# WASTEWATER TREATMENT USING SUPERCRITICAL WATER OXIDATION

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Prof. Grachev started his career in 1960s as an engineer, then as a lecturer at the Penza State Polytechnical Institute. In 1990 he was elected a People's Deputy, Deputy Chairman of the Committee on higher Education and Training at the Supreme Council of the Russian Federation. In 1993 – 1999 V. Grachev was the Chief of the Federation Council's Committee on Science, Culture, Education, Health and Ecology. In 1997 – 1999 he was elected a deputy of the State Duma, the Chairman of the Committee on Ecology. Prof. Grachev is an honorary member of the PACE. Since 2011 he has been the President of the Vernadsky Foundation.

Prof. Grachev is the author of 242 inventions, 625 published works, 29 monographs, 10 textbooks, 15 manuals.

## ANDREY ROZEN

Andrey Rozen is a D. Sc. in Engineering, the Head of "Welding, Foundry and Materials Chair at the Penza State University, Professor since 2003. Prof. Rozen is the Head of "Machine Engineering" Academic board at the Ministry of Education and Science of the RF. He has been an academic advisor of 10 research and development projects. Prof. Andrey Rozen's biography was included by the Swedish International Center into the bibliographic encyclopedia of Russia's high achievers "Who is Who in Russia" (2007). In 2010, Prof. A. Rozen was a holder of the Golden Galaxy diploma and golden medal awarded by the American Scientific Society for the development in the field of corrosion-proof materials.

## YEVGENIY VOROBYEV

Yevgeniy Vorobyev was born in Penza, Russia, in 1955. In 1977 he graduated from the Penza Polytechnic Institute with the degree in radiotechnics. Upon graduation he worked at the Penza radio manufacturing plant. In 1995 he graduated from the All-Russia Correspondence Finance and Economics Institute. In 2002 Y.Vorobyev defended his dissertation and was awarded the Cand. Sc. degree (PhD equivalent). He offered a verbal operation method for the systems analysis of complex sociotechnical systems. From 2009 to 2013 he was a principal investigator of "Sverkhkrit" research and development work (the Federal targeted program "Khimbiobezopasnost" (Chemical and Biological Safety).

The issue of wastewater treatment is highly relevant especially for metropolises and cities with the developed industrial infrastructure. In particular, effluents of industrial enterprises, using hydrocarbon materials or being engaged in their thermal processing, contain cyclic and aromatic compounds that have a very negative impact on the ecological environment. The technology of wastewater treatment by supercritical water oxidation (SCWO) is believed to be very promising.

By its dissolving capacity the supercritical water (T = 647.1 K; Pk = 22.06 MPa) is similar to the non-polar organic compounds, it hardly dissolves inorganics of the ionic nature and it completely miscibles with organic compounds, air and gaseous reaction products. In supercritical water organic toxicants can be oxidized by atmospheric oxygen to simple products, such as CO2, N2, etc. For all the tested toxicants the degree of their convertibility into simple products, as a result of oxidation, is more than 99.99 %, which is significantly higher than for the indicator of toxic combustion processes waste. Low temperature and the closure of the process eliminate the emission of hazardous substances into the atmosphere and the formation of dangerous oxides NOx and SO2.

Peculiarity of "supercritical" fluids is a continuous increase in their density (from the gas phase to the liquid-like one) without occurrence of heterogeneous equilibrium "liquid-gas" with increasing pressure. The boundary for the existence of the cluster of associated fluid molecules outlines the critical isotherm, which coincides with the percolation threshold.

An essential condition for the practical application of the method of supercritical water oxidation is a process automation, providing stability of the homogeneity multicomponent system boundaries. In addition, the development of technology is associated with the need to increase the service life of the reactor. At the temperatures and pressures used in the SCWO technology, under the influence of ionized halogen reactor materials corrode. Making the reactor of titanium alloys and bimetals of chromium-nickel alloys, tantalum cladded, is a significant obstacle to commercialization of the technology because of high cost of materials and limited resources in operational life.

However, the activities in this direction are constantly going on, both in the U.S. (Foster Wheeler Development Corporation, General Atomics), Japan (Mitsubishi Heavy Industries, LTD), and Russia in the field of basic and applied research, which laid the foundation for the engineering technological calculations.

A hardware solution of the SCWO installation has been implemented under the conditions of the following process flow diagram (Figure 1). Developed technical solutions have been implemented in a pilot SCWO installation. The technological part of the installation was comprised of the reactor and preparatory modules.

The installation includes the following technological systems: the raw materials and neutralized oxidant supply system, the preparation and mixture injection system, the SCWO mixture reactor system, the multistage system of gaseous products discharge, the division of the working mixture decay products with separation of solid and liquid phases, the recirculation system, and the ACS module . The estimated annual performance of the raw materials recycling complex is 1,200 tons per year. The estimated time of the annual operation of the reactor is 300 working days. The daily productivity of raw material processing is up to 4 tons per day.

The installation has a receiver unit for injection of the mixture into the reactor. One container is intended for storing the oxidant in the case it is needed, whereas another one is for storing the water used to provide the desired concentration of the mixture and compressing the working reactor. The pump unit provides pre-feeding of the mixture into the waste receptacle tank. The main oxidation processes take place in the reactor. The processed products are proceeded from the reactor into the separator and then to the receiver, and the capacity discharge tank. Cable channels (ducts) for the control and power of communication modules are laid along the perimeter.

The reactor unit design has: heating elements ensuring creation and support (if necessary) supercritical temperature, 18 kW, working mixture feeding injectors, a thermocouple for controlling the temperature inside the reactor and the temperature of the reactor vessel nozzle cover for supplying a gaseous oxidizing agent or withdrawing gaseous reaction products in the lower fitting part to output the reaction product condensed.

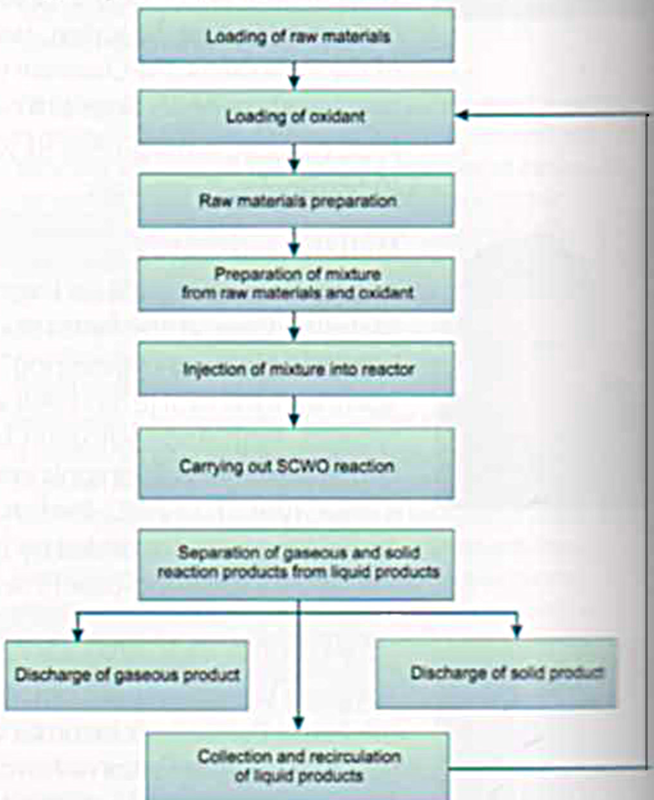



Fig. 1. Process flow diagram of SCWO processing

Units and components of the installation are connected to the process piping circuit, providing:

- Submission of the initial components for processing;

- Vapor-air mixture efficiency;
- Output of solid waste;
- Connection of the check valve;
- Connection of thermocouples – temperature sensors;
- Connection of remote strain gauges;
- Connection of the shut-off valves;
- Connection of the safety valves.

As the results of the calculations show, the composition and physico-chemical properties of the SCWO processing products vary depending on the time, temperature and pressure of the medium within the reactor zone. In this regard, an instrumental solution that provides control and stabilization process parameters is important. It is ensured by an automated control system. The installation is shown in Fig. 2, 3, 4.

Fig.2 Preparation module

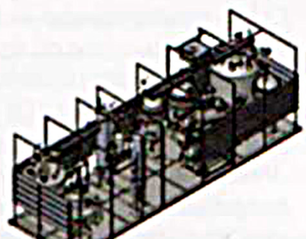


Fig. 3 Reactor module

Fig.4 Process modules transportation conditions

The installation consists of an automated control system (AMCS). Control signals are transmitted from the system unit through the electropneumatic controllers that transmit the pneumatic control action to the pneumatic shutoff valve.

The installation scheme provides for loading of up to 300 liters of waste at once. A processed product may have a viscosity up to 20 centistokes and contain up to 20% of suspended solids. In the waste receiving tank the stuff is heated till 80°C, dilution and supply of reagents are possible. Then the mixture is fed into the preparation reactor and from there it is injected into the SCWO reactor, providing the necessary pressure air, oxygen or an oxidizing agent solution.

Two reactors work in a parallel way. Release of the gaseous products from the reactor is done into a three-stage reactor condenser – separator. Dumping of solid waste from the separators and reactors is carried out into two receivers. In the final container condensation is formed, being recycled through the waste recovery (recuperation) line. The valve system is operated by pneumatics.

Since the process proceeds at high temperatures and pressures, its energy requirements in the time of starting and preparation of the equipment are relatively high (up to 75 kW). However, in the process of processing of the material with hydrocarbon groups, their heating up to the supercritical temperatures is possible due to the exothermic oxidation reactions without additional energy input.

Constructive-wise, the process module is placed in a standardized 40-foot container, High Cube Class, and meets all the requirements for transportation on public roads in a road trailer.

The reactor and process module can be mounted separately and upgraded for specialized tasks. The automatic control system unit is made as a separate module and is located at a distance of 25-30 meters from the hi-tech process module, providing comfort and safety and security for the operator, as well as protection of the management system hardware from an accidental exposure to the corrosive factors.

The operating process module is installed inside a closed container, in which the inputs are blocked when switching-in takes place, in order to avoid a possibility of admission of the operating personnel into the working area. The operating module is equipped with standardized communication pipeline connections for external loading of processed materials and unloading of recycled products from the process module. The process of loading and unloading of the module is controlled by the ACS unit in the automated mode.

The modular design of the SCWO installation allows applying it both in the fixed configuration, and in the mobile option. Time of deployment of the process unit does not exceed one shift. Feeding of neutralized waste can be done by universal tankers.

Technical specifications of the installation are given in Table 1.

The SCWO reactor is made of the materials resistant to corrosion caused by ionized halogen. Multilayer materials were developed by the authors of this article.

As a result of conducting extensive research, a multilayered metallic material with a "sacrificial pitting protection" is applied as a SCWO reactor material. The expected life of the reactor can be increased by 8 times.

Stability tests were conducted at the Penza State University. Initial assessment of toxicity and processed products was performed on Daphnia magna Straus, Scenedesmus quadricauda, on the "Ecolum" test system.

## SCWO installation technical specifications

Table 1

| Technical Specifications | Value |
|---|---|
| The volume of recyclables, m3/day | up to 5.0 |
| Operating mode | Long-term, cyclical |
| Cycle time (depending on the initial moisture content and calorific capacity of wastes) min. | 0.3-4.0 |
| The initial heating time of the reactor up to operating temperature, hour | no more than 6 |
| The primary source of heat energy | heating element |
| Consumption of diesel fuel, kg/hour | 2-5 |
| Power consumption, kW × h | no more than [illegible] |
| Installation weight, kg | 14635 |
| Overall dimensions, m (W×H×L) | 2.5×2.7×8.2 |
| Operating personnel | 3 persons per shift |

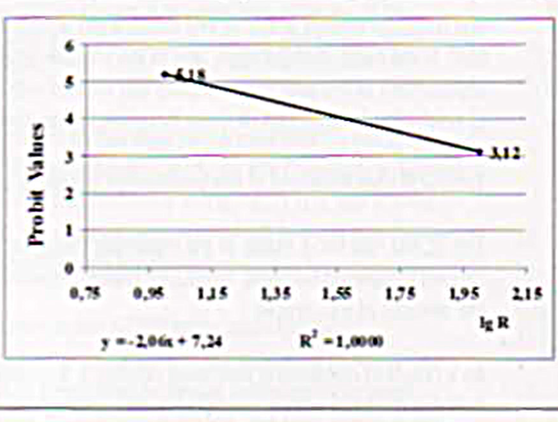
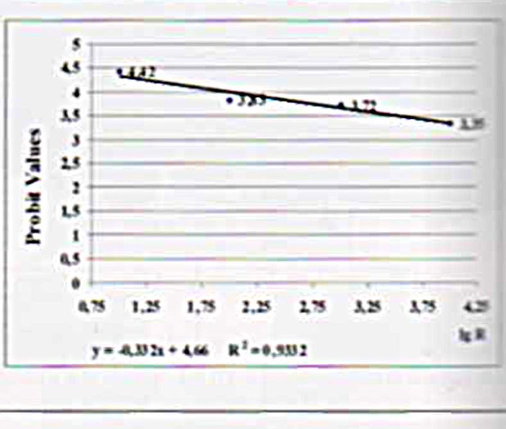
Experiments, conducted by bioassays, showed that the initial 10% aqueous emulsions of benzene, toluene, phenol require more than 10,000-fold dilution and belong to the hazard class 1 (extremely dangerous) for the environment.

Products of these emulsions on dilution harmless multiplicity (RBB) test objects is, in particular, for safe concentration dilution (SCD)10-96 for benzene is 51.14, phenol – 48.70, toluene – 47.96 times. This corresponds to the hazard class 4 (low hazard), which indicates a higher degree of environmental efficiency. Bioassay results are shown in Table 2.

Experimental measurements of the total content of polychlorinated dibenzo-n-dioxins and dibenzofurans in terms of 2,3,7,8-tetrachlorodibenzo-n-dioxin in samples of technological emissions into the ambient air were performed by gas chromatography-mass spectrometry [PND F 13.1.65-08]. Analyses chromatography-mass spectrometer Thermo Finnigan MAT 95XP.

The resulting total content ( TEQ and WHO-TEF toxicity coefficients) of polychlorinated dibenzo -n- dioxins and dibenzofurans in terms of 2,3,7,8 – tetrachlorodibenzo -n- dioxin samples industrial emissions SCWO – processing products equal to 3.9 pg/m3 do not exceed the maximum permissible concentration introduced by the EU – "TEQ Nm3" 0.1 nanogramm/m3 [" GN 2.1.6.014-94 . 2.1.6. Communal Hygiene. Atmospheric Air and Indoor Air , Sanitary Protection of Air . The maximum permissible concentration (MPC) of polychlorinated dibenzodioxins and polychlorinated dibenzofurans in air of residential areas. Hygienic standards " (approved by the State Committee on Sanitary and Epidemiological Inspectorate of the Russian Federation from 22.07.1994 N 7) Maximum Allowable Concentration (MAC) of Polychlorinated Dibenzodioxins and Dibenzofurans in Ambient Air].

Table 2

<table>
<tr><td></td><td>Dependence of mortality of Daphnia from dilution of waste samples (test object Daphnia magna Straus)</td><td>Dependence of mortality of algae from dilution of waste (test object Scenedesmus quadricauda)</td></tr>
<tr><td>benzene</td><td>
</td><td>
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## Results of bioassay of the baseline 10% aqueous emulsion of benzene, toluene, phenol and products of their recycling using the SCWO installation

| Substance | Condition | Test object<br>*Daphnia magna Straus* | Test object<br>*Scenedesmus quadricauda* | "Ecolum" test system | Hazard Class |
|---|---|---|---|---|---|
| | | Safe concentration dilution (SCD) | | | |
| | | $SCD_{10-96}$ | $SCD_{20-72}$ | for fluorescent bacteria | |
| Benzene | initial emulsion | more than 10000 times | more than 10000 times | all dilutions | Class 1 (extremely dangerous, SCD – more than 10000) |
| | emulsion derivatives | 51.14 times | 39.65 times | 1:100 | Class 4 (low-hazard, SCD – less than 100) |
| Toluene | initial emulsion | more than 10000 times | more than 10000 times | all dilutions | Class 1 (extremely dangerous, SCD – more than 10000) |
| | emulsion derivatives | 47.96 times | 37.93 times | 1:100 | Class 4 (low-hazard, SCD – less than 100) |
| Phenol | initial emulsion | more than 10000 times | more than 10000 times | all dilutions | Class 1 (extremely dangerous, SCD – more than 10000) |
| | emulsion derivatives | 48.70 times | 24.92 times | 1:100 | Class 4 (low-hazard, SCD – less than 100) |

Notes: SCD10-96 – harmless multiple dilution of water extracts, causing the death of more than 10% of test objects during 96-hour exposure

SCD20-72 –harmless multiple dilution of water extracts, causing the death of more than 20% of test objects during 72-hour exposure