International Journal of Mechanical Engineering and Technology (IJMET)
Volume 9, Issue 8, August 2018, pp. 32–45, Article ID: IJMET_09_08_004
Available online at http://www.iaeme.com/ijmet/issues.asp?JType=IJMET&VType=9&IType=8
ISSN Print: 0976-6340 and ISSN Online: 0976-6359

SUPERCRITICAL WATER OXIDATION OF ORGANIC POLLUTANTS

Vladimir Grachev
A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, 31, Bldg 4, Leninsky prospect, 119071, Moscow, Russia

Andrei Rozen
Department of Welding, Foundry and Materials Science, Faculty of Mechanical Engineering, Transport and Energy, Penza State University, 40, Krasnaya St., Penza, 440026, Russia

Evgeny Vorobiev
Department of Welding, Foundry and Materials Science, Faculty of Mechanical Engineering, Transport and Energy, Penza State University, 40, Krasnaya St., Penza, 440026, Russia

ABSTRACT

Calculated and experimental data for the automation of supercritical water oxidation (SCWO) technology and of registration the aggressive environment's corrosive effects on the installation's reactor have been obtained. The application of a new class of corrosion-resistant materials with a "sacrificial pitting protection" for a hardware implementation of the process, capable of widespread adoption of the SCWO, has been substantiated. Experimental evaluation of ecological purity of the process has been carried out.

Keywords: supercritical water oxidation, persistent organic pollutants, area of sustainable SCWO, corrosion caused by ionized halogen, multilayer metallic material with a "sacrificial pitting protection", bioassay, polychlorinated dibenzo-n-dioxins and dibenzofurans.

Cite this Article: Vladimir Grachev, Andrei Rozen and Evgeny Vorobiev, Supercritical Water Oxidation of Organic Pollutants, International Journal of Mechanical Engineering and Technology, 9(8), 2018, pp. 32–45.
http://www.iaeme.com/IJMET/issues.asp?JType=IJMET&VType=9&IType=8

1. INTRODUCTION

The issue of wastewater treatment and persistent organic pollutants (POPs) elimination is highly relevant especially for metropolises and cities with the developed industrial infrastructure [1]. 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 [2, 3]. The technology of

wastewater treatment by supercritical water oxidation (SCWO) is believed to be very promising [4, 5].

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 [6, 7]. 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 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 [6-13] and applied [14-17] research, which laid the foundation for the engineering technological calculations.

2. 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 [18]. Let us consider possible loss of stability by the homogeneous phase. This phase with initial parameters T_0, V_0, n_{10}, n_{20}, ..., n_{N0}, will be stable if for each isothermal variation the new state T_0, V_0, n_{10}, n_{20}, ..., n_{N0} will satisfy the following inequation:

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

where F – Helmholtz free energy, P – pressure, V – volume, μ – chemical potential, ni – 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:

$$[F - F_0 + S_0(T - T_0)]\, V_{0,n_{jo}} > 0 \qquad 2$$

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

Variations of the type:

$$\Delta V = kV_0 \qquad D_n = kn_{io} \qquad i = 1, 2, \dots N \tag{3}$$

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

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

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

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

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 (differential term, of 2nd order) is positive definite. At the critical point of stability (T_0, V_0, n_{10}, n_{20}, ..., n_{N0}) the quadratic form is positive semi definite. From this it follows that in this case the stability is determined by the properties of the differential term of 3rd order and of the expansion terms of higher orders.

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 reciprocally introduce vector Δn = (Δn1, Δn2, ..., ΔnN)T satisfying the following condition:

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

Determination of the critical point as the limiting stable state of the system requires a positive semidefinite quadratic form of its description, where 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 ΔV = 0 leads to the symmetrization of quadratic and cubic forms of terms in the equation for the description of the free energy. An equivalent result can be obtained by assuming Δnk = 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.

3. CALCULATION OF THE PROCESS' TECNOLOGICAL 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.

Initially the required number of 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 l of water and 0.1 l of fuel are required. Fuel mass per 1 liter of mixture is calculated by formula (10):

$$m_T = 0.1 \cdot \rho \quad (10)$$

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

Table 1 The content of components in 1l of the binary mixture

No.	Substance	Formula	M, g/mole	ρ, kg/l	V, l	m, kg	η, number of moles	y, mole fraction
1	Water	H_2O	18	1	0.9	0.9	64.29	0.983/0.986/0.982
2	Benzene	C_6H_6	78	0.879	0.1	0.088	1.13	0.017
3	Toluene	$C_6H_5CH_3$	92	0.87	0.1	0.087	0.946	0.014
4	Phenol	C_6H_5OH	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, 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).

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_2O	18	273	373	646.9	22.06
Benzene	C_6H_6	78	278.5	353	835	4.83
Toluene	$C_6H_5CH_3$	92	178	384	593	4.3
Phenol	C_6H_6O	94	455.0	314	694.3	6.13

on the principle of corresponding states by formulas (11, 12).

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

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

where y_i – mole fraction of the component.

On the basis of the found values of the critical points the values of the a and b coefficients for the Redlich-Kwong equation are calculated: formula 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	$2.216 \cdot 10^{-5}$

Next, the amount of binary mixture, required to cause supercritical behaviour in the unit, is calculated. The calculation is carried out by the Redlich-Kwong equation for a mixture of components (Equation 15)

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

where P – gas-vapor mixture pressure [Pa]; η – number of moles of the components; T – temperature [K]; V – volume of the reactor [m^3] (V = 0,027 m^3); 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.

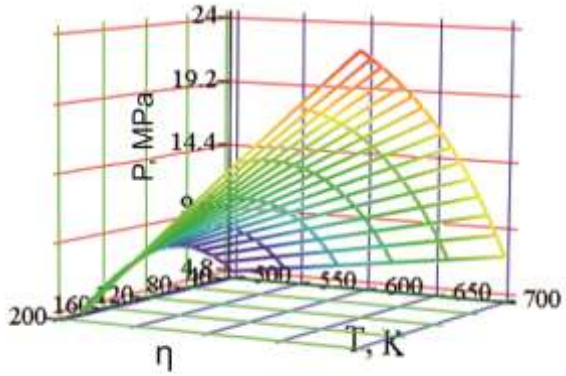

Figure 1 P = f (η,T) for the water-phenol mixture

The content of "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):

$$\eta_{o_2} = \eta_{fuel} \times \left(\alpha + \frac{\beta}{4} - \frac{c}{2}\right) \quad 16$$

where η_{O2} – 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 according to 3,4 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_{O2}, 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 CO_2, H_2O and O_2, which are calculated by formulas 17, 18, 19.

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

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

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

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

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):

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

Table 5 Composition of the SCWO products

Mixture	**η_{fuel}, mole**	**O_2 content, η(mole)/V(m^3) when in excess**		
		×2	×6	×10
Water/benzene	5.1	46.5/1.714	191.25/4.28	382.5/8.568
		$CO_2/H_2O/O_2$ 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
		$CO_2/H_2O/O_2$ 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
		$CO_2/H_2O/O_2$ concentration, mole/l		
		0.92/8.827/1.07	0.92/8.827/5.353	0.92/8.827/9.64

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

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

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

Table 6 Coefficients of the equation 21

Substance	**a**	**b**	**c**
CO_2	35.83	$9.04 \cdot 10^{-3}$	$-8.53 \cdot 10^{5}$
H_2O	21.69	$10.71 \cdot 10^{-3}$	$0.33 \cdot 10^{5}$
O_2	23.15	$3.39 \cdot 10^{-3}$	$-3.77 \cdot 10^{5}$

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

Table 7 Initial data for calculation of the maximum temperature SCWO

Mixture	**Q_{Vfuel}, MJ/mole**	**η_{fuel}, mole**	**$Q_{V\Sigma}$, MJ**	**Content of SCWO products: $CO_2/H_2O/O_2$ (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):

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

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 SCWO products are calculated by the formula (24) and are presented in Table 8.

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

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

Table 8 Values of the mole fraction (y_i) for 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 a_{Σ}, b_{Σ}, c_{Σ} coefficients for SCWO products are presented in Table 9.

Table 9 The a_{Σ}, b_{Σ}, c_{Σ} coefficients for SCWO products

Mixture	Excess of O_2								
	×2			×6			×10		
	a_{Σ}	$b_{\Sigma}\times10^3$	$c_{\Sigma}\times10^3$	a_{Σ}	$b_{\Sigma}\times10^3$	$c_{\Sigma}\times10^{-5}$	a_{Σ}	$b_{\Sigma}\times10^3$	$c_{\Sigma}\times10^{-5}$
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 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).

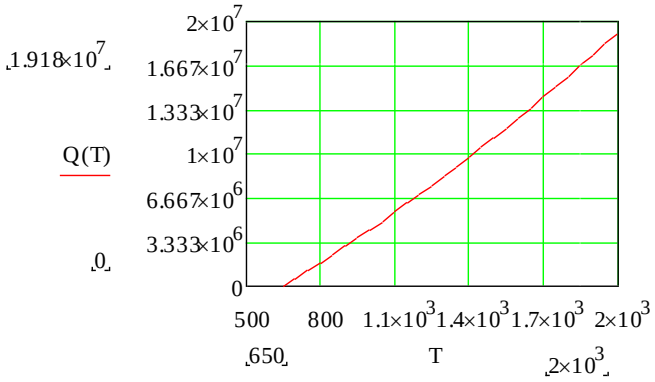

Figure 2 Determination of temperature for a water-benzene mixture when O_2 is in twofold excess

The results of the calculations are presented in Table 10.

Table 10 Temperature of products SCWO

Mixture	$Q_{V\Sigma}$, 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

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).

Basic data are presented 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_2O	646.9	22.06
O_2	154.6	5.08

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

Mixture	Excess of O_2,											
	×2				×6				×10			
	T_{cr}, K	P_{cr}, MPa	a	$b\cdot10^5$	T_{cr}, K	P_{cr}, MPa	a	$b\cdot10^5$	T_{cr}, K	P_{cr}, MPa	a	$b\cdot10^5$
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 SCWO products is calculated according to the determined values of Table 10, 12 by the Redlich-Kwong equation (Table 13).

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

Calculation data on SCWO critical parameters determine the values of the control signals of the process' automatic control.

4. HARDWARE SOLUTION

A hardware solution of the SCWO installation has been implemented under the conditions of the following process flow diagram (Fig. 2). 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, thermocouples for controlling the temperature inside the reactor and the temperature of the reactor vessel, nozzle covers for supplying a gaseous oxidizing agent/withdrawing gaseous reaction products and in the lower fitting part to output the reaction product condensed.

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.

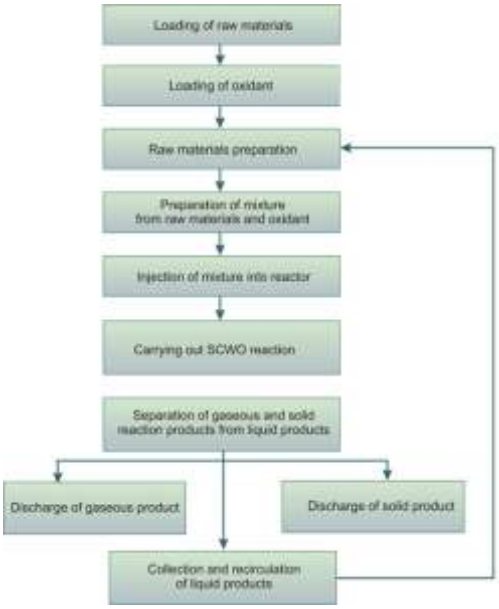

Figure 2 Process flow diagram of SCWO processing

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. 3.

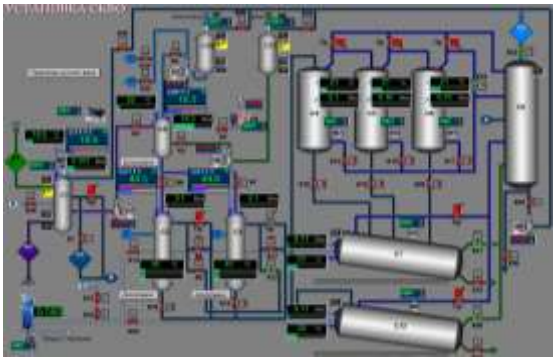

Figure 3 Ф1, ... Ф4 – filters; M1, M7, M8 – mixers; M2, ..., M6 – oscillators; H1, H2, H4, H6 – pumps; H3, H5 – compressors; C1 – preparatory vessel; C4, ..., C6 – expansion vessels; C7, C12 – solid waste tanks; C2, C3 – reactors; C8 – finishing tank; C9 – mixing tank; C10 – oxidizing agent tank; C11 – water tank; K1 ... K35 – valves; Pr1 ... WP4 – safety valves

The installation consists of an automated control system (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 14.

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 6300 hours were used [19].

Table 14 SCWO installation technical specifications

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 100
Installation weight, kg	14635
Overall dimensions, m (W×H×L)	2.5×2.7×8.2
Operating personnel	3 persons per shift

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 [20-22].

5. ENVIRONMENTAL ASPECTS OF THE PROCESS

Assessment of toxicity and processed products was performed on Daphnia magna Straus, Scenedesmus quadricauda, on the "Ecolum" test system [23-25].

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.

Dependence of logarithms of SCWO-processed waste samples dilution from probits of *Daphnia magna Straus* and *Scenedesmus quadricauda* mortality percentage is shown in Fig. 4. It has been found that dilution of waste samples in the ratio 1: 100, 1: 1000, 1: 10,000 has no toxic effects on the luminescent bacteria (toxicity index "T" is less than 20). Test objects' safe dilution ratio (SDR) has been defined for 10 and 20% mortality thresholds at 96-hour and 72-hour exposure.

Emulsions processing's products according to test objects' SDR, in particular for $SDR_{10\text{-}96}$, 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 15.

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 [26]. 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/m^3 [27].

5. CONCLUSION

1. The quality of engineering calculations on the distribution of internal stresses and temperature fields in the body of the reactors, as well as of the design documentation 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. Margin of the reactor walls' corrosive wear has been considered. The statutory definition 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 stated conditions of the plant, have been done. Estimates, modes of preliminary testing and monitoring of the intercrystalline corrosion, weld quality, styloscoping of the control unit welds' details have been determined.
3. According to the Corrosion Test Independent Laboratory at State Scientific Research Center –Scientific Production Association CNIITMASH, OJSC (Moscow), company of ROSATOM State Corporation, the corrosion resistance of the new material with "sacrificial pitting protection" is from 5 to 15 times higher than compared to conventional chromium-nickel stainless steels [19]. 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 obtaining the laminate by the explosion welding will increase slightly. Technological regimes, allowing obtaining three-, four-and five-layer composites per explosion.
4. According to the results of the studies on determination experimentally the hazard class of liquid by-products from processing the emulsion of benzene in water at SCWO unit, it is possible to draw the following conclusions:
   - Experiments on bioassays showed that the waste adversely affected the test organisms.
   - Required dilution of liquid products from processing the emulsion of benzene in water at the SCWO unit to a safe level for Daphnia ($SDR_{10\text{-}96}$) was 51.14 times, for algae ($SDR_{20\text{-}72}$) – 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.
   - Liquids products from the processing the emulsion of benzene in water at the SCWO unit, as industrial waste in accordance with the Ministry of Natural Resources' Order No. 511 of June 15, 2001, refers to class 4 of hazard (low hazard, SDR – less than 100) to the environment .

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