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Method of Supercritical Hydrothermal Oxidation for Neutralization of Persistent Organic Pollutants.

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ABSTRACT

Authors of the paper have obtained calculated and experimental data for the automation of the supercritical water (hydrothermal) oxidation technology and registration of the corrosive environment's influence on the installation's reactor. A method for calculating the content of organic substances and minimum amount of an oxidant required for the complete oxidation of harmful substances on the example of oxidation of a 10% aqueous solution of cyclic and aromatic compounds, which imitated industrial wastewater (binary mixtures of water with benzene, phenol, and toluene), has been elaborated.

Keywords: supercritical water oxidation, persistent organic pollutants, corrosion caused by ionized halogen, composite material with enhanced strength and corrosion resistance, bioassay, polychlorinated dibenzo-n-dioxins and dibenzofurans.

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INTRODUCTION

On the territory of Russia, countries of the near and far abroad there are more than 1.5 billion tons of accumulated toxic waste. And the amount of this waste is being multiplied year after year. At the same time there are no effective technologies for the anthropogenic waste management.

The international community is stepping up the disposal of persistent organic pollutants (POPs) and highly toxic substances and waste because they are long-range and are present throughout the world in ecosystems and the human body.

In the developed world, the main methods of highly toxic substances and waste disposal are burial and combustion. They account for 98% of all disposal methods. At the same time they are not environmentally friendly and pollute air, groundwater and soil.

Other disposal methods (biological treatment, chemical treatment, etc.) account for no more than 5-7% of the total amount. Their implementation is hindered by selectivity and high cost of these technologies.

In this regard, the technologies based on the methods of supercritical hydrothermal (water) oxidation (SCWO) are the most attractive.

SCWO involves waste treatment in a closed system with the use of oxidizing agents (oxygen, hydrogen peroxide, nitrites, nitrates, etc.) in an aqueous medium at temperatures and pressures above the critical point of water (374°C, 20.2 MPa). Under such conditions, organic substances easily dissolve in water and are oxidized to produce nitrogen, carbon dioxide, water, and inorganic acids or salts.

The effectiveness of this technology is proved by the fact that the destruction efficiency (DE) value exceeds 99.999% and the destruction removal efficiency (DRE) value is 99.9999% when processing, for example, chlordane and hexachlorobenzene (HCB) (according to the Ministry of the Environment of Japan, 2004). DRE for polychlorinated dibenzo-p-dioxin (PCDD) amounts to 99.9999%. In this regard, the US Congress allocates annually \$15-20 million on SCWO research.

SCWO technology is considered applicable to all POPs, such as waste water, oils, solvents, and solids with a particle diameter of not more than 200 microns (Japan Industrial Waste Management Foundation, 1999). Laboratory experiments on the destruction of polychlorinated biphenyls (PCBs) have shown that when applying the SCWO technology, the PCBs decomposition can be accompanied by the formation of high PCB concentrations (above one percent), even at operating temperatures.

According to the available data, emissions contain no nitrogen oxides or such acid gases as hydrogen chloride or sulfur oxides; in addition, the residues consist of water and solids if the waste being treated contains inorganic salts or organic compounds with halogens, sulfur or phosphorus.

Little has been reported on potential concentrations of undestroyed chemicals. If necessary, technological scheme allows recovering emissions and solid residuals for further processing.

An essential condition for the practical application of the SCWO method is a process automation that provides stability of the multicomponent system's homogeneity boundaries. In addition, the development of technology is associated with the need to increase the operational life of the reactor. At the temperatures and pressures used in the SCWO technology, under the influence of ionized halogen, reactor materials corrode intensively. Manufacturing of the reactor using titanium alloys and bimetallics of chromium-nickel alloys, tantalum clad, is a significant obstacle to commercialization of the technology because of high cost and limited operational life of materials.

However, the activities in this direction are constantly going on in the U.S. (Foster Wheeler Development Corporation, General Atomics), Japan (Mitsubishi Heavy Industries, LTD), and Russia in the field of basic (Valyashko, 2006; Gorbaty and Bondarenko, 2007; Lunin, 2007; Ivlev et al., 2007; Urusova, 2007; Landau and Lifshitz, 1964; Artemenko et al., 2010; Williams, 1981) and applied (Gumerov et al., 2007; Fedayeva et al., 2009; Vostrikov et al., 2008; Rozen et al., 2012) research, which laid the foundation for the

engineering calculations.

METHODS

Calculation of the multicomponent system's critical parameters

Thermodynamic conditions for the existence of the critical point corresponding to the multicomponent system can be summarized as follows (Heidemann and Khalil, 1980). Let us consider possible loss of stability by the homogeneous phase. This phase with initial parameters $T_0, V_0, n_{10}, n_{20}, \dots, n_{N0}$ will be stable if for each isothermal variation, the new state $T_0, V_0, n_{10}, n_{20}, \dots, n_{N0}$ will satisfy the following inequation:

$$\left[F - F_0 + P_0(V - V_0) - \sum_{i=1}^N \mu_{i0} (n_i - n_{i0}) \right]_{r_0} > 0 \quad (1)$$

where F – Helmholtz free energy, P – pressure, V – volume, μ – chemical potential, n_i – number of moles of the i -component. "0" index corresponds to the initial state. Absence of "0" index means arbitrarily altered state of the system.

The second condition should comply with the non-isothermal variation:

$$[F - F_0 + S_0(T - T_0)]_{V_0, n_{j0}} > 0 \quad (2)$$

This condition is satisfied since the isochoric heat capacity of the multicomponent system is positive. If the arbitrary change in the homogeneous phase leads to non-compliance of the inequations (1) and (2), the mixture's internal energy decreases and its separation into two or more phases occurs.

Variations of the type:

$$\Delta V = kV_0 \quad D_n = kn_{i0} \quad i = 1, 2, \dots, N \quad (3)$$

do not lead to the changes in the mole fraction and in the mixture's density, and therefore in pressure and chemical potentials. Hence, let us assume $\Delta V = 0$, which simplifies the equation (1):

$$\left[F - F_0 - \sum_{i=1}^N (\mu_{i0} \Delta n_i) \right]_{T_0, V_0} > 0 \quad (4)$$

At the critical point, the Helmholtz free energy can be expanded in a Taylor series:

$$\left[F - F_0 - \sum_{i=1}^N (\mu_{i0} \Delta n_i) \right]_{T_0, V_0} = \frac{1}{2!} \sum_j \sum_i \left(\frac{\partial^2 F}{\partial n_j \partial n_i} \right) \times \Delta n_i \Delta n_j + \frac{1}{3!} \sum_k \sum_j \sum_i \left(\frac{\partial^3 F}{\partial n_k \partial n_j \partial n_i} \right) \Delta n_i \Delta n_j \Delta n_k + \dots \quad (5)$$

The condition for the stability of the system's state at the critical point is the positive energy value at arbitrary changes in Δn . The stability of the system is retained if the quadratic form of its description in the last equation (second-order differential equation term) is positive definite. At the critical point of stability ($T_0, V_0, n_{10}, n_{20}, \dots, n_{N0}$), the quadratic form is positive semidefinite. It follows that in this case, the stability is determined by the properties of the third-order differential equation term and expansion equation terms of higher orders.

The necessary condition to reach the limit of the system's stability at a given point is that the matrix Q with elements

$$q_{ij} = \left(\frac{\partial^2 F}{\partial n_j \partial n_i} \right) \tag{6}$$

has a determinant equal to zero:

$$Q = \det(Q) = 0 \tag{7}$$

We may equivalently introduce vector $\Delta n = (\Delta n_1, \Delta n_2, \dots, \Delta n_N)^T$ satisfying the following condition:

$$Q \Delta \bar{n} = 0 \tag{8}$$

Determination of the critical point as the limiting stable state of the system requires a positive semidefinite quadratic form of the system's description, from which you can find vector Δn complying with the equation (8).

Plugging this vector in equation (5) retains the first expansion term and results in disappearance of the cubic term:

$$C = \sum_k \sum_j \sum_i \left(\frac{\partial^3 F}{\partial n_k \partial n_j \partial n_i} \right) \Delta n_i \Delta n_j \Delta n_k = 0 \tag{9}$$

The joint solution of the equations (7)-(9) defines a critical point of the multicomponent solution's state. At the same time the condition $\Delta V = 0$ leads to the symmetrization of the quadratic and cubic forms of equation terms in the equation for the description of the free energy. An equivalent result can be obtained by assuming $\Delta n_k = 0$, where k – index corresponding to any of the solution's components. But in this case, the quadratic and cubic forms in this equation will contain pressure derivatives and their symmetry will be lost.

Thus, solution of the equations (1)-(9) allows determining the critical parameters of the multicomponent systems' water oxidation and areas of sustainable SCWO process.

Calculation of the process' technological parameters

Calculation of the reaction mixtures is represented by the oxidation of a 10% aqueous solution of benzene, toluene, and phenol. On the one hand, they are highly toxic materials (hazard class 1), and on the other – are able to dissolve in large quantities in water (from 5 to 70 g/l). When heated above 60°C, phenol, in particular, can be dissolved in the water infinitely.

At first, the required number of the components of a "fuel"-water binary mixture is calculated to make a 10% (vol.) mixture.

For the preparation of 1 liter of a binary mixture, 0.9 liter of water and 0.1 liter of fuel are required (Table 1). Fuel mass per 1 liter of mixture is calculated by formula (10):

$$m_T = 0.1 \cdot \rho \tag{10}$$

where m_T – mass of the "fuel" [kg], ρ – density of the "fuel" [kg/l].

Table 1. The content of components in 1 liter of the binary mixture

Substance	Formula	M, g/mole	ρ , kg/l	V, l	m, kg	η , number of moles	y , mole fraction
Water	H ₂ O	18	1	0.9	0.9	64.29	0.983/0.986/0.982
Benzene	C ₆ H ₆	78	0.879	0.1	0.088	1.13	0.017
Toluene	C ₆ H ₅ CH ₃	92	0.87	0.1	0.087	0.946	0.014
Phenol	C ₆ H ₅ OH	94	1.06	0.1	0.11	1.17	0.018

The mole fraction of water is specified for a binary mixture with benzene/toluene/phenol, respectively. The total content of the components is 65.42/65.24/67.45/65.46 mole/l.

Next, the parameters of the binary mixture's critical point ($P_{cr\ mix}$, $T_{cr\ mix}$) are calculated. The calculation is made on the basis of the individual substances' critical parameters (Table 2) on the principle of corresponding states by formulas (11, 12).

Table 2. Parameters of the components

Substance	Formula	M, g/mole	T_{melt} , K	T_{boil} , K	T_{cr} , K	P_{cr} , MPa
Water	H ₂ O	18	273	373	646.9	22.06
Benzene	C ₆ H ₆	78	278.5	353	835	4.83
Toluene	C ₆ H ₅ CH ₃	92	178	384	593	4.3
Phenol	C ₆ H ₆ O	94	455.0	314	694.3	6.13

$$T_{cr\ mix} = \sum_i y_{ci} \cdot T_{ci} \quad (11)$$

$$P_{cr\ mix} = \frac{T_{cr\ mix}}{\sum_i y_i \cdot \frac{T_{ci}}{P_{ci}}} \quad (12)$$

where y_i – mole fraction of the component.

On the basis of the calculated values of the critical points, the values of the a and b coefficients for the Redlich-Kwong equation are calculated (formulas 13, 14).

$$a = \frac{0.42748 \cdot R^2 \cdot T_{cr}^{2.5}}{P_{cr}} \quad (13)$$

$$b = \frac{0.42748 \cdot R \cdot T_{cr}}{P_{cr}} \quad (14)$$

The results of the calculations are presented in Table 3.

Table 3. Critical points of the binary mixtures

Mixture	y , mole fraction	T_{cr} , K	P_{cr} , MPa	a	b
Water/benzene	0.983/0.017	650	20	15.914	$2.341 \cdot 10^{-5}$
Water/toluene	0.986/0.014	645	19.1	16.346	$2.433 \cdot 10^{-5}$
Water/phenol	0.982/0.018	646	21	14.924	$2.216 \cdot 10^{-5}$

After that, the amount of binary mixture, required to cause a supercritical behaviour in the unit, is

calculated. The calculation is carried out by the Redlich-Kwong equation for a mixture of components (Equation 15)

$$P(\eta, T) = \frac{\eta RT}{V - \eta b} - \frac{\eta^2 a}{\sqrt{TV}(V + \eta b)} \tag{15}$$

where P – gas-vapor mixture pressure [Pa]; η – number of moles of the components; T – temperature [K]; V – volume of the reactor [m³] (V = 0.027 m³); a and b – coefficients of the equation (Table 3). The form of the function P = f (η , T) for the water-phenol mixture is in Figure 1.

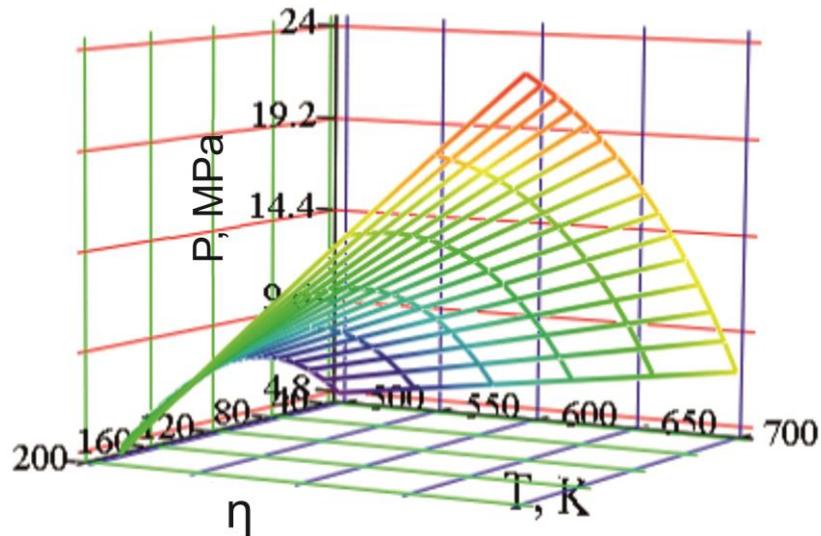


Figure 1. P = f (η , T) for the water-phenol mixture

The content of the “fuel” in the reactor and the minimum amount of oxygen, required for its complete oxidation, and the expected composition of the oxidation products are calculated. The calculation of the required amount of oxygen is carried out on the assumption of complete oxidation by formula (16):

$$\eta_{O_2} = \eta_{fuel} \times \left(\alpha + \frac{\beta}{4} - \frac{c}{2} \right) \tag{16}$$

where η_{O_2} – number of moles of oxygen; η_{fuel} – number of moles of “fuel” in the reactor; α – number of carbon atoms in the molecule of “fuel”; β – number of hydrogen atoms in the molecule of “fuel”; c – number of oxygen atoms in the molecule of “fuel”. The results of calculations are presented in Table 4.

Table 4. The mixture volume and the minimum oxygen content

Mixture	V _{mix} , l	η_{mix} , mole	η_{fuel} , mole	m _{fuel} , kg	η_{O_2} , mole	V _{O₂} , l (STP)
Water/benzene	4.586	300	5.1	0.398	38.25	856.8
Water/toluene	3.2	209	2.93	0.270	26.37	591
Water/phenol	3.514	230	4.14	0.389	28.92	648

To ensure complete oxidation, it is expedient to use excess oxygen. During testing it is expected to

provide 2, 6 and 10 fold excess. In this case, in the products of the “ideal” oxidation there will be present CO₂, H₂O and O₂, which are calculated by formulas 17, 18, 19.

$$C_{CO_2} = \frac{\eta_{fuel} \cdot \alpha}{V_r} = \frac{\eta_{fuel} \cdot \alpha}{27} = \left[\frac{mole}{l} \right] \quad (17)$$

$$C_{H_2O} = \frac{\eta_{fuel} \cdot \frac{\beta}{2} + \eta_{H_2O}^{init}}{V_r} = \frac{\eta_{fuel} \cdot \frac{\beta}{2} + 64.29 \cdot V_{mix}}{27} = \left[\frac{mole}{l} \right] \quad (18)$$

$$C_{CO_2} = \frac{\eta_{O_2}^{init} - \eta_{fuel} \cdot \left(\alpha + \frac{\beta}{4} - \frac{c}{2} \right)}{V_r} = \left[\frac{mole}{l} \right] \quad (19)$$

The results of the calculations of the SCWO products' composition are presented in Table 5.

Table 5. Composition of the SCWO products

Mixture	η_{fuel} , mole	When in excess		
		2	6	10
Water/benzene	5.1	O ₂ content, η (mole)/V(m ³)		
		46.5/1.714	191.25/4.28	382.5/8.568
		CO ₂ /H ₂ O/O ₂ concentration, mole/l		
		1.33/11.846/1.417	1.33/11.846/7.083	1.33/11.846/12.75
Water/toluene	2.93	O ₂ content, η (mole)/V(m ³)		
		25.74/1.181	158.22/3.544	263.7/5.907
		CO ₂ /H ₂ O/O ₂ concentration, mole/l		
		0.76/8.054/0.977	0.76/8.054/4.0883	0.76/8.054/8.79
Water/phenol	4.14	O ₂ content, η (mole)/V(m ³)		
		57.87/1.296	173.52/3.887	289.2/6.478
		CO ₂ /H ₂ O/O ₂ concentration, mole/l		
		0.92/8.827/1.07	0.92/8.827/5.353	0.92/8.827/9.64

Let us calculate the expected changes in pressure and temperature after the oxygen injection. Temperature calculation is performed under the assumption that all the heat released during SCWO will be used for the reaction mixture's heating. Therefore, the temperature is determined from the equation (20):

$$Q_{V\Sigma} = \eta_{\Sigma} \int_{T_0}^{T_K} C_V(T) dT \quad (20)$$

The dependence of heat capacity from temperature takes the form of equation (21):

$$C_V = a + bT + \frac{c}{T^2} = \left[\frac{J}{mole \cdot ^\circ K} \right] \quad (21)$$

Values of the coefficients for the calculation of the molar heat capacity are given in Table 6.

Table 6. Coefficients of the equation 21

Substance	a	b	c
CO ₂	35.83	9.04·10 ⁻³	-8.53·10 ⁻⁵
H ₂ O	21.69	10.71·10 ⁻³	0.33·10 ⁻⁵
O ₂	23.15	3.39·10 ⁻³	-3.77·10 ⁻⁵

Initial data for calculation of the maximum temperature (total heat of the reaction $Q_{v\Sigma}$ and composition of the SCWO products) is given in Table 7.

Table 7. Initial data for calculation of the maximum temperature of SCWO

Mixture	Q_{vfuel} , MJ/mole	η_{fuel} , mole	$Q_{v\Sigma}$, MJ	Content of the SCWO products CO ₂ /H ₂ O/O ₂ (mole) when O ₂ is in excess		
				2	6	10
Water/benzene	3.274	5.1	16.7	35.91/319.84/38.26	35.91/319.84/191	35.91/319.84/344
Water/toluene	3.923	2.93	11.5	20.52/217.5/26.4	20.52/217.5/110.4	20.52/217.5/237.3
Water/phenol	3.053	4.14	12.6	24.84/238.3/28.89	24.84/238.3/144.5	24.84/238.3/260.3

Integration of the equation (20) gives the formula for determining the SCWO maximum temperature (22):

$$Q_{v\Sigma} = \eta_{\Sigma} \left[a_{\Sigma}(T_K - T_1) + \frac{b_{\Sigma}}{2}(T_K^2 - T_1^2) - c_{\Sigma} \left(\frac{1}{T_R} - \frac{1}{T_1} \right) \right] \quad (22)$$

where, $Q_{v\Sigma}$ – total heat of reaction (Table 7); η_{Σ} – number of moles of the components in the SCWO products' mixture; a_{Σ} , b_{Σ} , c_{Σ} – coefficients in equation (21) for a gas mixture, calculated on the basis of additivity principle:

$$a_{\Sigma} = \sum_i y_i a_i \quad (23)$$

Coefficients b_{Σ} , c_{Σ} are calculated similarly.

The values of the mole fraction (y_i) for the SCWO products are calculated by the formula (24) and are given in Table 8.

$$y_i = \frac{\eta_i}{\eta_{\Sigma}} \quad (24)$$

where η_i – content of the SCWO products' component [mole], Table 7; η_{Σ} – number of the SCWO products [mole].

Table 8. Values of the mole fraction (y_i) for the SCWO products

Mixture	$Y_{CO_2}/Y_{H_2O}/Y_{O_2}$ (mole) when O ₂ is in excess					
	η_{Σ} , mole	2	η_{Σ} , mole	6	η_{Σ} , mole	10
Water/benzene	394	0.09/0.81/0.1	547	0.07/0.58/0.35	700	0.05/0.46/0.49
Water/toluene	264.4	0.08/0.82/0.1	348.4	0.06/0.624/0.317	475.3	0.06/0.236/0.704
Water/phenol	292	0.09/0.82/0.1	407.6	0.06/0.584/0.354	520	0.05/0.5/0.55

The values of the a_{Σ} , b_{Σ} , c_{Σ} coefficients for the SCWO products are given in Table 9.

Table 9. The a_z , b_z , c_z coefficients for the SCWO products

Mixture	Excess of O ₂								
	2			6			10		
	a_z	$b_z \cdot 10^{-3}$	$c_z \cdot 10^{-3}$	a_z	$b_z \cdot 10^{-3}$	$c_z \cdot 10^{-5}$	a_z	$b_z \cdot 10^{-3}$	$c_z \cdot 10^{-5}$
Water/benzene	23.109	9.828	-0.877	23.191	8.031	-1.725	23.112	7.04	-1.122
Water/toluene	22.967	9.844	-0.789	23.023	8.3	-1.201	23.566	5.457	-3.088
Water/phenol	23.325	9.935	-0.874	23.012	7.997	-1.654	25.369	7.672	-2.325

Temperature of the SCWO products was determined by the equation (22) on the assumption that all the heat generated during the reaction was used to heat the reaction mixture (Figure 2).

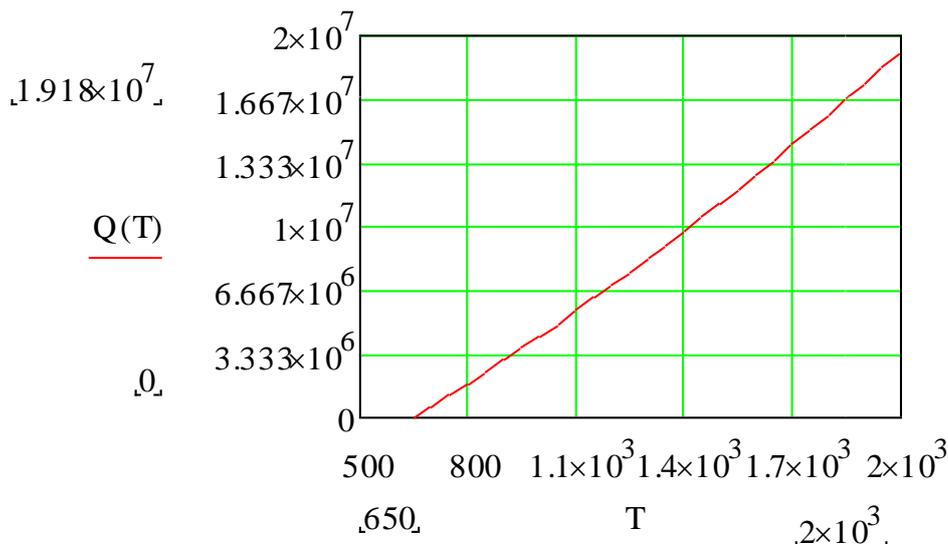


Figure 2. Determination of temperature for a water-benzene mixture when O₂ is in twofold excess

The results of the calculations are presented in Table 10.

Table 10. Temperature of the SCWO products

Mixture	Q_{vz} , MJ	Excess of O ₂					
		η_{Σ} , mole	2	η_{Σ} , mole	6	η_{Σ} , mole	10
Water/benzene	41.65	394	1850	547	1602	700	1669
Water/toluene	45.9	264.4	1880	348.4	1665	475.3	1482
Water/phenol	34.44	292	1888	407.6	1618	520	1386

The SCWO products' pressure is calculated by the Redlich-Kwong equation for a mixture of components (15). Coefficients of the equation are calculated by the formulas (11-14). Initial data is given in Table 11, the results of the calculations – in Table 12.

Table 11. Critical parameters of the SCWO products

Substance	T_{cr} , K	P_{cr} , MPa
CO ₂	304	7.39
H ₂ O	646.9	22.06
O ₂	154.6	5.08

Table 12. Values of the Redlich-Kwong equation's coefficients for the SCWO products

Mixture	Excess of O ₂											
	2				6				10			
	T _{cr} , K	P _{cr} , MPa	a	b·10 ⁵	T _{cr} , K	P _{cr} , MPa	a	b·10 ⁵	T _{cr} , K	P _{cr} , MPa	a	b·10 ⁵
Water/benzene	567	18.5	12.227	2.208	451	14.8	8.624	2.195	389	13.7	6.347	2.045
Water/toluene	570	18.8	12.192	2.184	471	15.5	9.178	2.189	280	9.9	3.196	2.037
Water/phenol	573	18.6	12.486	2.219	451	14.8	8.624	2.195	424	13.5	8.102	2.226

Pressure value for the SCWO products (Table 13) is calculated according to the values of Table 10, 12 by the Redlich-Kwong equation.

Table 13. Parameters of SCWO

Mixture	Excess of O ₂								
	2			6			10		
	η _Σ , mole	T, K	P, Mpa	η _Σ , mole	T, K	P, MPa	η _Σ , mole	T, K	P, MPa
Water/benzene	394	1850	285	547	1602	425	700	1669	697
Water/toluene	264.4	1880	172	348.4	1665	220	475.3	1482	319
Water/phenol	292	1888	197	407.6	1618	267	520	1386	332

The calculation data on the SCWO critical parameters determines the value of the control signals of the process' automatic control.

RESULTS

Hardware solution

A hardware solution of the SCWO installation has been implemented under the conditions of the following process flow diagram (Figure 3). 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.

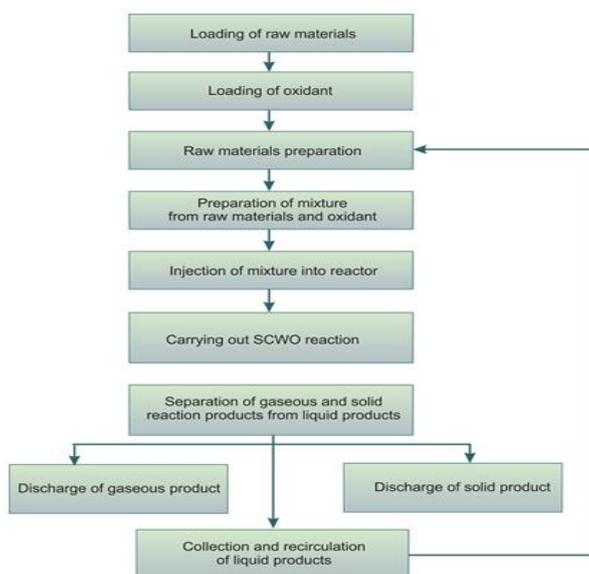


Figure 3. Process flow diagram of SCWO process

The installation includes the following technological systems: the neutralized raw materials and oxidizing agent supply system, the working mixture preparation and injection system, the SCWO reactor system for the working mixture, the multistage system of gaseous products discharge, the separation of the working mixture's decay products with separation of solid and liquid phases, the recirculation system, and the ACS (automated control system). The estimated annual performance of the waste 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 the waste 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 working mixture and compressing the 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 discharge tank. Cable channels (ducts) for the control and power units are laid along the perimeter.

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

Units and components of the installation are connected into the process chain by pipes that provide:

- Supply of the initial components for processing;
- Vapor-air mixture venting;
- Solid waste removal;
- Connection of the check valve;
- Connection of thermocouples – temperature sensors;
- Connection of remote strain gauge manometers;
- 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 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 of the process parameters is important. It is ensured by an automated control system (ACS). The installation is shown in Figure 4.

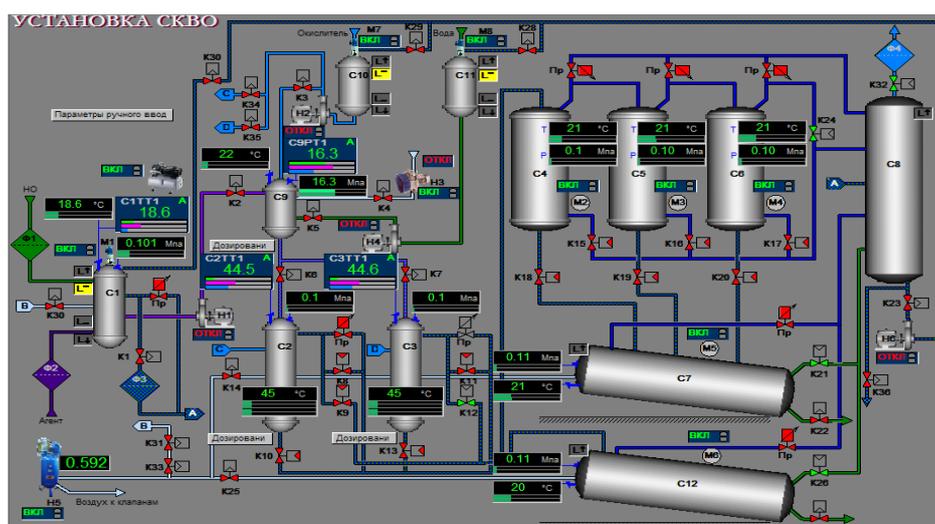


Figure 4. Common control scheme. $\Phi 1, \dots \Phi 4$ – filters; M1, M7, M8 – mixers; M2, ..., M6 – oscillators; H1, H2, H4, H6 – pumps; H3, H5 – compressors; C1 – preparatory vessel; C4, ..., C6 – expansion vessels; C7, C12 – solid waste tanks; C2, C3 – reactors; C8 – finishing tank; C9 – mixing tank; C10 – oxidizing agent tank; C11 – water tank; K1 ... K35 – valves; Pr1 ... WP4 – safety valves

The installation consists of an automated control system (ACS). Control signals are transmitted from the system unit through the controllers to the electropneumatic valves that transmit the control action through the pneumatic pipelines to the pneumatic shut-off valves.

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 mixture 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, the necessary pressure is provided by air, oxygen or an oxidizing agent solution.

Two reactors work in a parallel way. The gaseous products from the reactor are released into a three-stage condenser–separator. Solid waste is removed from the separators and reactors 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 occurs at high temperatures and pressures, its energy requirements during starting and preparation of the equipment are relatively high (up to 75 kW). However, when processing the material with hydrocarbon groups, their heating up to the supercritical temperatures is possible by means of the exothermic oxidation reactions, without additional energy input.

Constructive-wise, the process module is placed in a standardized 40-foot container, High Cube Class (Figure 5), and meets all the requirements for transportation on public roads in a road trailer.



Figure 5. SCWO installation process module, Penza State University

The reactor and process module can be mounted separately and upgraded for specialized tasks. The ACS unit is a separate module and is located at a distance of 25-30 meters from the process module, providing comfort and safety for the operator and 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 upon switch-on in order to avoid a possibility of admission of the personnel into the working area. The operating module is equipped with standardized pipeline connections for external loading of the materials being processed and unloading of the recycled products from the process module. The process of loading and unloading is controlled by the ACS unit in the automated mode.

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

Technical specifications of the installation are given in Table 14.

Table 14. SCWO installation technical specifications

Technical Specifications	Value
Volume of waste being treated, m ³ /day	up to 5.0
Operating mode	Long-term, cyclical
Cycle time (depending on the initial moisture content and calorific capacity of waste), 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, kWh	no more than 100
Installation weight, kg	14,635
Overall dimensions, m (W×H×L)	2.5×2.7×8.2
Operating personnel – operators	3 persons per shift

The SCWO reactor is made of the materials resistant to corrosion caused by ionized halogen. In the past, to solve this problem, titanium alloys and bimetals of tantalum-clad nickel-chromium alloys with service life up to 6,300 hours were used (Los et al., 2013).

As a result of extensive research, a multilayered metallic material with an "internal protector" is applied as a SCWO reactor material. Application of the composite material with enhanced strength and corrosion resistance together with the explosion welding technologies will increase the reactor's operational life more than 10-fold (Rozen et al., 2012; "Multilayer material with enhanced corrosion resistance (variants) and methods for preparing same", 2013).

Environmental aspects of the process

The toxicity of initial and processed products was evaluated for *Daphnia magna Straus*, *Scenedesmus quadricauda*, and the "Ecolum" test system ("Toxicity evaluation technique for water and water extracts from soil, sewage sludge, and waste according to Daphnia mortality and fertility change", 2007; "Toxicity evaluation technique for water, water extracts from soil, sewage sludge, and waste according to the change in the level of chlorophyll fluorescence and in the number of algae cells", 2007; "Integral toxicity evaluation for the surface, including marine, groundwater, drinking, waste water extracts from soil, waste, sewage sludge according to the change in the intensity of bacterial bioluminescence by 'Ecolum' Test System", 2010).

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

Dependence of logarithms of SCWO-processed waste samples dilution from probits of *Daphnia magna Straus* and *Scenedesmus quadricauda* mortality percentage is shown in Figure 6. It has been found that dilution of waste samples in the ratio 1: 100, 1: 1,000, and 1: 10,000 had no toxic effects on the luminescent bacteria (toxicity index "T" was less than 20). Safe dilution ratio (SDR) for the test objects has been defined for 10% and

20% mortality thresholds at 96-hour and 72-hour exposure.

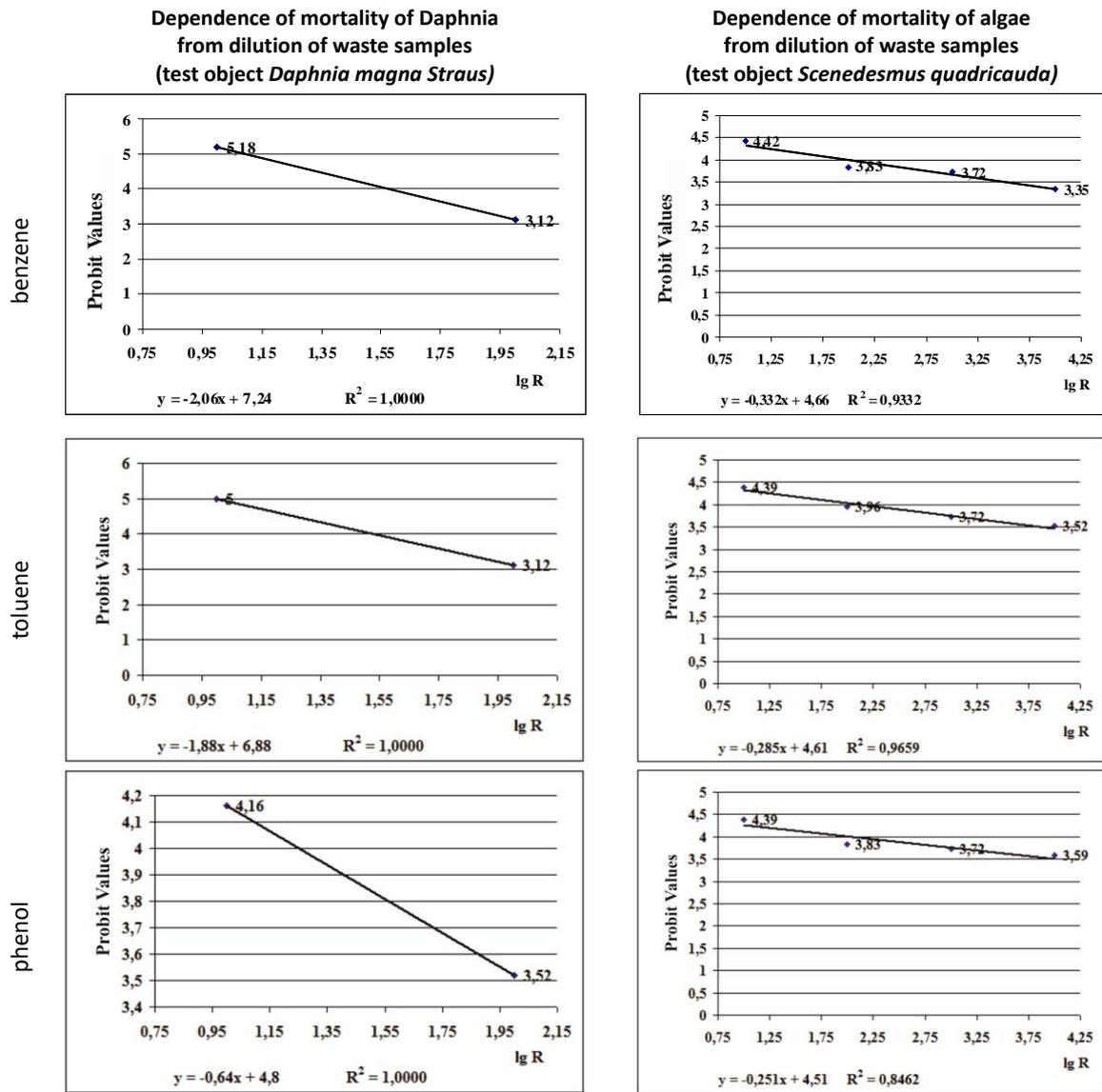


Figure 6. Dependence of test objects' mortality from dilution of waste samples

SDR for the products of the emulsions processing, in particular SDR₁₀₋₉₆, is 51.14 times for benzene, 48.70 times for phenol, and 47.96 times for toluene. This corresponds to the Hazard Class 4 (low hazard), which indicates a high environmental efficiency of the process. Bioassay results are shown in Table 15.

Table 15. Results of bioassay of the baseline 10% aqueous emulsion of benzene, toluene, and phenol and products of their recycling using the SCWO installation

Substance	Condition	Test object <i>Daphnia magna</i> Straus	Test object <i>Scenedesmus quadricauda</i>	"Ecolum" test system	Hazard Class
		Safe dilution ratio (SDR)			
		SDR ₁₀₋₉₆	SDR ₂₀₋₇₂	for fluorescent bacteria	
Benzene	initial emulsion	more than 10,000 times	more than 10,000 times	all dilutions	Class 1 (extremely dangerous, SDR more than 10,000)
	emulsion	51.14 times	39.65 times	1:100	Class 4 (low-hazard,

	derivatives				SDR less than 100)
Toluene	initial emulsion	more than 10,000 times	more than 10,000 times	all dilutions	Class 1 (extremely dangerous, SDR more than 10,000)
	emulsion derivatives	47.96 paza	37.93 times	1:100	Class 4 (low-hazard, SDR less than 100)
Phenol	initial emulsion	more than 10,000 times	more than 10,000 times	all dilutions	Class 1 (extremely dangerous, SDR more than 10,000)
	emulsion derivatives	48.70 times	24.92 times	1:100	Class 4 (low-hazard, SDR less than 100)

SDR₁₀₋₉₆ – safe dilution ratio of water extracts, causing the death of more than 10% of test objects during 96-hour exposure
 SDR₂₀₋₇₂ – safe dilution ratio of water extracts, causing the death of more than 20% of test objects during 72-hour exposure

Experimental measurements of the total content of polychlorinated dibenzo-n-dioxins and dibenzofurans in terms of 2,3,7,8-tetrachlorodibenzo-n-dioxin in the samples of technological emissions into the ambient air were performed by chromatography-mass spectrometry (“Quantitative chemical analysis of atmospheric air and emissions. Method of total content measurement of polychlorinated dibenzo-p-dioxins and dibenzofurans in terms of 2,3,7,8-tetrachlorodibenzo-p-dioxin in samples of industrial emissions into the ambient air by chromatography-mass spectrometry”, 2008). Analysis was performed by means of chromatography-mass spectrometer Thermo Finnigan MAT 95XP.

The obtained 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 in samples of industrial emissions into the atmosphere of the SCWO products equals to 3.9 pg/m³ and does not exceed the maximum permissible concentration introduced by the EU – 0.1 ng TEQ/Nm³ (“Communal hygiene. Atmospheric air and indoor air, sanitary protection of air. Maximum permissible concentration (MPC) of polychlorinated dibenzodioxins and polychlorinated dibenzofurans in the atmospheric air of residential areas”, 1994).

CONCLUSIONS

1. The quality of engineering calculations on the distribution of internal stress and temperature fields in the body of the reactors, as well as of the documentation design development is provided by the computer simulation using Delcam Power SHAPE and Delcam Art CAM software.
2. Thermal design of installations is elaborated taking into account the cycle time provided by the performance. The calculation of cyclic strength has been carried out. Corrosion allowance for reactors’ walls has been considered. The standard evaluation of the material’s corrosion rate under operation has been given. Calculations of the flow section and the permissible radius of curvature, confirming the possibility of transporting of the processed material at the expected rate in the given operating conditions of the installation, have been done. Estimates, modes of preliminary testing and monitoring of the intercrystalline corrosion, weld quality, styloscopy of the details of units’ control welded connections have been determined.
3. According to the Corrosion Test Independent Laboratory at State Scientific Research Center – Scientific Production Association CNIITMASH, OJSC (Moscow), company of the ROSATOM State Corporation, compared to the conventional chromium-nickel stainless steels, the corrosion resistance of the new material with “sacrificial pitting protection” is 10-fold higher and even more (Los et la., 2013). At the same time the obtained multilayer material is in the same segment as tantalum and platinum concerning performance characteristics, and at the same price segment as conventional chromium-nickel stainless steels. Its use value can be increased manifold, provided that the production costs associated with manufacturing of multilayer material by explosion welding will increase slightly. Technological regimes that allow manufacturing of three-, four-and five-layer composites per one explosion have been developed.
4. According to the results of the studies on determination experimentally the hazard class of liquid products from processing the benzene-in-water emulsion at the SCWO unit, it is possible to draw the following conclusions:
 - a. Experiments on bioassays showed that the waste adversely affected the test organisms.
 - b. Required dilution of liquid products from processing the benzene-in-water emulsion at the SCWO unit to a safe level for Daphnia (SDR₁₀₋₉₆) was 51.14 times, for algae (SDR₂₀₋₇₂) – 39.65 times; for luminescent bacteria, the minimum dilution ratio of the studied ones, at which the waste had no toxic

effect, was 1:100.

- c. Liquids products from processing the benzene-in-water emulsion at the SCWO unit, as an industrial waste in accordance with the Ministry of Natural Resources' Order No. 511 of June 15, 2001, refers to Hazard Class 4 (low hazard, SDR less than 100) for the environment.

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