 623–733 K and 733–873 K. Within these temperature intervals the benzene rings of the compounds constituting the waste undergo partial decomposition and oxidation.

Thus, the analysis made has confirmed that the waste consists entirely of organic compounds without mineral admixtures.

To carry out the first series of experiments with the bromine-containing waste, we prepared an aqueous solution with the 25% concentration of the bromine-containing mass, which was the solubility limit of this raw material at 293 K. This allowed us to combine controllable feed of the dispersed solution into the plasma heat-carrier flow with a sufficiently high concentration of the substance. Such a version has an advantage over the supply of solid dispersed particles, which is limited by their size and friability.

With this solution we conducted a series of experiments by changing the installation power and mass flow rate of the waste. In so doing, electric power changed from 94 to 120 kW, the flow rate of the plasma-forming gas was 4.7 g/sec and the flow rate of the waste was varied from 1 to 15.5 g/sec (Table 1).

After each experiment the waste gases were analyzed for bromine and toxic substances. Results for the former are given in Table 2. Toxic dioxins and carbon monooxide were not detected.

In the second series of experiments we investigated the possibility of increasing the efficiency of processing by using additives which modified the physicochemical properties of the solution. For this, we prepared a 75% solution of the waste in a polar organic solvent, with which three experiments were carried out to determine optimum conditions for processing. Electric power varied from 82 to 108 kW, the flow rate of the plasma-forming gas was 6 g/sec, and the flow rate of the waste changed from 5.6 to 12.5 g/sec. Though complete decomposition was observed, the substance did not burn out fully in the regime with a maximum rate of the waste, in which a great amount of unoxidized carbon settled in the scrubber. Operation parameters of the installation and results of chemical analyses of the waste gases are given in Tables 3 and 4.

The exhaust gases formed after plasma-chemical processing were analyzed for dioxins and their analogs, carbon monooxide and dioxide, as well as HBr. Dioxins were detected by the EPA 8270 method using a Hewlett–Packard GC/MS 5890/5972 mass-spectrometer. The gaseous phase formed in the plasma generator was allowed to pass through methanol, and then the methanol solution was investigated. In all experiments no dioxins were detected.

Once the gaseous mixture escaped from the plasma generator, it was analyzed for CO content with the aid of a MX-1320 high-resolution mass-spectrometer.

The content of HBr in the gas mixture formed was determined by the gravimetric chemicoanalytical method – by HBr titration with a silver nitrate solution followed by an analysis of silver bromide. In this case, HBr can be considered a useful product of processing of such waste, which is rather convenient and effective for further obtaining of pure bromine. As is seen, the yield of HBr in the first series of experiments with water-emulsion waste feed exceeds the HBr concentration in the version with the organic solvent almost by an order of magnitude when the plasma-chemical process proceeded with an excess of free carbon and CO and a lack of air. It is evident that vaporization and bromine reduction in an excess $H_2O$ atmosphere following the first version is the most efficient method of such processing.

**5. Conclusion.** High-temperature plasma processing of toxic halogen-containing organic waste at 4000-5000 K ensures their overall thermal decomposition to yield products of complete oxidation of the organics and related halogens in the form of HCl, HBr and so on, which are rather easily utilized and represent useful products of processing. Moreover, the danger of formation of secondary and particularly toxic compounds such as dioxins/furans, which can be reproduced in the cases of destruction of such waste by ordinary thermal methods, is eliminated.

## NOTATION

$N$, power; $G_{\mathrm{r.w}}$, raw-waste rate; $G_{\mathrm{p.g}}$, gas-flow rate for the plasma generator; $G_{\mathrm{c.g}}$, flow rate of the chilling gas; $T_{\mathrm{ch}}$, temperature in the mixing chamber; $T_{\mathrm{r}}$, reactor temperature; $T_{\mathrm{out}}$, temperature at the reactor outlet; $n$, experiment No.

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