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RESEARCH, DESIGN, CALCULATIONS, AND OPERATING EXPERIENCE

CHEMICAL PLANT

A NEW GENERATION OF HIGH-FREQUENCY OZONE GENERATOR

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Possessing a number of specific properties, for example, high reactivity and instability, ozone occupies a special place among traditionally employed oxidizing agents. In terms of oxidation power, ozone is second only to fluorine, and appreciably exceeds other widely used oxidizing agents. Oxidizing reactions with ozone are possible at normal pressures and temperatures.

A distinct advantage of ozone over other oxidizers consists in the fact that when used in an oxidizable medium, it does not leave oxidizer-reduction products that contaminate the substance being oxidized. The ozone is either completely consumed in the oxidation, or when it is partially consumed by the ozone-reduction product, exists as oxygen that is freely volatilized from any products being oxidized (an ecologically pure oxidizing agent). In a number of cases, this condition is found to be decisive in determining the possible use of some oxidizing agent, since separation of oxidizer-reduction products from the substance being treated frequently presents significant difficulty, and is occasionally not at all feasible.

Thus, use of ozone contributes to solution of the problem of the development of waste-free ecologically pure products.

Basic production processes in which use of ozone is technically and economically justified are as follows:

- purification (decontamination) of drinking water;
- cleaning of industrial discharges (in metallurgy and oil refining, at cellulose-paper combines, at automated washing plants, etc.;
- chlorine-free bleaching of cellulose;
- processing of liquid radioactive wastes, and recycling of worn tires; and
- ozone treatment of water for swimming pools.

According to foreign data, the ozone-demand level abroad amounted to 9700 kg/h in the mid-1990s; moreover, the priority was 6700 kg/h for France.

Ozone technology has come into the most widespread use for the purification of drinking water as a guaranteed complex solution to water-treatment problems – decolorization, deodorization, oxidation, and the rendering of organic compounds harmless.

Thirty countries currently treat natural water with ozone. In the mid-1990s, there were more than 600, 150, 130, 40, and 25 ozone-treatment plants in France, Switzerland, the Federated Republic of Germany, Austria, and Canada, respectively. In France, moreover, the water in urban water conduits is completely purified by ozone technology. The expected world demand for ozone may amount to approximately 30 tons/h for the purpose of water treatment over the next 20 years.

In Russia, ozone treatment is currently used at large-scale water-supply plants in Moscow and Nizhnii Novgorod with the use of imported equipment. Domestic equipment is used for water-supply plants in the cities of Birsk (Bashkortostan), Verkhnyaya Pyshma (Sverdlovsk Oblast), and Zavolzh'ye (Nizhnii Novgorod Oblast).

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Several methods of producing ozone are known:

• electrosynthesis in a gas discharge (barrier discharge);
• electrolytic;
• photochemical (under the action of ionizing radiation); and
• plasmochemical.

Analysis of modern foreign and domestic experience indicates that electrosynthesis in a gaseous discharge is the most economical and a comparatively simple means of producing ozone that can be used commercially. The efficiency of ozone production is therefore assessed on the basis of the specific energy output of ozone, i.e., the amount of ozone that can be produced per unit of expended electric power [kg/(kWh)], or with respect to specific power outlays (kWh/kg).

The theoretical limiting power output of ozone during its electrosynthesis in a gas discharge in oxygen is 0.53 kg/(kWh) (specific power outlays of 1.9 kWh/kg). The actual output is, however, appreciably lower – usually about 0.15 kg/(kWh); this corresponds to specific power outlays of 6.7 kWh/kg, since more than 90% of the electric power used is dissipated in the form of heat. Power indicators are increased by a factor of 2–2.5 for the electrosynthesis of ozone from air.

In terms of specific power consumption, the production of ozone by electrosynthesis in a gas discharge is the most economically suitable method.

OZONIA, Trailigaz, Wedeco, Schmidding-Werke (Germany), Degremont, and Sumitomo (Japan) are leading producers of ozonizer equipment. In Russia, the company Kurgankhimmash has been an establishment specializing in the production of ozonizers. All companies, with the exception of Sumitomo, market ozone generators with a tubular system of electrodes. The electrodes are composed of two coaxial tubes. The outer tube is fabricated from corrosion-resistant steel, and the inner one from glass with a thin layer of metal applied to the inner surface. The ozone generator consists of a large number of these electrode pairs assembled in a common housing.

The disadvantages of these ozone generators are as follows:

• one-sided cooling of the discharge gap;
• low frequency of the high-voltage supply (50–700 Hz);
• placement of a dielectric barrier on one side of the discharge gap (glass tubing metallized on the inside; and
• stringent requirements with respect to coaxiality of the steel and glass tubes, resulting in a sharp cost increase for their fabrication as the discharge gap is reduced to 1.0 mm and smaller, and high specific metal consumption.

The OZONIA Company has recently begun to use metallic tubes with a dielectric applied to their surface in accordance with the AT-95 technology as high-voltage electrodes. Use of the AT-95 technology has made it possible to lower the effective voltage to 4.5 kV, increase its frequency to 2000 Hz, and raise the output of ozone per unit area of electrode surface to 2.4 g/(h·dm^2).

The Japanese firm Sumitomo produces plate ozonizers with 250×300-mm electrodes with a two-sided barrier made from high-alumina ceramics. The discharge gap is 0.8 mm. Cooling is accomplished with air using heavy-duty fans. Maximum productivity does not exceed 4 kg/h. A disadvantage of this type of ozonizers is the high cost of the ceramic electrodes and their air cooling, which does not make it possible to carry out vigorous heat removal, leading to a significant increase in clearance dimensions.

Theoretical and experimental researches conducted in the 1980s and 1990s at the Moscow State University, the Moscow Institute of Power Engineering, and GUP VÉI have indicated that the limiting characteristics of ozone synthesis in a barrier discharge (a specific ozone output per unit of surface area, ozone concentration in the effective gas, and specific energy outlays) may be attained with an electrode system of the ozone generator, which approaches as closely as possible to an ideal system.

The following conditions must be fulfilled for this purpose:

• the electrode should have two-sided insulation and two-sided cooling;
• it is necessary to ensure an equidistant gap between electrodes, which is equal to 0.5 mm and smaller; and
• the frequency of the voltage supply should be increased to 8–10 kHz.

Despite the fact that studies in the field of ozonizer production are being conducted by approximately 25 large-scale firms over a period of at least 100 years, an ozone generator in which the enumerated conditions would be met has yet to be

TABLE 1

Outside diameter, mm	Inside diameter, mm	Height, mm
180	45	33
180	45	10
370	58	40
360	58	25.3
475	78	23

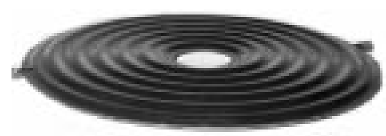

Fig. 1. Plate electrode for OVÉ-25 ozone generator.

developed. One of the principal causes of this situation consists in the fact that the predominant design of heavy-duty ozone generators is a device with tubular high-voltage electrodes (glass or metallic), which are arranged in a shell-and-tube heat exchanger under ground potential. This design does not make it possible to fulfill these conditions.

Research and development work conducted in the late 1990s by the company Kriogenmash and GUI VÉI [1–5] has made it possible to develop a three-dimensional thin-wall electrode design with a complex shape using high-precision forming of thin-sheet materials and their welding. A number of atypical structural and procedural problems caused by certain contradictions between stringent requirements for the accuracy of the curvilinear surfaces of adjacent electrodes in the ozone generator, which are mated at equal distances, and the possibility of their use for a bulk hollow thin-wall electrode design were solved in performing these studies. Five type sizes of plate electrodes were developed (see Table 1).

One of the designs developed for a plate electrode with a dielectric coating is shown in Fig. 1.

A composition of powdered glass enamel (more than 10 components), which has a coefficient of linear thermal expansion (CLTE) close to that of the electrode material, and, moreover, satisfies the requirements of electric insulation, has been developed in conjunction with the D. I. Mendeleev RKhTU:

• the loss tangent of the dielectric $\tan\delta < 7 \cdot 10^{-3}$;

• the dielectric constant $\varepsilon > 8$; and

• the intensity of the electric field corresponding to breakdown of the dielectric $E_{br} > 20$ kV/mm.

A procedure for the multilayer application of the powdered glass enamel in a high-voltage electric field (up to 70 kV) and its heat treatment in a special furnace has also been worked out.

Utilizing new technologies for both fabrication of electrodes, and also the development of a dielectric barrier, Kriogenmash and GUP VÉI have prepared experimental and experimental-commercial specimens of new resource- and energy-saving ozone generators employing a barrier discharge with a productivity to 2.5 kg/h and an ozone concentration of 20–25 g/m^3 (when operating on air) and 80–150 g/m^3 (when operating on oxygen); here, the specific output of ozone per unit of surface area of electrode reached 25 g/(h·dm^2).

During 2001–2002, Kriogenmash and GUP VÉI developed, fabricated, and tested an ozone generator with a productivity of 25 kg/h and a water-cooling system, which enter as component parts of an ozonizer in a modular-containerized version for the centralized water-supply system of Moscow in conformity with the resolution adopted by the Moscow City Government “On the organization of the production of domestic high-productivity ozonizers for centralized water-supply systems.” Based on the results of computational assessment of operating and economic indicators, we verified the effectiveness

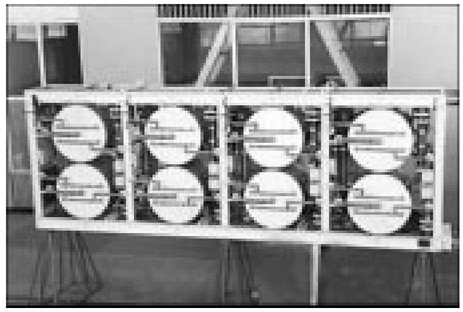

Fig. 2. OVÉ-25 ozone generator with productivity of 25 kg/h.

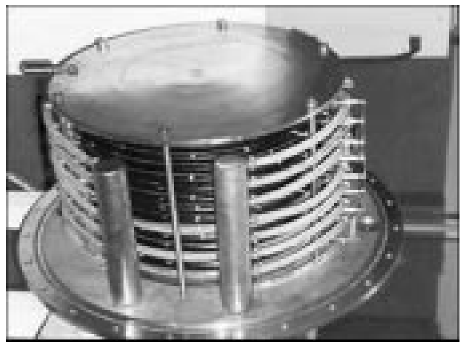

Fig. 3. Electrode block of OVÉ-25 ozone generator.

Fig. 4. OVÉ-25 ozone generator mounted in standard six-meter compartment.

of the development of ozonizers in the modular-containerized version (with complete factory readiness of the modules that enter into the plant) without the need for the building of capital structures.

The OVÉ-25 ozone generator consists of four autonomous ozonizer modules each with a productivity of 6.25 kg/h, which are placed on a common frame on which fittings and a pipeline are also secured (Fig. 2). Each ozonizer module is supplied from a 100-kW power source (supply voltage of ~4 kV, and nominal supply-voltage frequency of ~8 kHz).

Two blocks of electrodes enter as component parts of each ozonizer module. Two electrode assemblies in which plate electrodes are mounted are placed in each block of electrodes (Fig. 3). Each electrode is cooled by deionized water with a specific electrical conductivity of 3 μCm/cm and inlet temperature of +6°C. The distance between electrodes (discharge gap

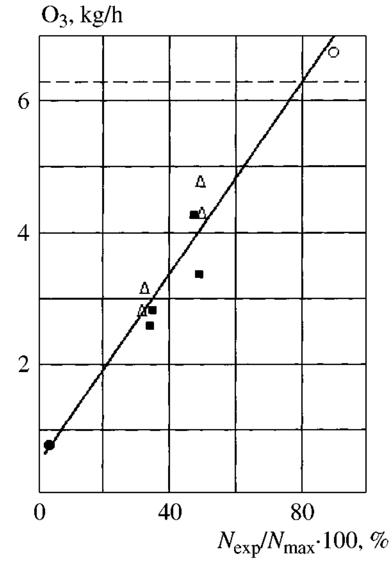

Fig. 5. Productivity of OVÉ-25 ozone-generator module as function of relative electric power supplied to electrodes: ——) expected; – – –) computed; ●, ■, ○, △) experimental data.

of 0.5 mm) is established using spacers. The oxygen or air is fed into the housing of the electrode block; they then proceed through the discharge gap in the direction from the periphery to the center, and pass through the central opening into a collector that gathers the ozone–oxygen or ozone–air mixture.

Figure 4 shows the arrangement of the ozone generator in a standard six-meter KT-M-OZON compartment. With an internal compartment width of 2174 mm, it was found possible not only to insert the ozone generator, but also ensure the assembly and disassembly of the electrode blocks, using a special adaptor.

Figure 5 shows the relationship between the productivity of one of the ozonizer modules and the relative electric power supplied to the electrodes. It is apparent that the design productivity of a single module (6.25 kg/h) is achieved at approximately 80% of the electric power input; this corresponds to the expected results. The joint operation of all four modules in the experimental-commercial ozonizer (modular-containerized version) installed at the Eastern Water-Supply Plant provides for an ozone output of 25 kg/h.

In the process of building an ozone generator with plate electrodes with a productivity of 25 kg/h, therefore, the following scientific-technical problems are solved:

• the three-dimensional hollow thin-wall design of the plate electrode is fabricated by the method of high-precision forming, which ensures repeatability of the geometry of the effective surface with a significant cost reduction for electrode fabrication;

• the length of the discharge gap between electrodes is reduced to 0.5 mm with the condition that this value remains constant over the entire discharge zone; this makes it possible to lower energy outlays and improve the operational reliability of the dielectric barrier;

• two-sided application of the dielectric barrier and two-sided cooling of the electrodes, which ensure vigorous heat abstraction from the discharge zone, are realized; this eliminates decomposition of the ozone due to overheating of the surface;

• a low nominal working voltage (~4.0 kV) is produced, and the nominal frequency of the supply voltage is increased to 7–8 kHz; and

• a specially developed glass enamel applied to the surface of an electrode by the method of electrostatic spraying, which for a layer thickness of 0.5 mm, ensures high electric characteristics of the ozone generator, is used as a dielectric barrier.

Implementation of the above-enumerated technical solutions has made it possible to obtain a high output of ozone per unit of surface area of electrode – up to 25 g/(h·dm^2). For comparison, the OZONIA Company, which has developed the most modern process for the fabrication of tubular electrodes in accordance with the AT-95 technology, has attained a specific ozone output of 2.4 g/(h·dm^2). This large difference in these parameters makes it possible to build domestic equipment that is more compact and lighter, and, of course, more competitive.

As compared with the ozone generator manufactured by the OZONIA Company (up to 10 kV), the lower supply voltage (~4.0 kV) of the ozone generator with plate electrodes makes it possible to justifiably look forward to greater reliability and longer service life of domestic ozonizers. The two-sided dielectric barrier and two-sided cooling of the plate electrode, as well as the possibility of selecting a dielectric coating with certain properties enable us to rely on the fact that the problem of control and optimization of the gas discharge will be successfully resolved in the near future. This will significantly increase ozone output from a unit of surface area of electrode and will lower specific energy outlays.

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