ELECTRICAL SURFACE TREATMENT METHODS

Influence of Long-Term Operation of Electrolytes on the Composition, Morphology, and Mechanical Properties of Surfaces Produced at Deposition of Co–W Coatings from Citrate Solutions

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Abstract—A comprehensive study has been conducted on the composition of a citrate electrolyte used to produce Co–W coatings that contains (mol/l) the following: cobalt sulphate (0.2), sodium tungstate (0,2), citric acid, sodium citrate, boric acid (pH 6.5) at both its storage and long electrolysis (up to $Q \approx 17$ A hour/l). The influence of the degree of operation, the electrolyte agitation, and current volume density on variations in its composition, as well as on the coating composition and microhardness is shown. The observed variations arise from the Podlaha–Landolt induced codeposition mechanism as applied to the used electrolyte composition and electrolysis modes.

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The induced codeposition of refractory metals (W, Mo) with metals of the iron group (Fe, Co, Ni) [1–3] makes it possible to produce amorphous (nanocrystal) coatings that are unique under certain conditions and possess corrosive and mechanical properties [2, 4–11]. Specifically, the deposition of Co–W alloys from citrate investigated electrolyte at elevated temperatures [9–12] allows one to produce coatings in which wear characteristics are better under conditions of dry friction than coatings made of electrolytic chromium and titanium nitride [6, 11]. Co–W coatings with these characteristics were deposited from an almost neutral citrate solution with addition of an boric acid and the same concentration as cobalt sulphate and sodium tungstate (0.2 mol/l) [9–12].

The possibility of the practical implementation of such solutions is substantially governed by the invariance (or change) of their properties after the long-term operation of the investigated electrolyte. This work is devoted to the solution of the problem.

EXPERIMENTAL

General outlines of the experiment. Long-term operation was conducted in an electrochemical cell with a nonseparated anode and cathode spaces. An investigated electrolyte of the following composition was used (mol/l): $Na_2WO_4 \cdot 2H_2O$, 0.2; $CoSo_4 \cdot 7H_2O$, 0.2; $C_6H_8O_7$ (citric acid), 0.04; $Na_3C_6H_5O_7$ (sodium citrate), 0.25; H_3BO_3 , 0.65. Electrodeposition on flat steel specimens with different areas was conducted from this inves-

tigated electrolyte at a current density of $i_c = 1 \text{ A/dm}^2$ and a solution bulk temperature of $T_0 = 60^{\circ}\text{C}$.

The electrodeposition was conducted in three sets of experiments with different current volume density varied by the change of the deposited coating area. The investigated electrolyte volume in the cell was 100 ml. The maximum area of the covered surface was 8 cm². Obviously, the current maximum volume density i_v was 0.8 A/l in the first set of experiments; in the second and third sets, it was 0.4 and 0.2 A/l, respectively. A graphite platelet with constant surface area situated parallel to the cathode plane was an anode. Deposition was conducted on one side of the steel plate, while the other was isolated.

The experiment design included two types of electrodes (cathodes), i.e., indicators (IE) and electrode accumulators (AE). The first type of electrodes were deposited with an amount of passed charge such that the thickness of the obtained coating was ~15–20 μ m. For these electrodes, the electrodeposition current efficiency and the morphology of the surface, as well as its composition and microhardness, were determined depending on the degree of the investigated electrolyte operation *Q* (A hour/l). The current volume density only changed (based on variations in the cathode surface area) in the case of deposition on indicator electrodes.

Deposition on accumulator electrodes was carried out after deposition on IEs. This operation was meant for the maximum (controlled) removal of the initial products



Fig. 1. Cobalt concentration in the electrolyte versus the degree of its operation.

(ions Co^{2+} and tungsten ions) from the solution. After deposition on AEs, deposition on IEs was conducted and the current efficiency, coating morphology, and composition were recorded, but from the solution with the higher degree of investigated electrolyte operation.

In the first and second sets of experiments ($i_v = 0.8$ and 0.4 A/l), deposition was carried out under the conditions of stirring the solution using a magnetic agitator during deposition on both IEs and AEs.

In the third set of experiments ($i_v = 0.2 \text{ A/I}$), deposition on IEs was carried out in the absence of stirring, while deposition on AE was conducted with stirring. The results corresponding to sets I–III are shown by points *1*, *2*, and *3* in Figs. 1, 2, and 7–10. A design of the IIIrd set of experiments is presented in Table 1 as an example.



Fig. 2. Tungstate concentration in the electrolyte versus the degree of its operation.

The solution pH and concentration of W and Co in the investigated electrolyte were determined prior to every stage of deposition on IEs. The same measurements were conducted in the initial investigated electrolyte before its operation. Because the partial evaporation of the investigated electrolyte occurred during the experiment, some water was periodically added to maintain a constant volume of 100 ml. This procedure was applied after each stage of electrodeposition (on IE, then on AE, etc.).

Analysis of the solution. An analysis was conducted at regular intervals (after deposition on AE) of the solution to evaluate the content of Co^{2+} using the procedure [13, p. 677] and WO_4^{2-} [13, p. 600], as well as the solution pH. Cobalt and tungsten ions were determined by the photocolorimetric method, which measures the opti-

Number in order	Electrode	S, cm^2	I, mA	<i>t</i> , hour	Presence of agitation	Q, A hour/l	ΣQ , A hour/l
1	IE	2	20	2	w/a (without agitation)	0.4	0.4
2	AE	8	80	3	a (agitation)	2.4	2.8
3	IE	2	20	2	w/a (without agitation)	0.4	3.2
4	AE	8	80	3	a (agitation)	2.4	5.6
5	IE	2	20	2	w/a (without agitation)	0.4	6
6	AE	8	80	3	a (agitation)	2.4	8.4
6	IE	2	20	2	w/a (without agitation)	0.4	8.8
7	AE	8	80	3	a (agitation)	2.4	11.2
8	IE	2	20	2	w/a (without agitation)	0.4	11.6
9	AE	8	80	3	a (agitation)	2.4	14.0
10	IE	2	20	2	w/a (without agitation)	0.4	14.4

Table 1. Co–W coating electrodeposition conditions during the long-term operation of the electrolyte (the IIIrd set, $i_v = 0.2$. A/I)

cal density of the solution Co^{2+} using nitroso R-salt and WO_4^{2-} after its reduction of Sn(II) and Ti(III) to W(V) (with the formation of the appropriately colored complex) [13]. In both cases, calibration graphs were constructed from the solutions that contained not only Co^{2+} and WO_4^{2-} , but rather all components of the investigated electrolyte solution at the concentrations in which they are used in the investigated electrolyte.

The utilized investigated electrolyte was also analyzed before electrolysis (before its operation) as before electrolysis the investigated electrolyte was held for ~1 month in the closed flask. It was found that the concentration of both Co^{2+} and WO_4^{2-} evaluated by the above-described methods turned out to be smaller than the initial one (0.2 mol/l). Thus, the determined concentration of Co^{2+} was 0.179 \pm 0.004, while that of was WO_4^{2-} 0.150 × 0.004 mol/l. To elucidate the causes of the observed decrease in the measured concentrations, a spectrophotometric analysis was conducted on the initial solution (Perkin Elmer Lambda 25 spectrophotometer, cell width of 10 mm). The absorption spectra of the initial solution were registered a few hours after its preparation, as well as after 2 weeks and ~1.5 months. In addition, the absorption spectra of the solution were registered during long-term electrolysis after different values of the passed charge.

Analysis of coating surface. The morphology, chemical composition, and mechanical properties of the obtained coatings varied with the amount of the passed charge (Q, A hour/l). A number of methods were used with the aim of analyzing them, including the following:

1) The surface morphology was investigated using scanning electron microscopy (SEM TESCAN).

2) Local element analysis was conducted on the X-ray accessory to the scanning electron microscope (INCA Energy EDX). Because local element analysis was used (surface regions with diameters of several micrometers were examined and the ray penetration depth was of the same order of magnitude), the presented results are the average of three measurements.

In some cases, the results of scanning electron microscopy showed discrepancies in the surface morphology in different regions. In this case, different regions were examined according to the abilities of local element analysis.

Estimation of surface microhardness. Depending on the degree of investigated electrolyte operation, the microhardness of the coatings determined at various loadings by a Vickers indentor (50 and 100g) was estimated using a PMT-3 microhardometer.

RESULTS AND DISCUSSION

Variation in investigated electrolyte composition during operation. The fact that the determined concentration of both Co^{2+} and WO_4^{2-} in the initial investigated electrolyte turned out to be lower than the given value is the most noteworthy peculiarity of the used method of solution analysis, as was mentioned above. Moreover, the determined concentration of the ions under study during the investigated electrolyte operation grew (at relatively small values of passed electricity, Figs. 1 and 2). At higher values of Q, there occurred the lowering of concentration of both Co^{2+} and WO_4^{2-} . The values of Qat which the above-mentioned lowering was observed depended on the current volume density. At smaller values, the determined concentration peaked at lower Q(Fig. 2); it was most pronounced for the variation of WO_4^{2-} concentration in the investigated electrolyte (Fig. 2).

Another peculiarity of variations in the investigated electrolyte composition is that, during electrodeposition on IEs under conditions without agitation (the third set of experiments), more drastic changes in the WO_4^{2-} concentration and less drastic changes in Co²⁺ concentration were observed (Figs. 1 and 2). As will be shown later, according to the results of the coating composition measurements, the presence of agitation increases the cobalt concentration in the coating and decreases the tungsten concentration, causing the observed difference in the reduction rate of the concentration of the main components of the investigated electrolyte. The pH of the investigated electrolyte changed only slightly up to $Q \approx 10$ A hour/l; its value was in the range pH 6.5-6.9. This is indicative of the high buffer capacity of the solution due to the insertion of boric acid into the investigated electrolyte composition, as boron is not found in the coating.

Measurements of the investigated electrolyte absorption spectra showed that cobalt is a constituent of the citrate complex (absorption peak at $\lambda = 531$ nm, Fig. 3). The sodium tungstate citrate solution is colorless and does not absorb in the visible spectrum. As for cobalt–tungsten investigated electrolyte, two absorption peaks are observed in the visible spectrum, i.e., at 531 nm, which corresponds to the absorption peak of the cobalt citrate complex, and at $\lambda = 716$ nm, Fig. 4. It is not improbable that the second peak is caused by the formation of the appropriate cobalt-tungsten heterocomplex (heterocomplexes and possibly heteropolycomplexes) in the solution.

It is important to note that, estimation by the variations in the absorption spectra during the long-term storage of the investigated electrolyte, the composition of the solution changes. Specifically, the absorption peak at $\lambda =$ 716 nm is broadened and absorption increases in the range of 620–640 nm (Fig. 4).

In the course of operation, the absorption peak reduces at $\lambda = 531$ nm corresponding to the variation of the cobalt citrate complex concentration and almost disappears at $\lambda = 716$ nm (Fig. 4).



Fig. 3. Absorption spectrum of the solution containing cobalt salt, citric and boric acids, and sodium citrate in relation to the solution cobalt salt and boric acid with concentrations corresponding to their concentrations in the electrolyte.



Fig. 4. Absorption spectra of nonoperated electrolytes that are (1) newly prepared (2. after 2-3 weeks; 3. within a month) and operated (4. up to 5 A hour/l; 5. final solution of the second set).

Influence of the degree of investigated electrolyte **operation on the morphology and composition of the coatings.** As was pointed out above, in the experiments for the given (initial) composition of the investigated electrolyte (and temperature), a constant current density of electrodeposition of 1 A/dm^2 was used [2]. It can be seen from the polarization curve obtained for the initial (nonoperated) investigated electrolyte composition (Fig. 5) that

this density is close to the limiting current density. The nature of this current density was not studied specially; however, if it is taken into account that the curve presented in Fig. 5 is obtained in unstirred investigated electrolyte and suggested that the measured current (in the range of limiting one) is diffusion current, then the value of the current limiting density must increase in the presence of stirring. Thus, at the fixed electrodeposition current density, the surface morphology must change, as with stirring, electrodeposition will occur at $i < i_{lim}$, where i_{lim} is the density of the cathode limiting current of diffusion.

In reality, with stirring (Figs. 6a and 6b), the morphology of the obtained surface differs substantially from that observed after electrodeposition at the same current density without stirring (Fig. 6c). In the latter case, the formation of a coating with spheroidal structure is observed, whereas, in the first two cases, the structure is more crystal-shaped. This effect is fairly well known in practice for both electrodeposition and electrodissolution (see, e.g., [14]). In these cases, at $i < i_{lim}$, a pronounced crystallinity is observed and, at $i \ge i_{lim}$, more uniform electrodeposition (electrodissolution) occurs, as, in this case, the principal resistance to the transfer is concentrated inside the diffusion boundary layer. This results in smoother surfaces (to the extent that they appear polished). The coatings obtained with electrodeposition without stirring (at the used current density) had a shiny appearance and, with stirring, they were matte.

However, not only does the morphology of coatings change with stirring, but their composition also vary substantially (Figs. 7 and 8). The presence of agitation that increases (obviously) the value of the limiting current causes a reduction in the tungsten concentration in the coating (Fig. 7) and growth in the cobalt concentration (Fig. 8). It should be noted that, up to certain (high enough) values of Q, the concentration of tungsten in the coating grows with increasing Q, while that of cobalt decreases (or is close to constant) (Figs. 7 and 8).

The causes for changes in the coating composition with investigated electrolyte agitation will be examined



Fig. 5. Polarization curve of the cathode induced electrodeposition from the electrolyte under study (potential is given in relation the saturated Ag/AgCl electrode).

later when discussing the how the codeposition of cobalt and tungsten is induced. Nevertheless, it is evident that the growth in the tungsten content in the alloy with an increase in Q and reduction in cobalt concentration is due to the drastic change in the cobalt citrate concentration as compared to tungstate during the operation. Bearing in mind that the coating composition is close to stochiometric for Co₃W [9], it is obvious that the cobalt concentration should subside in the solution at a substantially higher rate than tungsten; the measurements of the investigated electrolyte concentration also support this. Thus, if, after ~10 A.hour/l, the concentration of WO₄²⁻ in the

solution is reduced to ~0.16 mol/l, the concentration of WO₄ in the Solution is reduced to ~0.16 mol/l, the concentration of Co^{2+} is reduced to 0.065 mol/l (Figs. 1 and 2, the first set of experiments).

Upon analyzing the obtained data, it can be stated that they are intrinsically noncontradictory. This is also confirmed by the fact that neither the concentration of cobalt in the solution nor its concentration in the coating, as well as concentration of tungsten in the coating, depend on the current volume density (the distinction between different sets of experiments is due solely to the presence or absence of stirring). The above conclusion is supported by the data of Table 2, in which the results of the



Fig. 6. Microphotos of the surface of Co–W alloys obtained at 1 A/dm² after 3.2 A hour/l for the Ist (a), IInd (b) and IIIrd (c) sets of experiments.



Fig. 7. Change in tungsten concentration in the coating versus the degree of electrolyte operation.

coating composition study obtained at Q = const (3.2 A hour/l) are presented. It can be seen that alterations are only observed at the transition to the third set of experiments without stirring during deposition on the IEs.

Influence of changes in investigated electrolyte composition on current efficiency. Differences in the electrodeposition conditions with and without stirring are also manifested in variations in the electrodeposition current efficiency (Fig. 9). At the accepted value of the electrochemical equivalent (0.311 mg/kl [7]), the efficiency was substantially higher with stirring; in this case, it amounted to as much as ~87%. Without stirring, the peak value of current efficiency was ~75%. In addition, the current efficiency value (η) did not depend on the current volume density (coincidence of values for the first and the second sets of experiments (Fig. 9)) and decreased when Q increased, which occurred to a greater extent in the case without stirring during electrodeposition.

The reason for the observed changes can be understood if the above-mentioned hypothesis (see the previous section), according to which the observed cathode limiting current (Fig. 5) is a limiting diffusion current and the main reaction at $i > i_{lim}$ is a secondary reaction of evolving hydrogen (water decomposition), is accepted. Then, the increase in i_{lim} at i = const must reduce the

Table 2. Composition of coatings (wt %) produced in the electrolyte after its operation up to Q = 3.2. A hour/l

No	Set of experiments	W	Со
1	Ι	33.1 ± 1.0	66.6 ± 0.9
2	II	33.7 ± 0.2	66.3 ± 0.2
3	III	49.4 ± 0.9	50.6 ± 0.9



Fig. 8. Change in cobalt concentration in the coating versus the degree of electrolyte operation.

hydrogen current efficiency and increase the metal current efficiency, which is observed in the experiment. Correspondingly, the dilution of the investigated electrolyte according to the main components of the solution (citrate, cobalt, and tungstate) due to its operation must reduce the value of i_{lim} , thus decreasing the metal current efficiency and increasing the secondary reaction current efficiency, which is also seen in the experiment (Fig. 9). The presented analysis results also indirectly support the hypothesis that the observed current limiting density is diffusion.

Coatings microhardness. The results of measurements of the obtained surface microhardness displayed in Fig. 10 correlate well with the findings of previous investigations, as well as with the data on changes in the coating composition with the variations in the electrolysis conditions presented in this work. These data are evidence that a clearly defined correlation exists between the tungsten concentration in an alloy and the coating microhardness. In fact, the microhardness increases (to certain values of Q) in comparison to the coatings obtained with its use in the presence of an increasing tungsten concentration in the surface layer without stirring (compare results shown in Figs. 7 and 10). The tungsten concentration and microhardness (regardless of the presence or absence of stirring) increase relative to the degree to which operation increases (up to a certain limit) (Figs. 7 and 10).

The acceptable accuracy of microhardness determination is noteworthy, as it is the same (within the limits of measurement error) for measurements with different current volume densities (Fig. 10). Since the coating composition also does not depend on the current volume density (Figs. 7 and 8), the correlation between the tungsten content in the alloy and the microhardness of the coating is clear. Moreover, it is seen that, at fairly high Q,



Fig. 9. Influence of the degree of electrolyte operation on current efficiency.

the microhardness decreases with an increasing degree of investigated electrolyte operation; this is observed at Q > 8 A hour/l with stirring (the first and the second sets) and at Q > 4 A hour/l without stirring (third set).

It should be also pointed out that, for coatings obtained with stirring, the microhardness values do not depend on the loading amount, which indicates its homogeneity (through the depth). The coatings obtained in the absence of stirring were less homogeneous. The microhardness values measured at a loading of 50 g were $\sim 20\%$ higher than for double loading (values obtained with a loading of 50 g are shown in Fig. 10). It should also be taken into account that the roughness of coatings obtained with stirring was higher than without it, which in turn can influence the obtained values of microhardness.

It was shown above that, with stirring, deposition occurred at $i < i_{lim}$, while, without stirring, it occurred at $i \sim i_{lim}$ (at small Q). In addition, it is evident that variations in the concentration of tungstate and cobalt citrate during operation should reduce i_{lim} ; this reduction has a stronger effect on the process in the case without stirring. For this reason, the growth of Q under these conditions substantially reduces the current efficiency (Fig. 9), as well as microhardness (Fig. 10).

As can be seen from the results of studying the surface morphology with stirring at up to ~8 A hour/l, the morphology hardly changes. Moreover, only tungsten and cobalt enter the composition of the coating; the concentration of tungsten rises with growth in the degree of operation (Figs. 11a and 11b). At $Q \sim 13$ A hour/l, the investigated electrolyte composition changes such that qualitative deposition becomes impossible (Fig. 11c). In this case, the microhardness decreases and substantial heterogeneity is established over the deposited surface (Fig. 10).



Fig. 10. Influence of the degree of electrolyte operation on coating microhardness.

In the absence of stirring (though the surface is enriched by tungsten (Fig. 7) and smoother (Figs. 6c, 12a, 12b) than that obtained with stirring), at a certain degree of operation, some areas appear with increased carbon (as well as oxygen and other components of the solution) contents; the number of these areas increases with increasing degrees of operation (Fig. 12). A comparison of the findings of the element analysis presented in Fig. 12, as well as the values of microhardness (Fig. 10), shows that the presence of these surface areas is due to the capture of the investigated electrolyte components and is the reason for the reduction in microhardness under the conditions of deposition at $i \approx i_{lim}$. As can be seen from the microphotos and the results of the surface analysis, cobalt and tungsten are deposited on the main surface of the alloy and the increased content of carbon and other components of the solution only occur at certain points. Obviously, deposition under the conditions of $i \approx i_{lim}$ is optimum in regards to the composition of coatings and their physical properties; however it is simultaneously maximally sensitive to variations in the investigated electrolyte composition during its operation. If the deposition is carried out at $i < i_{lim}$, then the tungsten concentration in the coating and microhardness will be smaller; furthermore, the current efficiency will be higher and the mechanical properties of the coatings will be less sensitive to changes in the solution composition.

The appearance of coatings is the qualitative indicator of the electrodeposition with $i \sim i_{lim}$ or $i < i_{lim}$. In the first case the coating is shiny and in the second one it is matte.

On the interaction between the electrodeposition mechanism and the composition, morphology, and mechanical properties of tungsten–cobalt coatings. The observed peculiarities of the influence of electrodeposition conditions on the composition and proper-

(a)				(b)			(c)		
	Spectrum 1	<u>З0 µт</u>		+ Spect	rum 1 30 µm		Spectrum 1	орана 30 µm	
Element	Wt %	At %	Element	Wt %	At %	Element	Wt %	At %	
Со К	66.70	86.21	Co K	56.02	79.90	СК	5.14	18.98	
W M	33.30	13.79	W M	43.98	20.10	O K	11.21	31.08	
Total	100.00	100.00	Total	100.00	100.00	Na K	4.96	9.57	
		J	L		I	S K	1.24	1.71	
						Fe K	1.67	1.33	
						Co K	37.26	28.04	
						W M	38.53	9.29	
						Total	100.00	100.00	

Fig. 11. Microphotos and element content in coatings produced in the electrolyte after passing (A hour)/l: (a) first set, 0.8; (b) second set, 8.0; (c) third set, 12.8.

ties of the obtained deposits can be interpreted if the induced codeposition mechanism is known. As applied to the used investigated electrolyte composition and conditions under which the alloys are obtained, the discovered peculiarities, i.e., the influence of stirring and changes in the composition, morphology, and properties of coatings with variations in the degree of operation, can be explained if the Podlaha-Landolt mechanism is accepted [15]. According to this mechanism, the metal citrate of the iron group (in this case, cobalt citrate [CoCit⁻]) plays a dual role. First, the deposition of cobalt occurs as a direct result of this process; secondly, it plays the role of a catalyst of codeposited component electrodeposition (in this case, tungsten). As applied to obtaining the Co-W alloy, the pattern appears to be as follows:

$$[CoCit]^{-} \underbrace{Co_{(s)} + Cit^{3-}}_{WO_{4}^{2} + 2H_{2}O + 2\overline{e}}$$
(a)
$$[CoCitWO_{2}]_{ads}^{-} + 4OH^{-} (b)$$
$$|+2H_{2}O + 4\overline{e}$$
$$W_{(s)} + CoCit^{-} + 4OH^{-} (c)$$

Taking into account that a parallel reaction of hydrogen evolution occurs, the reaction takes the following form:

$$H_2O + \bar{e} \longrightarrow \frac{1}{2}H_2 + OH^-.$$
 (d)

As is mentioned in [15], the presented reactions are only patterns and do not reflect, for instance, the exact composition of the participating complex ions, including the intermediate adsorbed heterocomplex [CoCit⁻WO₂]⁻. Moreover, the presented pattern shows the following:

1. The relation of the rates of competing reactions (a) and (b, c) will determine the relationship between components in the alloy.

2. Stirring will increase the partial current of the stage, which is quicker as in this case where concentration restrictions on the sum electrochemical process rate are possible.

If the reaction (a) is suggested quicker then the total process rate (current density), which is fairly high, this stage will be limited by the diffusion rate and the observed limiting diffusion current (Fig. 5) will be determined by the rate of cobalt citrate complex supply. Furthermore, with $i = i_{lim}$, the complex surface concentration will be determined by its regeneration rate in accordance



Fig. 12. Microphotos and element content in coatings and their spectral characteristics obtained at electrodeposition from the electrolyte under study (third set of experiments) after passing (A hour)/l): 6.4 (a, b), 11.6 (c, d). The analyzed parts of the alloy surface are indicated in the microphotos.

with reactions (b) and (c). In other words, the stirring velocity will increase the rate of reaction (a); the partial current of this reaction and, correspondingly, the cobalt content in the alloy at the expense of the tungsten content decrease, which is observed in the experiment.

Thus, it may be thought stated that the observed values of i_{lim} are the limiting diffusion currents of reaction (a), i.e., they are determined by the rate of CoCit⁻ delivery to the electrode surface. At $i < i_{lim}$ (in the experiments with stirring described below), the alloy structure should change independent of the increase in the cobalt content. In this case, at $i < i_{lim}$, in parallel with the generation of Co₃W (as a consequence of the joint occurrence of reactions (a–c)), crystalline cobalt will be generated, which is confirmed by the data presented in [9], where it is shown that, under the described conditions (investigated elec-

trolyte, temperature, electrodeposition at i = 1 A/dm²), crystal cobalt enters the composition of coatings in parallel with Co₃W; furthermore, at electrodeposition with current density i = 1 A/dm², it is absent and the amorphization of the coating is observed.

Obviously, the peculiarities of the morphology of the coating (Fig. 6, visual observations indicating whether shiny or matte surfaces were obtained) are indirect evidence for the mechanism (a–b) provided that stage (a) is diffusively controlled.

During the process of the long-term operation of the investigated electrolyte, the foremost reduction occurs in the concentration of cobalt in the solution, as its amount in the alloy is larger (in at %). Hence, i_{lim} should decrease and, during operation, the current efficiency will diminish (Fig. 9) peaking without stirring, as, in this case, its





value is smaller. The values of the alloy current efficiency must be smaller in the case of the absence of stirring, as i_{lim} decreases and the part of the reaction d grows.

It seems expedient to carry out electrodeposition at $i \approx i_{lim}$ (in the used investigated electrolyte) from the point of view of obtaining the minimum surface roughness and higher values of microhardness, as well as the corrosion characteristics of the surface. However, this sometimes causes more rigid requirements for the change in investigated electrolyte composition and cobalt concentration, which determine the value of i_{lim} . In electrodeposition it is usually advantageous to use operating current densities that are half the value of the limiting diffusion current [16], as, at $i \rightarrow i_{lim}$, treeing is

observed and, at $i > i_{lim}$, powders are generated. It is apparent that this conclusion cannot be extended to the practice of induced codeposition.

The rigidity of requirements for the change in composition manifests itself in particular in the fact that, if deposition occurs at $i \approx i_{lim}$ (in our case, absence of stirring at i = 1 A/dm²), the allowable degree of the investigated electrolyte operation is sharply limited without corrections. In the experiments described above, this value is Q > 4 A hour/l and the concentration of cobalt and tungstate varies moderately, with the values being close to each other (~0.16 and 0.14 mol/l, respectively). At Q >4 A hour/l, i_{lim} is reduced substantially, causing the quality of coatings (Figs. 11 and 12) and their microhardness

As for the observed abnormalities in the change in concentrations of the salt of cobalt and tungsten (reduction during storage in the investigated electrolyte without current passing and growth in the course of electrolysis, Figs. 1 and 2), it may be suggested that the reduction of WO_4^{2-} by cobalt citrate to heterocomplexes may occur, not only as an electrochemical process (reaction 9b), but also as a chemical process. Then, anode oxidation becomes possible with the generation of WO_4^{2-} and CoCit⁻ (i.e., the reverse occurrence of reaction (b)) during electrolysis). If this is really the case, then the reaction current efficiency must reduce the growth in current anode density, as, with the increase in i_a , the prevailing evolution of oxygen will be observed on the carbonic anode. Thus, the range of Q at which growth in the WO_4^{2-} concentration is observed in the investigated electrolyte is reduced with the decrease in the current anode density. It is precisely this effect that is seen in the experiment (Fig. 2), as, in the second set of experiments (as compared with the first one), the current volume density was reduced, which means that, with the same surface area of the anode, the anode current density was lower.

The possible mechanism of reduction suggests that the complex generated by reaction (b) (or chemically) may be a complex with a charge transfer. The advanced mechanism is a hypothesis and further research is necessary to prove it. The same is also true for the proof of the nature of the cathode limiting current. Some measurements under controlled hydrodynamic conditions are necessary to support it.

CONCLUSIONS

A comprehensive study has been conducted on the composition of a citrate investigated electrolyte used to produce Co–W coatings containing the following (mol/l): cobalt sulphate (0.2), sodium tungstate (0.2), citric acid, and boric acid (pH 6.5) at both its storage and long electrolysis (up to $Q \sim 17$ A hour/l.) With and without agitation. It is shown, during the storage of the investigated electrolyte without current, heterocomplexes containing tungsten and cobalt are generated. The presence of these components (possibly heteropolycomplexes) reduces the determined concentration of WO₄^{2–} and citrate Co(II) in the investigated electrolyte, which may increase during electrolysis (up to certain values of

Q) due to the oxidation of their anode with the generation of WO_4^{2-} and Co(II).

It is found that agitation at $i = \text{const} (1 \text{ A/dm}^2)$ substantially influences alloy composition and the morphology and microhardness of the coating.

The observed changes are the result of applying the induced codeposition Podlaha–Landolt mechanism to the investigated electrolyte composition and electrolysis modes.

It is shown that optimum conditions of electrodeposition achieve deposition at a current density corresponding to the limiting diffusion current of the reduction of cobalt citrate while achieving the maximum tungsten concentration in the alloy and maximum values of surface polishing and microhardness. However, these electrodeposition conditions are rather sensitive to variations in the investigated electrolyte composition during its long-term operation.

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> ELECTRICAL PROCESSES IN ENGINEERING AND CHEMISTRY

The Effect of an Electric Field on Plane Wall Cooling

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INTRODUCTION

One of the most efficient and promising ways to intensify thermal exchange is to use electroconvection phenomena [1]. Under the effect of an external electric field, free space charges are formed in a dielectric fluid; during their motion, these charges entrain a neutral medium, intensively agitating it. In the process, electrohydrodynamic flows are formed at a certain field density; as this density increases, a transition from a laminar to a turbulized flow mode is observed. Flow velocities, depending on the electrophysical properties of the working material, can be as high as 1 m/s. As a rule, for the process to be intensified, electroconvection is used to agitate a heat carrier, which results in a decrease in the thickness of the thermal boundary layer and an increase in the coefficient of the wall heat transfer to the fluid.

In the present paper, an electric field is used to form a heat carrier flow directed perpendicularly to a heat transfer surface which is simultaneously turbulized.

EXPERIMENTAL SETUP AND INVESTIGATION TECHNIQUE

The experimental setup (Fig. 1) comprises a working chamber, a heater feed circuit, a circuit intended for measuring the temperatures of a heat-releasing surface and a heat carrier, high-voltage circuits, and a thermostat to stabilize the temperature of the working material.

The working chamber 1 is a vertical cylinder 150 mm in diameter and 110 mm high made of stainless steel and having three windows. Two windows are designed for observing and recording electroconvection, whereas window 2 is intended for introducing a metal cartridge housing a copper–constantan thermocouple 3 which fixes the temperature of the working medium. A highvoltage electrode 4 is fixed in the upper removable cover of the chamber made of plexiglass. The temperature of the fluid heat carrier was kept constant with the help of the thermostat 5 connected to the refrigerator 6.

The high-voltage electrode 4 was made as a mesh from insulated wires with perforations from the side of the counter electrode 7.



Fig. 1. Block diagram of the experimental setup.



Fig. 2. Dependence of the heat transfer coefficient on voltage in different high-voltage electrode geometries: (1) $1.5 \varnothing$ 1.5 mm mesh (from stainless steel wires 0.1 mm in diameter); (2) plate; (3) mesh from insulated wires 1 mm in diameter with perforation.

The heat surface 7 and the face of a brass rod 840 mm in diameter and a diaphragm 80 mm in diameter and 0.1 mm thick were one unit. This design was used to minimize heat spread over the diaphragm.

Junctions of differential thermocouples were located at specified distances from the heat-releasing surface along the rod axis. Cold thermojunctions were submerged in transformer oil and placed in a Dewar vessel with melting ice. Via a two-pole switch 9, the thermojunctions were connected to an Sh-300 combination logging tool. The ohmic heater 10 connected to a source of stabilized voltage was mounted in the lower part of the brass rod. The supplied electric power was measured with the wattmeter W.

An AII-70 half-wave rectifier was used as a high-voltage source. An S-196 kilovoltmeter was connected to the high-voltage circuit to measure the potential drop between the heat-releasing surface and the high-voltage electrode.

The experiment started with washing of the working chamber and its subsequent filling with transformer oil. With the help of the stabilized voltage source, the required power to the heater was reached, whereas the thermostat ensured the required working medium temperature. A specified electric potential was supplied to the electrodes.

The system was kept under voltage until a stationary state characterized by an electromotive force of thermocouples constant in time was achieved. After the thermocouple readings were recorded, the system was readjusted for a new stationary mode by varying the potential difference at the electrodes, all other parameters being the same.



Fig. 3. Heat transfer coefficient α vs. interelectrode gap d, $T_{\rm f} = 324$ K.

The sequence of operations was preserved in experiments performed at different electric field densities, heat carrier temperatures, high-voltage electrode geometries, and interelectrode gaps.

EXPERIMENTAL RESULTS AND CONCLUSIONS

The efficiency of plane wall cooling depends substantially on the counter electrode (high-voltage electrode) geometry (Fig. 2), which drastically affects the heat carrier electrostatic charging. The latter was more intense in the regions of maximum electric field density, in particular, at perforations [1]. The dielectric fluid is charged by a meshlike charge. Under the effect of Coulomb forces, the medium is electroconvectively turbulized, this turbulization increasing with an increase in voltage (curve 3, Fig. 2). Contrary to mesh and plane electrodes (curve 1, Fig. 2), a mesh with perforations pumps the heat carrier perpendicularly to the wall [2] and transports it away from the interelectrode gap (IEG), which increases the hear transfer coefficient α by a factor of 7 as compared to natural convection.

When IEG narrows (d < 3 mm), the distances between perforations, the heat-releasing surface, and the mesh become comparable. Each perforation begins playing the role of an individual electrode, analogous to a needle one [1], which lowers the velocity of dielectric fluid pumping. Hydraulic resistance of the interelectrode gap increases; the intensity of heat carrier agitations decreases; and, as a result, heat transfer deteriorates (Fig. 3).

An increase in the heat carrier temperature $T_{\rm f}$ (Fig. 4) and of the temperature drop ΔT (i.e., the difference between wall and fluid temperatures) (Fig. 5) in the case



Fig. 4. Heat transfer coefficient vs. voltage at different heat carrier temperatures $T_{\rm f}$, K: (1) 308; (2) 324; (3) 341.

of a mesh electrode yields an increase in the heat transfer coefficient. Electrical conduction increases, viscosity of the transformer oil decreases with temperature [1], and turbulization and pumping of the working medium increase. In the process, we observe some weakening of the dependence of α on ΔT at large temperature drops (Fig. 5), which seems to be attributed to saturation of electrostatic charging of the fluid dielectric due to thermal heterogeneity.

CONCLUSIONS

Utilization of a mesh electrode with perforations was found to significantly accelerate the process of plane



Fig. 5. Heat transfer coefficient α vs. temperature drop, $T_{\rm f}$ = 324 K.

wall cooling. The heat transfer coefficient increases by a factor of 7, which is attributed to simultaneous turbulization and heat carrier pumping perpendicularly to the heat-releasing surface and, consequently, away from the interelectrode gap.

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ELECTRICAL PROCESSES IN ENGINEERING AND CHEMISTRY

Application of Plasma-Solution Treatment for Modification of Bast Fibers

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Abstract—Delignification processes of rough bast fibers under the action of face discharge were studied. The residual lignin content in the fiber and the fiber mass loss were determined after the plasma–solution and subsequent short chemical treatment with reduced alkalinity. This two-stage treatment was shown to be an effective delignification method for bast fibers, since the delignification degree amounts to 68% for flax, 64% for hemp, and 39% for jute fibers.

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INTRODUCTION

The processing of cellulose materials is based on multiple technological processes in various industrial branches. The application of plasma-solution methods with an aim to modify cellulose-containing materials may be of considerable interest because they involve both the high plasma chemical activity and the selectivity of processes, which occur in solutions. In particular, the application of plasma-solution treatment to modify rough bast fibers, which, in recent years, have become widespread in the textile market, is, in our opinion, rather promising. The aim of modifying bast fibers is to supply them with properties necessary for their joint processing with other kinds of raw materials (cotton, wool, and man-made fibers). The modification of hemp and jute technical fibers, as well as of waste products of flax scotching, is of great interest from both practical and economical points of view. These fibers possess high hygroscopic and hygienic properties, durability, and resistance to UV radiation; this stimulates the search for possibilities to produce new kinds of textile raw materials on their bases.

The main admixtures in bast fibers are of the same nature and their content does not vary significantly. Lignine is one exception, whose content amounts to 4-5% in flax fiber, 5-7% in hemp fiber, and exceeds 12% in jute fiber [1, 2]. In particular, the high lignine content defines the durability and roughness of technical fibers. By forming rough bonds with a cellulose component, lignin reinforces elementary fibers and ties them in long, strong complex bunches. It is necessary to destroy rough bast bunches to elementary and thin complex fibers, which involve four to five elementary fibers.

Lignin is a natural polymer of complex structure. Its basis consists of phenylpropane structures linked by sim-

ple ether and carbon–carbon bonds; therefore, it is highly resistant to base action. To reach the necessary degree of lignin elimination (not less than 50%), the bast fibers are subjected to treatment in basic solutions (5–10 g/l of sodium hydroxide) for 2–3 h at a temperature of no less than 100°C. However, even fairly severe treatment conditions (base concentration 15 g/l) do not result in the elimination of lignin from hemp, and especially jute, fibers to the necessary degree. Thus, when specially chosen delignifying preparations are applied, which are used to chemically modify bast fibers, the maximal degree of lignin elimination amounts to 55% for flax fibers and 38% for hemp fibers [3, 4].

It is rather promising to use a plasma–solution system to delignify rough bast fibers. The kinds of plasma–solution systems, their physical properties, chemical effects, and possible technological applications are discussed in detail in [5–7]. The possibility to initiate and accelerate traditional oxidation processes in electrolyte solutions by

Table 1. Lignin content in the treated fibers

	Residual lignin content, %						
Fiber	Initial After plasma–solu- fiber tion treatment*		After plasma–solution and alkaline treatments				
Flax	4.0	3.6	1.3				
Hemp	5.8	4.9	2.1				
Jute	15.2	14.8	9.3				

* Duration of treatment is 20 min.



Fig. 1. Scheme of the face discharge setup. (1) Electrolyte solution, (2) electrodes, (3) glass tube, (4, 5) circuit for radiation registration, (6) plasma zone.

virtue of plasma activation is described in [8]. In this paper, the generation of chemically active particles in plasma-solution systems and the efficiency of the use of primary active particles in plasma and plasma-solution systems at atmospheric pressure are analyzed. Moreover, in [8] a principal possibility has been demonstrated to use plasma-solution systems for intensification of delignification processes of natural polymer materials, since the active particles involved in bleaching and delignification processes of cellulose materials and the particles formed in aqueous electrolyte solutions under the discharge action possess a similar composition. To reach the greatest modification effect in the treated material, it is necessary to apply this type of plasma-solution system where the plasma zone is generated immediately in the solution volume and reactions of the activated solution can be combined with a direct plasma action on the modified material [9].

The aim of this paper is to evaluate the possibility to use a plasma–solution treatment with an face discharge [6] to delignify flax, hemp, and jute fibers.

EXPERIMENTAL METHOD

The scheme of the plasma–solution system, where an face discharge is used, is shown in Fig. 1.

The treatment of shredded fibers (2–4 mm) was performed in a glass reactor (reactor volume of 1 l), Fig. 2. The cellulose material was placed in the solution and treated for 10–25 min. The residual lignin content was determined in the treated fibers using the sulphuric acid method [10]. The discharge current in the ignition moment amounted to 1 A when NaOH (0.4 g/l) was used as a working solution, while that for tap water amounted to 0.2 A. Electrodes were made of graphite.

RESULTS AND DISCUSSION

The data presented in Table 2 show the influence of plasma–solution treatment on the solubility of bast fiber lignin.



Fig. 2. Scheme of the reactor for face discharge treatment of polymer materials. (1) Electrodes, (2) plasma zone, (3) solution with treated material, (4) magnetic mixer.

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Table 2. Lignin content in the bast fibers after plasma–solution treatment dependent on the initial solution temperature

Fiber	Initial	Residual lignin content after plasma–solution treatment, %				
11001	content, %	Initial solution temperature 20°C	Initial solution temperature 90°C			
Flax	4.0	3.8	2.2			
Hemp	5.8	4.8	3.8			
Jute	15.2	14.8	10.2			

* Treatment conditions: NaOH concentration is 0.4 g/l; duration of treatment is 20 min.

The presented data show that the lignin content in bast fibers changed insignificantly after one-stage plasma–solution treatment. The degree of delignification of the flax, hemp, and jute fibers did not exceed 10, 15, and 3%, respectively. However, as a result of subsequent base treatment for 60 minutes with a reduced base concentration (5 g/l), the degree of the elimination of lignin reached 68, 64, and 39% for the flax, hemp, and jute



Fig. 3. Delignification degree of the fiber as a result of twostage treatment versus the duration of plasma–solution activation. (1) Flax, (2) hemp, (3) jute.

fibers, respectively. This significantly exceeds the parameters obtained using specially chosen delignifying preparations used to chemically modify bast fibers. Thus, the maximal degree of the lignin elimination amounted to 55% for flax fibers, while that for hemp fibers amounted to 38% [3, 11]. Under the conditions of plasma-solution treatment, some hidden destructive processes are initiated that lead to the weakening of a significant part of chemical bonds in lignin macromolecules; this determines its destruction and intensive dissolution of significant part of it at the stage of chemical treatment. Therefore, to ensure the necessary degree of lignin elimination from fibers with high degree of lignification, it is appropriate to use a two-stage scheme of the modification process. The first stage involves a preliminary activation of lignin destruction via fiber treatment in a base medium (0.4 g/l) in the discharge zone. The second stage involves a 60-minute chemical fiber treatment with a base solution of sodium hydroxide with concentration of 5 g/l at 100°C.

The dependences of the delignification degree of the fibers on the duration of plasma–solution activation are shown in Fig. 3.

As was mentioned above, the lignin content in fibers immediately after the plasma–solution treatment reduces insignificantly, though increase in its duration influences the subsequent alkaline fiber treatment. Evidently, though remaining in the structure, lignin undergoes significanty destructive changes, the degree of which increases with an increase in the dose of the plasma– solution treatment. It should be mentioned that the solution temperature at the beginning of treatment exerts a significant influence on the lignin destruction. The most effective process occurs at an initial temperature of 90°C (Table 2).

Some danger exists that, under the action of discharge, together with the activation of the lignin dissolution, destruction processes in the fiber can occur [11] that negatively influence its strength parameters. Therefore, the influence of the duration of discharge action on the total fiber mass loss was studied (Table 3).

The data provided in Table 3 characterize the influence of the discharge treatment on the degree of purification of the fibers from general admixtures. Evidently, the discharge action initiates not only the lignin destruction, but also the destruction of the total complex of associated substances. The combined action of a short-term plasma–solution (10–15 min) and chemical (60 min) treatment allows one to reach the same degree of fiber purification as treatment in an alkaline solution at 100°C for 2–3 h (dependent on the fiber kind) [12]. However, flax and hemp fibers lose about 20% of their mass after 25-minute activation in the plasma–solution system and subsequent alkaline treatment. It was stated in papers [3, 12], which are related to the chemical modification of bast fibers, that, in order to ensure the safe from the

	Fiber mass loss, %								
Treatment duration, min	Flax		Не	mp	Jute				
	After plasma– solution treatment	After plasma– solution and alka- line treatments	After plasma– solution treatment	After plasma– solution and alka- line treatments	After plasma– solution treatment	After plasma– solution and alka- line treatments			
10	2.1	11.4	4.6	12.0	1.5	6.8			
15	4.7	12.4	6.9	13.8	4.3	10.8			
20	6.1	13.5	9.0	18.0	6.2	14.4			
25	7.9	20.1	11.1	21.4	8.5	16.9			

 Table 3. Influence of duration of plasma–solution treatment on the bast fiber mass loss

point of view of conserving the cellulose component, the limiting values of the fiber mass loss are 12–13 and 14–18% for flax and hemp fibers, respectively. Hence, the optimal duration of the plasma–solution treatment in the studied system should not exceed 10–15 min for flux fibers, 15–20 min for hemp fibers, and 25–30 min for jute fibers. This duration of the plasma–solution activation was chosen for fiber treatment in water. The obtained results are presented in Table 4.

It can be seen that at the discharge treatment without alkali application, the delignification degree reaches 52.5% for flux fibers and 55% for hemp fibers; this is a rather high figure of lignin elimination for these cellulose materials. For jute (delignification degree 22%) this treatment was not sufficient; to increase its efficiency, alkaline media should be used alongside with delignifying preparations at the both stages and the process duration should be increased.

Thus, the results of carried out investigations have shown that the main admixtures in bast fibers, in particular, lignin, undergo deep destructive changes in the process of plasmochemical treatment. The treatment results in the destruction of admixtures and their elimination

 Table 4. Lignin content in the fiber after plasma–solution treatment in water

Fiber	Duration of plasma–solution treatment, min	Initial lignin content in the fiber, %	Lignin content after two-stage treatment, %
Flax	10	4.0	1.9
Hemp	15	5.8	2.6
Jute	25	15.2	11.8

from the middle lamellae, which fasten together elementary fibers in the bast bunches. Hence, this allows one to reach the goal to modify bast raw materials, to split rough complex fibers into elementary and thin fibers with technical parameters that permit their further processing as a textile raw material. The plasma–solution treatment, together with improved traditional technologies, can be an effective delignification method of bast fibers.

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ELECTRICAL PROCESSES IN ENGINEERING AND CHEMISTRY

Enhancement of the Operating Efficiency of Oil Wells by Electrical Treatment of the Bottom-Hole Area

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Abstract—Characteristic properties of secondary oil recovery with the application of electrical treatment of the bottom-hole area of wells are considered. Special attention is focused on the electroosmotic method. The data of a laboratory experiment confirming efficiency of the electroosmotic treatment of the bottom-hole area for oil production are given.

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INTRODUCTION

One of the key problems of the oil producing industry is incomplete (as a rule, at most 40%) primary oil recovery from oil stratum. For some oil strata containing high-viscosity oil reserves, owing to intrinsic potential energy of the stratum, no more than 10-15% may be recovered. Subsequently, with a view to enhance the efficiency of the oil reservoir, the oil stratum is additionally treated by secondary methods. The main ones are related to oil displacement by injection of various aqueous solutions through additional well injectors; this makes it possible to increase oil production by 15-20% [1].

In oil strata, oil saturates voids, fissures, and caverns between solid fractions of the formation that build oilbearing strata. Most oil deposits are situated in sedimentary rocks, which are good oil reservoirs. The producing zone of a stratum contains, in addition to oil, residual water. In the majority of reservoirs it amounts to 20–30% of the pore space volume [2].

In all parts of the world, there are many neglected or abandoned reservoirs that still contain a fair amount of oil. An increase in oil recovery by just 1% is equivalent to a new pool discovery.

In physicochemical terms, oil is a mixture of carbohydrates and organic compounds. The density of oil is $820-950 \text{ kg/m}^3$, the electric conductivity ranges $10^{-6}-10^{-14} \text{ S/m}$, and the electrokinetic potential is usually 40– 150 mV [3].

In addition to hydraulic methods, the capabilities of secondary treatment of stratum with physical fields are studied—thermal, ultrasonic, magnetic, high-frequency, and electromagnetic, as well as their combinations [1]. Along with traditional secondary techniques for enhancement of efficiency of oil reservoirs, the methods based on electrical treatment of both reservoirs as a whole and the bottom-hole area, being immediately adjacent to the oil producing well, are obviously promising [4].

ANALYSIS OF KNOWN ENGINEERING SOLUTIONS

The analysis of published and patent information makes it possible to select the following techniques and methods of electrical treatment of oil reservoirs.

Direct, alternating, and high-frequency current is applied for heating of oil stratum and generation of electrophoresis phenomena. In the presence of strata with quartz sand, upon passing of a high-frequency current, a piezoelectric effect takes place, i.e., vibrations of quartz sand grains and, accordingly, an increased inrush of oil from the strata [5].

Before commencement of operation, the area near the producing well is treated by a unipolar electric current. A positive result is obtained owing to a set of electrokinetic effects. Herein, an increased permeability of strata is maintained after the electric current action has terminated [6].

The area near the producing well is treated by electric current for heating of this area up to a temperature that eliminates boiling of pore water [7].

The combined electroosmotic and thermal action of direct electric current is used for formation of a mineralized channel in the oil-bearing stratum; for this purpose, after wells have been connected to a power supply, a mineralized liquid is supplied to the cathode well, and the current value is restricted by the mineralized liquid boiling temperature [8].

The electrophoresis phenomenon is used where a producing well is connected to the positive pole of a power supply and an additional electrode is connected to the negative pole [9].

By means of passing of alternating electric current below the bottom-hole area, the ground is heated to 130–150°C; the formed temperature front forces oil toward the producing well [10].

The permeability of a bottom-hole area adjacent to the producing well is controlled by pulse current. An increase in the permeability is obtained owing to disintegration of cementing agents in thin capillaries that limit the filtration rate [11].

The bottom-hole area of a producing well is treated with heteropolar pulse electric current with an amplitude up to 3000 A, with a relative pulse duration of 1–3, and with a pulse-decay rate of 10–150 ms. A positive effect is obtained not only owing to electrokinetic and thermodynamic effects but also owing to the resonance properties of the oil-bearing stratum [12].

Generation of a direct current voltage of 150–450 V and a current density of 0.1–10 A/cm² between the anode electrode and the producing well (cathode) causes chemical and ion-plasma processes; as a result, hydrogen and alkali are evolved on the well casing (cathode), contributing to a decrease in the surface tension of the oil film and to dissolution of residual dead oils [13].

A combined action of direct and alternating current with an amplitude ensuring initiation of oxidation– reduction reactions in oil, for decomposition of polycyclic compounds contained in it into compounds with low molecular weight and oil hydrogenation, is applied [14].

One more method is the use of a combined action of direct electric current and an electrolyte solution (aqueous solution of NaCl or inorganic acids) supplied to perforated anode electrodes under a pressure of 1.5–5 atm [15]. This method allows electroosmotic displacement of oil toward the producing (cathode) well in oil strata with low water saturation.

The analysis performed shows the wide variety of methods and techniques of electrical treatment. Each of them requires additional study of efficiency and feasibility of application, which certainly cannot be done within the bounds of one paper. Therefore, henceforth, we will confine ourselves to the methods based on the use of electroosmotic forces, which appear in capillary porous media under the influence of direct electric current. In some cases, these methods may appear to be more efficient than hydraulic ones.

ELECTROOSMOTIC TREATMENT OF THE BOTTOM-HOLE AREA OF AN OIL RESERVOIR

A positive effect of the application of electroosmosis for water–oil displacement as compared to hydraulic displacement may be observed when the oil reservoir is finely porous.

Pore water is an aqueous electrolyte solution. On the boundary of capillaries, a double electrical layer is formed; its diffusive portion consists, as a rule, of positive cation ions. The concentration of cations appears to be higher than that of anions; therefore, in the course of electroosmosis, the net flux of the water will be directed from the anode to the cathode. One of the distinctive features of electroosmosis, in comparison with standard hydraulic filtration, is another dependence of water velocity on pore radius. In the most general case, it is possible to consider two models of distribution of two liquids (water and oil) in the pore space. In the first case, particles of water and oil alternate in the pore space; in the second case, the two liquids are situated parallel to the pore surface. Thereupon, in the first case, we can speak of electroosmotic displacement under water inflow to the oil stratum from the outside; in the second case, we speak of cooperative electroosmotic flow of the two liquids under the electric field action [4].

Practical application of the electroosmotic method requires significant energy input. Power consumption is determined by the voltage of the direct-current power supply and by the spreading resistance between anode and cathode electrodes.

Figure 1 depicts possible diagrams of formation of an electroosmotic flow to the bottom-hole area of a producing well, where 1 is the direct-current power supply, 2 is the producing well, 3 is the additional well, 4 is the oil-bearing stratum, 5 is the cathode electrode, 6 is the anode electrode, 7 is the insulating insert, and 8 is the additional ground electrode.

If a direct-current power supply is connected directly to the upper bases of wells, then most of the current (and, accordingly, of the electric energy) is consumed for treatment of ground layers that do not contain oil (Fig. 1a). The connection of the power supply to the lower parts of wells, with isolation of the latter from the main well, is more energy-conserving (Fig. 1b). The use of a ground anode electrode instead of an additional well (Fig. 1c) leads to a significant increase in spreading resistance and, as a consequence, to outrageously high energy consumption. It is possible to achieve minimum energy expenditure if exclusively the bottom-hole area near the producing well is subjected to electroosmosis instead of the whole oil stratum. In addition, pumping equipment in placed in the producing well; therefore, in the majority of cases, it is impossible to move electric cables and electrodes down to its lower part. Thus, the methods of electroosmotic treatment of the bottom-hole area shown in Figs. 1d and 1e are best of all for practical application and minimum energy consumption. Herein, owing to considerably lower electric resistivity of a metal well (in comparison with neighboring ground), the base of a producing well will operate as a bipolar electrode; as a result, a considerable decrease in the spreading resistance between anode and cathode electrodes is obtained.



Fig. 1. Diagrams of the direct-current power supply connection for formation of an electroosmotic flow to the bottom-hole area of a producing cell.

LABORATORY EXPERIMENT

With a view to prove the possibility of minimization of power consumption with the use of the electroosmotic method for enhanced oil recovery according to the diagrams in Figs. 1d and 1e, a laboratory experiment was carried out; its results are presented below.

The diagram of the laboratory setup is shown in Fig. 2. In plastic box 1, a four-layer medium is situated. The layer c is an oil-saturated mixture, the layers b and d are clay, and the layer a is paraffin. The thicknesses of the layers are the following: c = 15 cm, d = 5 cm, b = 10 cm, and a = 1 cm. Perforated metal tubes 2 are at a distance of 40 cm from each other. Anode and cathode electrodes 3, being metal cylinders with a diameter of 4 mm and a length of 10 mm, are situated at a distance of 5 cm from the nearest perforated tube. The upper parts of the perforated tubes are shut with isolating closures 5. From container 6, 1% salt brine 7 is supplied to the oil-bearing stratum. The brine, having passed through the oil-bearing stratum, through branch pipe 8 enters reserve tank 9.

The laboratory experiment was carried out in three stages.

In the first stage, with switches K_1 and K_2 being off, from container 6, through perforated tubes 2, 1% aqueous solution of NaCl was filtered through the oil saturated stratum c. Herein, from branch pipe 8, an analogous clear aqueous solution of NaCl was supplied to tank 9 for 10 min.

In the second stage, the switch K_1 was on, and a current of 100 mA flowed between the electrodes. Within



Fig. 2. Diagram of the laboratory setup.

1.5 min after the beginning of the electroosmotic treatment, oil began to appear. After 35 min, the power supply was switched off; in the process, the liquid filtration rate decreased approximately by a factor of 10, and the output of oil completely ceased. Then, the power supply was switched on again by means of the switch K_1 , and the filtration rate achieved its previous value with simultaneous appearance of oil.

In the third stage, after a half-hour disconnection of the power supply, voltage was fed by switching on K_2 between additional electrodes 3 placed in close proximity to perforated metal tube 2 (the switch K_1 was off). Simultaneously, from container 6, a 1% aqueous solution of NaCl was filtered. A picture identical to the second stage of the laboratory experiment was observed.

Thus, the laboratory experiment confirms the possibility of applying electroosmosis with a view to increase oil yield without using wells as electrodes [16].

CONCLUSIONS

(i) Application of the electroosmotic treatment of both oil reservoirs and the bottom-hole area of wells is most efficient for finely porous oil-bearing strata. In this case, the electroosmotic filtration to a producing well is more efficient than the hydraulic one.

(ii) With a view to minimize energy consumption in the course of electroosmotic treatment, electrodes for formation of an electroosmotic flow should be situated proximately to the producing well (in the bottom-hole area). In this case, the latter must operate as a bipolar electrode.

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ELECTRICAL PROCESSES IN ENGINEERING AND CHEMISTRY

Application of Pulsed Electrical Discharge lamps for Bactericidal Treatment

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Abstract—A bactericidal treatment analytical analysis of the potentialities of pulsed UV lamps has been carried out. A comparison of traditional low- and high-pressure mercury lamps has been performed. Devices with pulsed xenon lamps are characterized by higher power consumption, lower resources, and higher exploitation expenditures than low-pressure mercury lamps. Xenon lamps may be used in equipment or under conditions in which the mercury presence is barred.

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INTRODUCTION

Bactericidal treatment of water, air, and surfaces by means of ultraviolet (UV) radiation is an ecologically safe, economical, and convenient method that results in highly efficiency disinfection free of harmful effects on water and air [1–3]. As a source of bactericidal UV radiation [1–4], an electric arc in the mercury vapor is usually used. Low-pressure lamps have a high coefficient of efficiency (CE) (35-50%) for the transformation of electric energy into UV radiation with a wavelength of 254 nm at a discharge linear power up to 2-3 W/cm. High-pressure lamps have a low CE (10-15%) in the region of bactericide UV. However, their power is an order of magnitude higher than that of low-pressure lamps. A major drawback to the mercury bactericidal lamps is the presence of metallic mercury. Low-pressure mercury lamps contain 3-10 mg of mercury, while highpressure lamps contains hundreds milligrams. A permanent improvement of the ecological safety requirements and the introduction of additional restrictions for the use of metallic mercury prompted the development of new sources of bactericidal UV radiation. Recently, a new generation of low-pressure UV lamps was devised with amalgam as the source of mercury vapor. The main portion of mercury here is in a bound state (amalgam) and only 0.03 μ g per lamp is in a free state; therefore, the vapor pressure of mercury at temperatures of up to 50°C is lower than the maximum permissible concentration (MPC). This type of lamps is considerably safer than the luminous lamps used for lighting. Amalgam lamps have a high CE (35–45%) and resources of 12000–16000 h.

At present, UV radiation sources free of mercury have been devised based on pulse discharges in the rare gases and their mixtures with halogens¹ (excimer mixtures) [2–5], the radiation spectrum of which contains a considerable amount of UV radiation. Since the peak power of the radiation pulse of a xenon lamp can equal 3-10 MW, the natural question emerges of whether there is any difference between the bactericidal media treatment by UV radiation of this pulse lamp and a normal mercury lamp. The wide spectrum of pulse discharge also suggests another question of whether or not the visible range of a pulse radiation influences the disinfection process. Investigations of disinfection by pulse radiation have shown that, when the radiation pulse exceeds the threshold power, in addition to the usual bactericidal effect, an additional mechanism of the action of UV radiation on microorganisms can occur, i.e., pulse heating [6–9]. In the present paper, both mechanisms, the conditions of their origin, and potentialities of the pulse systems in a disinfection treatment have been analyzed.

MECHANISMS OF PULSE RADIATION DISINFECTION

1. Bactericidal UV Radiation

UV radiation in the bactericidal range of 205–315 nm always produces a bactericidal action, which is characterized by UV photon absorption by DNA molecules inside the cell and the disintegration and formation of bonds. As a result, a microorganism loses its reproduction ability. The curve of the efficiency of the bactericidal action of UV radiation with regard to wavelengths agrees well with the absorption curve of UV radiation by DNA molecules. The peak of this curve is in the region of 265 nm [1–3]; therefore, the radiation of low-pressure mercury lamps with wavelengths of 254 nm has a high bactericidal effectiveness. The number of surviving microorganisms N exponentially decreases with growth in the absorbed energy (bactericidal dose D), $N = N_0 \exp(-kD)$, where N_0 is an initial number of microorganism

¹L. M. Vasilyak, *Surf. Eng. Appl. Electrochem.*, 2009, no. 1, pp. 30–40.

ganisms and k is a constant that characterizes the degree of sensitivity of a given type of microorganism to UV radiation. The size of UV dose necessary for a tenfold reduction depends on the type of microorganism and, for many bacteria and viruses, lies within the range of 2–20 mJ/cm² [1 and 3]. For the majority of practical applications, the value of bactericidal dose *D* is determined, not by the peak value of radiation intensity, but by the integral of bactericidal irradiance $E(\lambda, t)$ with respect to the time of exposure t [1–4] as follows:

$$D = \iint E(\lambda, t) S(\lambda) (d\lambda) dt,$$

where λ is a wavelength, $S(\lambda)$ is the relative bactericidal efficiency with respect to a wavelength. Figure 1 depicts an example of the determination of bactericidal efficiency in the case of a pulsed xenon lamp $S_{\lambda} I_{\lambda}$, as well as therelative spectral curve of bactericidal action S_{λ} and the distribution of the radiation energy spectrum of a pulsed xenon lamp within the range of 200–300 nm I_{λ} .

2. Pulse Overheating of Microogramisms

The question of distinctions between the action of a pulse and continuous radiations was investigated in the United States and Germany [6–14], Russia [15, 16], Japan [17, 18], Iran [19], Canada [20], and other countries. The first investigations of the disinfection process using powerful pulsed lamps were carried out in Japan and the pulse technique was patented in 1984 [17]. Those early studies assumed that, in the powerful action of a pulse, both UV radiation and visible light participate in disinfection. However, after 15 years, it was proven that, in the pulse radiation disinfection process, the main contribution is from UV photons [6-9].

At present, it has been determined that pulse radiation can produce a bactericidal effect. The mechanism of its action upon microorganisms depends on the power peak density of UV radiation; furthermore, each type of microorganism has its own value of threshold peak power. According to the obtained data [6 and 7], the process of disinfection by pulse radiation is constituted by two parts, one of which is the generally known action of bactericidal UV radiation, while the other is the destruction of microorganism, caused by its overheating in the process of UV radiation absorption. At the peak density of UV radiation power below the threshold, disinfection is only defined by UV radiation in the bactericidal range of 205–315 nm and the degree of disinfection depends on the integral bactericidal dose in accordance with the above formula.

At high densities of pulse radiation, when the total power density of UV radiation in the spectral ranges of A, B, and C (200–400 nm) is above the threshold, the rate of radiation power supply exceeds the rate of the decrease in thermal energy due to a microorganism into the environment, which causes the microorganism to overheat and, subsequently, disintegrate [7]. It has been proven experimentally that the radiation in the visible

spectral region introduces no significant contribution into the heating of microorganisms. The level of necessary power density depends on the thermal resistance of the microorganisms being exposed and their surrounding environment. For stable disintegration, the heating should exceed 130°C, which causes irreversible changes, including liquid boiling inside the microorganism and being ejecting from it. An example of this destruction is presented in Fig. 2 with mold spores (Aspergillus Niger) being exposed to radiation by two pulses with a peak density of UV radiation of 33 kW/cm² [7]. The broken empty capsule is clearly seen. According to calculations [7], for the pulse heating of E. coli bacteria to these temperatures, it is necessary to obtain a peak density of the radiation power across the treated surface of 10³ W/cm² in air and 10⁴ W/cm² in water (Fig. 3). As follows from calculations, the heating is already apparent at values of 10^2 W/cm² in air and 10^3 W/cm² in water, since, for many types of microorganisms, heating to 70°C is critical. Overheating depends on the environmental properties. For water, the radiation powers should be higher, since heat irradiation from a microorganism in water is higher than in air. For this reason, the overheating and disintegration of microorganisms on paraffin or wax surfaces are higher than on the metal surface. It should be noted that, at such high densities of the pulse energy, melting of

It should be noted once again that the primary contribution to microorganism heating comes from UV radiation, not visible light or infrared radiation. Most likely, this is due to the adsorption of UV radiation at a smaller depth in comparison to visible light or infrared radiation. Furthermore, this is stipulated by the fact that, at a target

the paraffin surface has been observed [6-7].

Fig. 1. Determining bactericidal efficiency of a pulsed xenon lamp $S_{\lambda} I_{\lambda}$. *I* is the relative spectral curve of bactericidal action, S_{λ} . *2* is theradiation energy distribution along the spectrum of pulsed xenon lamp in 200–300 nm range, I_{λ} . *3* is the product of $S_{\lambda} I_{\lambda}$.





Fig. 2. Pulsed radiation influence upon *Aspergillus Niger* spores. Scale indicated in photos. (5A) initial spores; (5C) single *Aspergillus* spore after being exposed to two pulses of radiation with a peak power of 33 kW/sm². The top of the spore is torn by overheated intracellular liquid, which was out from inside the spore. A crater of ejected remnants forms around the spore [6, 7].

dimension equal to a micron or less, the processes of photon distribution or absorption will be influenced by the wave nature of the light and long-wave photons will have a greater propensity to dissipate and encircle a microparticle than UV photons. It has been shown experimentally that the pulse overheating and microorganism destruction can be also achieved by the application of only soft UV radiation from the A and B regions (280– 400 nm) with an intensity above threshold, which results in disinfection without the use of hard bactericidal UV radiation from region C (200–280 nm).

In addition to the peak power value, it is necessary to provide the target with a power supply that is sufficient for heating. If the pulse is very short, e.g., less than 1 μ s, the time may be insufficient to heat the microorganisms. In other words, in order to ensure overheating, it is necessary to additionally provide radiation pulse power, with a higher power supply than the thermal drop due to the microorganisms in the surroundings and an absorbed dose of energy sufficient to heat microorganisms to a



Fig. 3. Calculated heating temperatures for *E. coli* bacterium with respect to the power peak density H (W/cm²) of UV radiation in air (1, 2) and water (3, 4) for two pulse durations: 100 (1, 3) and 1ms (2, 4) [6 and 7]

high temperature. Taking into consideration the shortterm nature of these temperatures, they may be insufficient to disintegrate the spore and certain types of bacteria. Just as in normal heating, there should be a definite exposure time for the disintegration of all microorganisms of a certain type.

UV RADIATION SOURCES

The main factors that determine the efficiency of UV radiation sources are bactericidal efficiency, the bactericidal flux of the lamp, resources, the drop in the bactericidal flux of the lamp by the end of its service life, compactness, the costs of the trigger-pulse and power supply units (start-control devices), safety, and techniques for applying the bactericidal radiation source.

The use of bactericidal gas-discharge lamps, where the main radiation element is a mercury atom, is determined by the fact that it has a resonance electronic transition with a radiation wavelength of 253.7 nm, which is close to the maximum of the bactericidal sensitivity curve. In low-pressure mercury and amalgam lamps, the CE of the transformation of the lamp's input electric power into radiation on the wavelength of 253.7 nm amounts to 35–50% [1–3], which comprises over 90% of the total UV radiation. In these sources, the pressure of the rare gas equals 800-5000 Pa, while the mercury vapor pressure equals 10-15 Pa. Due to the thriceincreased linear power of UV radiation in comparison with the low-pressure mercury lamps, amalgam lamps enable one to efficiently solve the problems of the bactericidal treatment of air, water, and surfaces. The use of electronic compact start-control devices (SCDs), which operate at frequences of 20-50 kHz, gave us the opportunity to increase the lamp's CE, i.e., the SCD system, as well as to extend the service life of the lamp to 16000 h and vary the electric power of the lamp in the process of its operation. The high bactericidal CE, applicability of the SCD, resources of over 1000–1600 h, and relatively cheap cost expanded the use of low-pressure mercury and amalgam lamps.

The arc discharge at a high pressure of mercury vapor, i.e., 10^3-10^5 Pa, has a lower CE in the region of bactericidal UV radiation of 15% and, considering the bactericidal efficiency curve, this value is reduced to 10–11% [4]. As a matter of fact, all industrially produced bactericidal high-pressure mercury lamps emit UV radiation with wavelengths of less than 200 nm, which causes the formation of highly toxic ozone. Low-pressure mercury lamps are mainly produced from borosilicate glass or special kinds of quartz, which constrict the short-wave radiation and eliminate the formation of ozone, which favorably distinguishes them from ozone-forming lamps.

The main purported advantage of pulse xenon lamps is the high peak power of their pulse, which equals 5-50 MW at a pulse duration of $1-200 \,\mu s$. Initially, xenon lamps were developed for the purpose of enhancing solid-state lasers; later, they were also used for disinfection. The spectral composition of radiation depends on the density of the discharge current (Fig. 4) [6, 7] and lamp switching circuit. The 200-300-nm wavelength range comprises 25-30% of the total radiation within 100-1100 nm and 40% of the entire UV range. Correspondingly, the bactericidal efficiency will amount to 10–13% of the total lamp radiation. Figure 1 presents the bactericidal efficiency of a pulse xenon lamp. The obtained result well agrees with the data for the xenon lamps of type #[INP]#-7/120 and #[IFP]#-8000 [1, 3]. Taking into consideration the escape losses of the lamp bulb and thermal losses, the bactericidal efficiency will be around 10% of the contributed into the lamp electric power. The wide radiation spectrum of the pulse xenon lamps is a drawback rather than an advantage, since its short-wave region may provoke undesirable ozone formation, subsidiary chemical reactions, and the formation of compounds harmful for human beings. In order to reduce the radiation intensity in a short-wave spectrum region, it is necessary to decrease the current density in the lamp (Fig. 4), in which case the peak power also decreases. Additional protective films are also used alongside special sorts of quartz. However, this considerably increases the cost of the lamp and reduces the resources due to the adsorption of UV radiation by the quartz bulb.

The service life of the pulse xenon lamps is determined by the number of flashes a lamp can produce. The higher the pulse power, the lower the number of lamp actions, which vary from 10^3 to 10^8 pulses. The average power of a lamp is controlled by changes in the repetition frequency of the pulses. At a frequency of 30 Hz and resources of 10^8 pulses the time of continuous operation of the lamp equals less than 1000 h. In practice, UV radi-



Fig. 4. Radiation spectrum of pulsed xenon lamp at a current density of 6.5 (1) and $1 \text{ kA/cm}^2 (2)$.

ation drop in the pulsed lamps amounts to 25-50% by the end of the service life.

For switching on a pulsed xenon lamp, two main electric circuits are used that have pulse capacitors for energy storage. In one of the circuits, the pulsed lamp is constantly connected with a capacitor and the lamp is constantly supplied by a high operating voltage of 1– 5 kV. To initiate a discharge, a high voltage pulse with an amplitude of 10-30 kV is supplied to the lamp from a special circuit and triggers an electric breakdown. In the other circuit between the energy storage capacitor and the lamp, there is a high-voltage switch, for instance, a spark gap or a thyratron. The use of a switchboard increases the cost of the pulse power source and decreases its resources. The application of powerful high-voltage devices considerably enlarges the dimensions and complexity of the power source for pulse lamps and imposes high requirements on the safety measures in the process of equipment exploitation.

Thus, UV radiation pulse sources are characterized by a high peak power (up to 50 MW), a bactericidal efficiency of UV radiation of around 10%, service life of about 1000 h, and a bulky high-voltage power source. Lamps with a high specific load, such as high-pressure mercury and pulse xenon lamps, demand intensive heat removal, which makes constructing equipment on their bases complicated in comparison to equipment with lowpressure mercury or amalgam lamps.

POTENTIALITIES OF PULSE UV DISINFECTION

1. At a pulse energy lower than threshold $(1-3 \text{ kW/cm}^2)$, the pulse sources of UV radiation may be used in a disinfection zone similarly to the usual bactericidal lamps. In this case, the bactericidal action depends on the share of UV radiation in the bactericidal range, which is about 25% of a total pulse of radiation [2–4, 6] and about 40% of UV radiation in all UV ranges (A, B,

and C) [6]. In accordance with the current manual, the bactericidal action of UV radiation can be determined, not by the peak value of radiation intensity, but rather by the integral of bactericidal irradiance over a period of time according to the above formula. Correspondingly, the bactericidal efficiency and bactericidal CE of energy transformation of the pulsed lamps will be 10–13% of the total lamp radiation [4], which is several times lower than those of low-pressure mercury lamps and approximately corresponds to high-pressure mercury lamps. Nevertheless, the use of pulsed lamps may be necessary at particular plants and under conditions where the presence of mercury is not permitted or for the purpose of reliable ecological safety.

If room air is disinfected using a pulsed lamp with lowfrequency flashes, it may cause problems. Air in rooms is agitated by ventilation and convective streams with typical rates of air motion of no more than 0.1–0.2 m/s to make the people in the room feel comfortable. The radiation of one pulse source efficiently disinfects the air around it. However, due to a considerable diminution of radiation intensity with distance, the pulse source has an insignificant effect on distant areas. As a consequence, the total period of treatment should be long enough to agitating the room air and the number of pulses should be high, which makes the advantages of a powerful pulse source almost nothing. It should be noted that the efficiency of disinfecting room air using low-power, stationary, open irradiators has been proven by long-term practice [1, 3, 21]; additionally, the optimal power values of continuous UV radiation for most of types of accommodations in use have also been determined in practice. With permanent radiation, all water or air will receive a certain average dose of UV radiation.

At a low frequency of flashes, a similar situation may occur also with air or water being disinfected in a flow regime, e.g., in enclosed devices, where radiation is performed in an entirely closed chamber that air or water passes through. Due to the insufficient exposure time of the medium being treated in the radiation zone, it is necessary to achieve a fairly high frequency of flashes to reliably disinfect the air or water being exposed.

Thus, if UV radiation power density is less than the threshold, the only advantage of the pulse source is its ability to disinfect in a very short (in comparison with a mercury lamp) period of time, e.g., in medical materials or a packaging [11–14, 22].

2. At a UV radiation power density higher than the threshold $(1-3 \text{ kW/cm}^2)$ and at a sufficient pulse duration, additional possibilities of disinfection appear, since both of the above mechanisms will commence operating; the efficiency of disinfection may be greatly increased. The pulse thermal disinfection or sterilization can be performed concerning microorganisms, resistant to bactericidal UV radiation. Moreover, the additional possibility arises to sterilize food substances, biological solutions, medical materials, contact lenses, or some other samples simply by soft UV radiation from A and B regions [6, 7, 14]

if hard bactericidal radiation from the C region cannot be used because of the undesirable chemical reactions or sample damage it causes, e.g., in medications or food substances. It is possible to sterilize a packaging material and the samples inside the packaging by the pulse UV radiation, passing through the packaging material [5–8, 11 and 13]. There have been a number of investigations [15] in which the pulse UV radiation from A and B regions were applied with medical aims to treat surface wounds and sores.

However, the results may be unsatisfactory if the conditions for using the method differ from the experimental conditions. The disintegration of a thermal microorganism is fundamentally different from how bactericidal UV radiation acts on DNA. Therefore, the efficiency of disinfection obtained experimentally at small distances from the pulse source with an intensity that exceeds the threshold cannot be extrapolated for long distances, since UV radiation intensity per a unit of area reduces, and the mechanism of thermal destruction produces no effect. The required radiation energies will be set too low and the efficiency of disinfection will be too high. For example, let the peak UV radiation power be 5 MW and the lamp length be 0.5 m. If the tests are carried out at a distance of 10 cm from the lamp axis, then estimating a cylindrical source, the peak density of UV radiation will be $1-2 \text{ kW/cm}^2$, which is sufficient for the onset of the thermal destruction of microorganisms in air or on the surface. At a 2-m distance, the source approximates a point; therefore, the radiation density is inversely reduced to the distance squared and, at most, equals 20-50 W/cm², which is considerably lower than the threshold. Hence, thermal destruction produces no effect. In order to achieve overheating in the case of an open source used for disinfecting air and with a distance between the walls of the room of 4 m, the UV radiation pulse power should equal ~500 MW, which is unattainable for the existing pulsed lamps. Consequently, overheating cannot be fully achieved to disinfect a room using single, open, pulsed irradiators.

3. The work on water and air decontamination as a result of destroying microorganisms using pulse radiation heating are at the stage of experimental investigation. The basis for regulating their application has not yet been developed and there are no recommendations or methods for designing and utilizing industrial devices. The minimal values of radiation power peak density for disintegrating various microorganisms have not been determined and the dependence of these values on the environmental conditions and duration of radiation pulses has not been defined. The types of microorganisms needed to reliably evaluate the quality of the equipment have not been selected.

For the practical use of the pulse thermal method to disintegrate bacteria and spores, a set of statistically reliable experimental data on the required power fluxes of the pulse radiation for disintegration of each type of microorganisms and their environmental dependence, the rate of growth of the radiation power pulse, and the duration of the pulse action upon a microorganism, is necessary; taking into consideration the short-term action of heating, it may be insufficient to disintegrate spores and certain types of bacteria. It is necessary to conduct experiments with each type of microorganism. Today, this type of database only exists for continuous UV radiation on a wavelength of 254 nm. One cannot draw a direct analogy between the doses required for disinfection by mercury and pulse lamps, since the doses of the pulse radiation may differ from those of arc mercury discharge. For instance, based on the data presented in [23, 24], it is evident that, for certain types of microorganisms, the required doses of pulse UV radiation may be both higher and lower than the doses at a continuous UV radiation. The method of thermal destruction of microorganisms using pulse UV radiation requires additional investigations to determine its applicability in regards to small-sized objects of 100-300 nm, e.g., viruses, which are commensurable with a wavelength of UV radiation.

EXAMPLES OF PULSED LAMPS EQUIPMENT

At present, in all the devices, pulse lamps with discharge in rare xenon have been used. A number of firms, such as LightStream (United States); PurePulse Technologies, Inc. (United States); Xenon Corporation; Steribeam (Germany); and Melitta (Russia) offer pulse xenon lamp devices for bactericidal treatment.

LightStream produces equipment for water decontamination at a consumption of 80–800 m³/h. One xenon lamp is used with a pulse power of 6 MW at a pulserepetition frequency of 1-30 Hz. The average power of UV-C radiation is 2400 W and power consumption is 15 kW, which is equivalent to CE = 16%. The required UV dose is defined by integration along the whole spectrum and by the time of pulse action, with no accompanying benefits (including the pulse overheating mechanism) attributed to the pulse radiation. Naturally, this kind of system is less efficient than low-pressure lamps in the transformation of electrical energy into UV radiation; however, they contain no mercury. A similar approach to determining the bactericidal dose of UV radiation and its efficiency has been accepted in the equipment made by the Xenon Corporation.

German Steribeam equipment is produced based on the effect of destruction during pulse overheating in the form of closed boxes. These products are intended for disinfecting medical products; solutions and instruments; food items; packaging; and various surfaces for the food, medical, and fragrance industries. Xenon flash lamps are used with total powers of 800 J, pulse durations of 250 μ s and the portion of UV radiation in the C region (UVC) comprises 12–15%, while UVB makes up 10–12% and UVA comprises 10–15%; the share of all UV radiation is 40–42%. The total dose across a sample surface is 500–800 mJ/cm² and the UV radiation intensity across a sample surface is 2–4 kW/cm². Since, in closed boxes, a sample is located at a preset distance from the lamp, the radiation intensity and UV dose across the sample surface will exceed the threshold values; therefore, one can maintain with confidence that both of the disinfection mechanisms work. The equipment is not meant for the treatment of large volumes or flows of liquid and gas by overheating.

The open pulse irradiators Alfa-01 and Alfa-05 designed by "Melitta-UV" (Russia) are meant for the treatment of air or surfaces in the rooms. In this case the power density of the pulse radiation will depend on the room dimensions, a distance to the source and on the source location. In the registration certificate of Alfa-01, it is indicated that the pulse-repetition frequency is 2.5 Hz, power consumption is 2 kW, and productivity is $5000 \text{ m}^{3}/\text{h}$ with the assumption that disinfection covers a 100 m³ room. The estimations show that, at a peak radiation power of Alfa-01, which is 2-10 MW in a 60-100-m³ room, the peak density of the radiation power in the total spectral range on the surfaces of walls is 50- 200 W/cm^2 , which is lower than the threshold implementing the thermal destruction mechanism. Therefore, the efficiency of disinfection in these rooms will depend wholly on the bactericidal dose of UV radiation received. The disinfection efficiency will depend upon the rate of air agitation in the room, similarly to a case of the lowpower mercury lamp. Let us make a comparison between the power consumption between a pulse and continuous sources. For the 99% disinfection of a 100-m³ room by Alfa-01, the recommended treatment time is 1.5 min, which corresponds to an electric power consumption of 180 kJ. Using mercury lamps, according to RD [1], for a 99% disinfection of air in the UV range, the power consumption amounts to 260 J/m³ or 26 k/J for a 100-m³ room, which is considerably lower than Alfa-01 power consumption. In order to obtain the same result with lowpressure mercury lamps within the same amount of time, their UV power will be around 300 W and, at the 30-40% efficiency of mercury UV lamps, their capacity will be than 1 kW.

Thus, the use of pulsed lamps for the bactericidal treatment of open rooms, air, or water has no advantages in comparison with traditional low-pressure mercury lamps. It is not advisable to apply pulse sources with a low pulse as the repetition frequency for treating room air and water or air currents due to the impossibility of producing a bactericidal dose in the full volume exposed to treatment.

EXPLOITATION OF DISINFECTION PULSED SYSTEMS

In the pulse method of water and air disinfection, the power expenditures are similar or even higher than those with low-pressure mercury lamps. In practice, it is also necessary to consider the losses in systems of a pulse power supply; for example, in the power supply unit of an L7684 lamp made by the Japanese firm Hamamatsu, the losses equal 50%, as compared with an average

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Parameters of mercury	and	pulsed xenon	lamps for	bactericidal treatment
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Parameters	Low-pressure mercury lamp	High-pressure mercury lamp	Amalgam lamp	Pulsed xenon lamp
Quantity of metallic mercury in the lamp, mg	3–10	100–300and more	0.00003 in vapors	no
CE of bactericidal radiation (considering the curve of bactericidal efficiency), $\%$	30–40	8–11	30–40	8–10
Lamp resources, thousands of h	12–16	3–5	12–16	1 (at 30-Hz frequency)
Power source resources, thousands of h	50	50	50	1–5
Power source mass, kg	0.2	5-10	0.5	5–30
Power source cost, euro	5-10	200-400	50-100	5000-10000
Guaranteed disinfection of the room air or the flows of water and air	Yes	Yes	Yes	Pulse repetition frequency should be high enough. At a low pulse repetition frequency certain volumes will not get the required UV radiation dose
Possibility of overheating steriliza- tion mechanism use	No	No	No	Allows to sterilize UV radiation resis- tant microorganisms, as well as solu- tions and objects inside the packaging
Formation of ozone and other sec- ondary substances	No	Yes	No	Yes
Simplicity of exploitation	+	+	+	– Highly qualified personnel required
Exploitation safety	+	– Ozone formation	+	– High voltage (5–15 kV); Ozone formation
Exploitation expenditures	Low	Low	Low	High
Basic regulations	Available	Available	Available	Not available

power lamp. Another essential fault of the given method is the very high cost of the equipment. At a similar power consumption (2 kW), Melitta pulse sterilization equipment costs 12000 euro, while that made by Steribeam costs 88000 euro and the cost of low-pressure amalgam lamps with the same power consumption does not exceed 1100 euro. The resources of the pulsed xenon lamps, pulsed capacitors, and dischargers depend on the discharge parameters and equals $10^5 - 10^8$ pulses or approximately 100–1000 h of continuous operation and, for technological applications, the resources should amount to 8000–10000 h. Equipment with a pulsed UV radiation source so far fails to compete with traditional low-pressure mercury lamps in large-volume water and air disinfection systems in regards to their power and financial expenditures are concerned. However, for the bactericidal treatment of materials and packaging by soft UV radiation, as well as for systems in which the use of the mercury devices is barred, xenon lamps are obviously the most acceptable option.

The application of powerful, high-voltage, pulsed technical equipment considerably enlarges the dimensions and complexity of the power supply for pulsed lamps, involves the increased safety requirements, requires highly qualified operating personnel, and increases the exploitation expenditures.

The basis for regulating the application and exploitation of the industrial devices has not yet been developed to disinfect water and air by destroying microorganisms through pulse radiation heating and the types of microorganisms needed to reliably evaluate the equipment quality have not yet been selected.

The main characteristics and potentialities of bactericidal treatment by mercury and pulsed xenon lamps are presented in the table.

CONCLUSIONS

1. Disinfection by pulse radiation depends on the peak power and pulse duration of UV radiation. At a power lower than the threshold (of $1-3 \text{ kW/cm}^2$), the decontamination is performed by bactericidal UV radiation, the required dose of which is determined by integrating the radiation pulse according to the time and bactericidal spectrum. The efficiency with which pulsed xenon lamps transform electric power into UV radiation is several times lower than that of ecologically safe amalgam lamps and can be used either under specific conditions when mercury is barred or to enhance the ecologi

cal safety. If the power of pulsed UV is less than the threshold, then the only advantage is the possibility of disinfecting over a short period of time, e.g., for medical materials or packaging.

2. At UV radiation pulse power being higher than a threshold, $1-3 \text{ kW/cm}^2$, there occurs another sterilization mechanism, with a microorganism overheating destruction as a result of being exposed to UV radiation in A,B,C spectral ranges. The radiation in the visible and infrared spectral regions makes no considerable contribution to microorganism heating. At a power exceeding the threshold, thermal sterilization can be performed at a distance of no more than 10–15 cm from the lamp. This mechanism allows for the following reasons:

a) sterilization of the microorganisms resistant to bactericidal UV radiation, e.g., mold;

b) decontamination and sterilization by soft UV radiation from A and B regions only, if the hard bactericidal radiation from the C region is prohibited because it provokes certain undesirable chemical reactions or damages the sample;

c) sterilization of the samples inside a transparent packaging.

It is possible to sterilize biological solutions, medical materials, contact lenses and other samples, surfaces, food items, packaging material, and samples inside the packaging by UV pulse radiation that penetrates the packaging material. At long distances (~1 m) from the lamp the overheating mechanism produces no effect, considering the existing powers of the lamps.

3. It is not recommended to use pulse sources with low pulse repetition for air decontamination in rooms or flows of water or air, since there is no guarantee that the bactericidal dose is affects the entire decontaminated volume.

4. The work on decontaminating water and air by destroying microorganisms using pulse radiation heating are at the stage of experimental investigations. The bases for regulating their application has not been developed; recommendations and designing methods, as well as methods for using industrial devices, have not been determined; the minimal values of the power radiation peak density in the disintegration of various types of microorganisms and the dependence of these values on the environmental conditions have not been defined; and the types of microorganisms needed to reliably estimate the equipment quality have not been chosen. The method of thermal destruction by pulse UV radiation cannot be recommended for wide applications as long as these problems are not solved.

5. The cost of the equipment with pulsed xenon lamps exceeds the cost of that based on amalgam lamps by an order of magnitude. Pulsed xenon lamp devices are characterized by a higher power consumption, low resources, and high exploitation expenditures; furthermore, they require high direct voltage (~5 kV) and pulse voltage (up to 30 kV) and high-voltage wires are highly dangerous.

Highly qualified operating personnel are required for the exploitation and maintenance of pulsed devices.

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ELECTRICAL PROCESSES IN ENGINEERING AND CHEMISTRY

Peculiarities of Temperature Dependences of Superconducting Critical Current Density in YBSO Films in Weak External Magnetic Fields

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Epitaxial films of a high-temperature superconductor YBa₂Cu₃O_{7- δ} (hereinafter YBCO), whose c axis is oriented perpendicularly to a substrate, are known to be characterized by high (~(1–4) \times 10⁶ A/cm² at temperature T = 77K) critical current densities j_c [1], which are two to three orders of magnitude higher than corresponding values of j_c in the most perfect monocrystals [2]. Evidently, this is associated with more efficient mechanisms of vortex lattice pinning, but there is no consensus of opinion concerning this mechanism. Pinning on point inclusions of a foreign non-superconducting phase (e.g., Y_2O_3)[3], surface pinning on film thickness inhomogeneities [4], and pinning on quasi-one-dimensional defects (namely, non-superconducting nuclei of edge and screw dislocations formed in a YBCO film during its growth and piercing it through) [5–10] are suggested as possible versions. Though all these mechanisms contribute to pinning of vortices in films grown under different conditions, to determine a governing mechanism, it is necessary to perform additional studies as, e.g., in [11], but taking into account the proposed correction.

In the experiments, we used YBCO films whose *c* axis was oriented normal to the plane that were grown on monocrystal SrTiO₃(001) substrates (5 × 5 × 0.5 mm) using pulsed laser ablation of a ceramic stoichiometric target with a KvF laser with the wavelength $\lambda = 248$ nm. The measurements were performed for two films: F1 with the thickness *D* = 125 nm and F2 with *D* = 112 nm. The dependences of the superconducting current critical density *j*_c(*H*, *T*) on the temperature *T* and on the dc magnetic field *H*, normal to the film plane, were determined by measuring the temperature dependences of the magnetic moment *m*(*H*, *T*) with a SQUID magnetometer within the range of external fields from 5 mT to 2 T. For a ring superconducting film with the radius *r* and thickness *D*, the primary magnetization *M*(*H*, *j*_c) was found in

[12]. Taking into account that m = MV, where $V = \pi r^2 D$ is the film volume, for the magnetic moment, we have

$$m(H, j_{c}(T)) = j_{c}(H, T)Dr^{3}\frac{2}{3}$$

$$\times \left[\arccos\frac{1}{\cosh x} + \frac{\sinh x}{\left(\cosh x\right)^{2}}\right] \equiv j_{c}(H, T)Dr^{3}\frac{\pi}{3}F(x),$$
⁽¹⁾

where $x(H, T) = H/H_c(T)$, $H_c = j_c(T) D/2$ is the characteristic field of the magnetic flux penetration into the sample (magnetization saturation field), and F(x) is the function of magnetization saturation for a thin $(r \ge D)$ disk. Since contrary to thickness the disk diameter does not enter the argument of the function F(x), the latter should weakly depend on the film shape. Further on, we assume that Eq. (1) is applicable for films of other shapes (e.g., for a square one) if we replace the radius with some characteristic (for the given shape) size r_{eff} .

In the state of magnetization saturation, when $x \ge 1$, $F(x) \approx 1$ and the critical current density is simply proportional to the magnetic moment

$$j_{\rm c}(H,T) = \frac{3m(H,T)}{\pi D r_{eff}^3}.$$
 (2)

By comparing Eq. (2) with that for the magnetic moment of a rectangular film in a saturated critical state [13], we can easily see that, for a square film, $r_{eff} = (a/2)(4/\pi)^{1/3} \approx (a/2) \times 1.08$, where *a* is the side of the square. Note that the absolute value of j_c determined on the basis of the proposed technique depends on both the sample thickness *D* and its lateral dimension and shape (via r_{eff}^{-3}).

Figure 1 shows the temperature dependences of the magnetic moment for the F1 film obtained at different magnetic fields. Similar results were qualitatively observed for the F2 film as well. It is apparent from Fig. 1 that the overwhelming part of the measured temperature range and fields falls in the magnetization saturation mode (monotonic decrease in the magnetic moment with the field growth at a fixed temperature). In



Fig. 1. Dependences of magnetic moment *m* on temperature for F1 film measured at external magnetic fields of (\Box) 5, (\bigcirc) 15, (\triangle) 35, (\bigtriangledown) 70, (\diamond) 200, (\lhd) 500, and (\triangleright) 2000 mT.

this region, to convert the magnetic moment *m* into j_c , we can use Eq. (2). At the same time, for the fields H < 10 mT in the region of low temperatures (below 80 K), we observe a deviation from monotony which shows itself in the intersection of the curves m (H = const) at different H (for 5 and 15 mT at 74 K in Fig. 1). To restore the true value of j_c using the measured *m* in this temperature and field range, it is necessary to take into account a correction for incomplete saturation of magnetization determined by the function F(x) (1). To do this, it is convenient to invert the function S(x) = F(x)/x in view of the monotony of which $j_c(m)$ is unambiguously defined from Eq. (1) and is

$$j_{\rm c}(H,T)$$

$$=\frac{2H}{D}\frac{1}{S^{-1}\left[\frac{3m(H,T)}{2\pi Dr_{eff}^{3}}\right]}=\frac{2H}{D}\frac{1}{S^{-1}\left[\frac{3m(H,T)}{Da^{3}}\right]},$$
 (3)

where $S^1(x)$ stands for the function inverse to S(x). The dependences recalculated using Eq. (3), namely, $j_c(H = \text{const}, T)$, together with the corresponding experimental data for m (H = const, T), in 5 and 15 mT fields are shown in Fig. 2. It is apparent from the figure that, for the data obtained in the 15 mT field (even more so in stronger fields), Eq. (3) within the entire temperature range is reduced to Eq. (2), whereas, for the data obtained in the 5 mT field and at temperatures below 80 K, it is necessary to use Eq. (3).

Thus, the present paper gives the results of experimental studies of temperature dependences of the critical current density $j_c(H, T)$ for thin epitaxial YBSO films grown by laser ablation on a monocrystal STO substrate. The technique of converting the experimental temperature dependence of magnetization into the dependence of



Fig. 2. Temperature dependences of magnetic moment *m* (symbols) and critical current densities calculated from them with Eq. (3) (lines) for F1 sample in (\Box , solid line) 5 mT and (∇ , dashed line) 15 mT fields.

the critical current on temperature taking into account corrections for incomplete magnetization saturation is presented. It allows expansion of the field of application of this technique for lower fields and temperatures.

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ELECTRICAL PROCESSES IN ENGINEERING AND CHEMISTRY

Study of Hydrodynamic Pressure in the Limited Region of a Tube under Explosion of a Microconductor

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Abstract—Hydrodynamic processes in the limited region of a tube under explosion of a microconductor are studied. In particular, hydrodynamic loading on the tube wall is considered. **DOI:** 10.3103/S1068375509010074

INTRODUCTION

In a number of technologies that use electric explosion of a microconductor as a power supply, polyethylene cartridges are applied [1]. One of these technologies is beading of tubes in grids of heat-exchange apparatuses. In this case, a cylindrical-form polyethylene cartridge filled with water is placed into the tube; a microconductor is situated along the symmetry axis of the cartridge. After electric explosion of the microconductor, a cavity filled with plasma, i.e., a discharge channel, is formed. The intensely expanding cavity (the stored energy of electric explosion may achieve 40 kJ) generates a shock wave, which influences the tube wall and deforms it. However, an intense motion of liquid along the tube axis leads to a rapid decrease in pressure in the liquid and, therefore, to a loss of quality of the obtained compound. By limiting the axial velocity of water expansion, for example, by installing additional weights on the end faces of the cartridge, one can increase the time and, hence, intensity and uniformity of loading of the tube.

Some results of study of the hydrodynamics of microconductor electric explosion in a cartridge placed into a tube, for a model law of electric power injection, are given in [2].

In the present work, we consider the hydrodynamic load on the wall of a tube and on disks covering the cartridge, one of which is fixed, and the other moves along the tube to the fixed rigid barrier. Herein, the electric power injected into the discharge channel is obtained according to experimental data (according to measured dependences of current and voltage in the discharge channel on time).

FORMULATION OF THE PROBLEM

We assume that the tube wall is absolutely rigid, as well as one of the bases of the cylindrical cartridge (discharge chamber). The disk covering the cartridge from the other side is inflexible and fixed. A microconductor is situated along the symmetry axis (Fig. 1). The liquid filling the discharge chamber is ideal and compressible; the channel is filled with ideal low-temperature plasma.



Fig. 1. Diagram of the region under study: (1) tube surface; (2) rigid fixed disk; (3) rigid mobile disk; (4) barrier; (5) microconductor.



Fig. 2. Electric power injected into the discharge channel.



Fig. 3. Pressure distribution along the tube surface at t, μ s: 5 (1); 15 (2); 25 (3).

MATHEMATICAL FORMULATION OF THE PROBLEM

In the region of liquid limited by the plasma–water contact area and the surface of the cylinder with absolutely rigid lateral face and one of the bases and the second rigid base, moving friction-free by the law of motion for a rigid body, it is necessary to solve a system of twodimensional nonlinear equations of gas dynamics, written in the cylindrical coordinate system, in combination with the binomial constitutive equation [3]. On the absolutely rigid surfaces, the normal component of the liquid velocity vector is stipulated to be equal to zero; on the mobile disk, the velocity of liquid is identical with that of the disk motion. On the plasma–water contact area, the fulfillment of the condition of energy balance is required [4]. The mathematical formulation of the problem is described in detail in [2].

The law of electric power injection into the discharge channel specified in this work is given in Fig. 2. The microconductor length l = 45 mm, the inner tube radius $R_k = 8.5$ mm, the mobile disk weight m = 5 g, and its initial distance from the barrier $\delta = 5$ mm.

RESULTS OF THE PROBLEM SOLUTION

Some results of the problem solution are presented in Figs. 3–5. In construction of the computational grid, the coordinate origin was placed at the microconductor center; the Oz axis was placed along its symmetry axis (the z coordinate increases from left to right); the Or axis coin-



Fig. 4. Pressure distribution over the radius of the mobile (solid lines) and fixed (dashed lines) bases of the cylinder at t, μ s: 5 (I); 20 (2).



Fig. 5. Pressure in the discharge channel and at the points on the mobile (solid lines) and fixed bases of the cylinder: (1) pressure in the channel; $(2-2^{\circ}) r = R_k$; $(3-3^{\circ}) r = 0.5 \times R_k$.

cides with the cylinder radius passing through the coordinate origin.

Expansion of the discharge channel, which appears as a result of the microconductor electric explosion, leads to formation of a shock wave in the liquid surrounding the channel and to the disk motion. This wave, together with waves reflected from the surfaces of the tube and the disk, creates a complex wave pattern. Mobility of one of the disks leads to perturbation of the flow unidimensionality, which is characteristic of a cylindrical discharge chamber with fixed bases and a microconductor placed along the symmetry axis, whose length is equal to that of the chamber. At the moment when the shock-wave front reaches the tube surface ($t \approx 5 \,\mu$ s), values of the pressure on the cylinder lateral surface near the bases differ by 10.5% (Fig. 3, curve 1). The nonuniformity of the distribution of the parameters of the liquid over the axial coordinate gradually extends over the whole discharge chamber (Fig. 3, curves 2, 3).

Radial distributions of pressure over the surface of the cylinder bases, as well as other hydrodynamic characteristics, differ significantly from the moment of the discharge channel expansion (Fig. 4). The pressure distribution along the fixed base levels rapidly enough; the one along

the mobile base remains nonuniform during the whole time period under consideration (up to $t = 50 \,\mu$ s).

The second pressure maximum in the discharge channel is higher than the first one. It is formed as a result of superposition of the pressure wave generated by the discharge channel (energy injection still continues) and the wave reflected from the tube wall (Fig. 5, curve 1). After the electric power injection has terminated, the pressure in the channel varies insignificantly.

The highest pressure in liquid is achieved near the tube wall and the mobile disk (Fig. 5, curve 2). The value of the first maximum here is lower by approximately 10% than in the symmetric region near the fixed base (Fig. 5, curve 2'). However, the subsequent maxima of pressure near the mobile base are considerably higher. The highest value is obtained here at the moment of the disk collision with the barrier, since there takes place a superposition of two reflected waves: from the surface of the tube and the disk. The pressure oscillation period here is lower than in the similar region near the fixed boundary, because the discharge channel expansion rate is higher and, therefore, the time of the pressure wave transit from the discharge channel to the tube surface is less. The radial coordinate on the mobile disk achieves a value exceeding $0.5 \times R_k$; hence, the pressure at this point on the mobile disk surface (Fig. 5, curve 3) is identical to the pressure in the discharge channel (Fig. 5, curve 1). The radial coordinate on the fixed base of the cylinder achieves the maximum value at the moment of arrival of the pressure wave reflected from the tube wall, and it varies insignificantly from this point on. However, the area occupied by plasma on both bases of the cylinder is quite considerable, since the discharge channel volume is comparable with the liquid volume (the cartridge volume is 10.2 cm^3 ; the discharge channel volume at the moment of count termination is 1.9 cm^3). That is, in addition to the hydrodynamic influence, the disks, particularly the mobile one, are appreciably affected by plasma.

CONCLUSIONS

In order to obtain uniform hydrodynamic loading of the tube surface, it is necessary to limit the treated region by fixed additional weights.

Adjusting position of the mobile disk and the barrier, one can obtain high values of pressure on specified regions of the surface of the tube and the disk.

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ELECTRICAL PROCESSES IN ENGINEERING AND CHEMISTRY

Loading Effect at Oxygen Plasma Etching of Fabric of Polyethylele Terephtalate Monofilament Fibers

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Abstract—The results of studying the effect of loading under the low-temperature action of oxygen plasma on the surface of Italian fabric of polyethylene terephthalate monofilament threads are presented. Gravimetric and mass-spectrum techniques (mass spectrometer IPDO-2A) were used in this work. When the contact times of the plasma with the sample are less than the characteristic times of chemical reactions, the contact time determines the specific rates of heterogeneous processes. The reciprocal influence of heterogeneous and volumetric processes only becomes appreciable when the contact times of the plasma with the sample exceed the characteristic times of chemical reactions. As a result, the specific rates of etching, of oxygen consumption from the gas phase, and of the formation of gaseous products decrease with the increase in the reactor load ratio; however, the correlation of the destruction channels does not change. Compared to the air plasma, oxygen plasma was found to be more stable to the loading effect in a wide range of discharge parameters.

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INTRODUCTION

A loading effect was observed in the case of air plasmochemical etching of fabric of polyethylene terephtalate (PETP) complex fibers in a wide range of the discharge parameters [1]. A chemically reacting plasma was found to be a strongly nonlinear system possessing numerous and variable feedback channels. Gas elimination changes the plasma properties and, hence, the target process kinetics. The interrelated influence of the parameters and the load determines the regularities of the elimination of reaction products.

The mechanisms of the plasma-oxidative destruction of lavsan fabric in the oxygen and air discharges are similar in many aspects [2] for a low reactor load. Nevertheless, a substantial difference exists, i.e., the noticeable influence of heterogeneous chemical reactions in the air plasma on the reagent (oxygen atoms) concentration in the gas phase.

It was demonstrated in [3] by the example of woven materials of various synthetic fibers that the kind of thread interweaving and the surface density of fabrics can exert a strong influence on the rate of plasma etching. The authors of [4] investigated the plasma destruction of PETP fabrics with various structures (domestic fabrics of complex fibers and Italian fabrics of monofilament single threads with various kinds of interweaving and density) in the oxygen discharge. The results have demonstrated that the difference in the etching rates of fabrics is related to the difference between the geometrical and the effective (real) surface of material subjected to the action of active particles. Specific rates of mass loss, oxygen consumption, and formation of gaseous products, calculated taking into account the total fiber surface for fabrics of various structure, agree well with each other and with the PETP film etching rate. It should be noted that the effective surface of fabrics of the same structure in the general case is different at the plasmolysis in oxygen and in air.

The aim of the present work is to investigate the influence of the loading effect on kinetics of a stationary etching process and formation of gaseous products under the oxygen plasma action on the surface of fabric of monofilament PETP fibers.

EXPERIMENTAL METHOD

Experiments were performed by virtue of the installation, the scheme of which is presented in [5]. The experimental conditions and parameters of plasma treatment were the same as described in [1]. The linear velocity of the gas flow was maintained constant in one series of the experiments and amounted to 30 cm/s; in another series of the experiments, it varied from 10 to 100 cm/s. The object of the research was an Italian fabric SAATELENE 6264 of monofilament PETP fibers. The fabric parameters determined using a scanning electronic microscope Tesla BS-300 were as follows: the fiber diameter of 64 μ m, the fiber spacing of 100 μ m, and the specific density of 5.83 mg/cm^2 . The length of the fabric cylinder generatrix was varied within the range of 2-18 cm. The geometrical area of the treated material increased from 20.5 to 184 cm² and the fraction of the reactor surface covered with the fabric increased from 6 to 56%. As was mentioned above, the effective fabric surface area differs from its geometrical surface area. For



Fig. 1. Rate of the mass loss of the monofilament fabric versus the reactor load ratio.

a low reactor load (up to 10%), when the same plasmaforming gas is used, the effective area of the studied monofilament fabric is ~3.3 times less than for a complex fabric; the effective area for fabrics of the same structure differs approximately by a factor of two for etching in oxygen and air discharges [4].

The mass loss in the samples was determined by periodic weighing on an analytical balance WA-34. The weighing accuracy was 1×10^{-4} g. The composition of gaseous etching products, the rate of their formation, and the rate of reagent consumption were analyzed using an IPDO-2A mass spectrometer with a PMO-4S sensor.

RESULTS AND DISCUSSION

According to the results of mass-spectral measurements, oxygen is consumed for all experimental conditions; the destruction products are molecules of CO_2 , CO, H_2O , and H_2 .

The average rates of the mass loss W, determined as the ratio of the mass loss of the total sample to its geometrical area, are shown in Fig. 1 for a pressure of 100 Pa and a discharge current of 80 mA. In Fig. 2 the rate of O₂ consumption and the rate of formation of gaseous products (W_i) under the same conditions are presented. The yields of gaseous products per one reacting O₂ molecule ($\varphi_i = W_i/W_{O_2}$) are shown in Fig. 3. The specific rates of all the processes decrease (mass loss becomes less by a factor of two when the load increases by a factor of nine) and tend asymptotically to a constant value. The sum molar fraction of the products in the gaseous products from 0.13 to 0.47, though the yields of the gaseous products per one reacting O₂ molecule remain constant.



Fig. 2. Rates of the O₂ consumption (1) and formation of $CO_2(2)$, CO(3), $H_2O(4)$ and $H_2(5)$ versus the reactor load ratio.

These results have been compared with the data obtained for the case when the effect was studied for the reactor loading with a complex PETP fabric in the air plasma for the same discharge parameters [1]. This comparison is valid because the regularities of plasma-oxidative destruction of PETP fabrics of various structure are similar for low loads; for the same minimal load (20.5 cm²), the etching rate for a lavsan fabric in air does not much exceed (1.5 times approximately) the etching rate for a monofilament fabric in oxygen.

In the air plasma, less changes in the gas phase composition determined according the sum molar fraction of the products (from 0.21 to 0.31) lead to a more significant loading effect; the specific rate of the mass loss decreases by a factor of approximately five. The correlation of the material destruction channels changes in favor of the channel with CO and H₂ formation. Even a large amount of treated material (a so-called "high load") is a smaller perturbation for oxygen plasma than a low load for air plasma. This situation is probably associated with the fact that the polymer destruction during air etching is mainly a plasma-oxidative process and the loading effect should be more pronounced when the product fraction with respect to the reagent (oxygen) is greater. Actually, when the amount of the treated material increased by a factor of 8 or 9 in the region behind the sample, the ratio of the sum partial pressure of the etching products to the partial pressure of O_2 molecules increased from 0.15 to 0.88 in the oxygen discharge and from 3 to 14 in the air discharge. Simultaneously, the molar fraction of O₂ consumed from the gas phase for the discharge processes increased from 0.11 to 0.43 and from 0.52 to 0.71 in oxygen and in air, respectively. Moreover, one should recall that, according to the composition of particles and volume processes that occur, the oxygen plasma is a less



Fig. 3. Yields of $CO_2(1)$, CO(2), $H_2O(3)$, and $H_2(4)$ per one reacting oxidant molecule versus the reactor load ratio.

complex system than the air plasma in that it possesses a smaller number of feedback channels. For example, in the case of modeling the gas activation processes in low-pressure plasma with an aim to determine the composition of neutral particles, the examined kinetic schemes consisted of 43 and 88 reactions in oxygen and air, respectively [6]. One of the main chemically active components of oxygen plasma is oxygen in its atomic form. The atoms serve as an energy source to initiate heterogeneous reactions and as a chemical agent facilitating both formation of functional oxygenated groups on the surface and their destruction (etching). In addition to the dissociation channel of O_2 by direct electronic stroke, in air discharge, new dissociation channels also arise. These

reactions involve $N_2(A^3\Sigma_u^+)$ and $N_2(B^3\Pi_g)$ excited states. As a result, the flux of $O(^3P)$ atoms on the reactor wall diminishes significantly less than one might expect based on the decrease in the concentration of O_2 molecules in the initial plasma-forming gas [6].

Some features of the situation observed in the case of the loading effect study resemble the situation observed in the study of polymer destruction regularities in O_2 mixtures with inert gases (N₂ and Ar). For various studied film polymers (PETP, PP, and PE), when the oxygen content in the plasma-forming gas diminishes, its more intensive consumption in the reactions occurs and, in the gas phase, the fraction of products whose formation demands less oxygen (CO and H₂) increases [7, 8]. The rate of these processes sharply increases for the oxygen content in mixtures by less than 10–20%. Evidently, competitive processes take place that involve atomic and molecular oxygen in the gas phase.

The loading effect in O_2 discharge was studied in a wide range of the discharge parameters (pressure of 50–200 Pa and current of 20–110 mA) at the constant linear



Fig. 4. Rate of the mass loss of the monofilament fabric versus the gas consumption;

velocity of the gas flow. The experimental data have demonstrated that the effect in general retains for all the discharge parameters. Namely, when the amount of the treated material increases, the specific rates of the mass loss, the oxygen consumption, and the elimination of the gaseous etching products diminish. The yields of the gaseous reaction products per one consumed O_2 molecule do not substantially change within the data scattering limits.

The loading effect can manifest itself as a dependence of the etching rate of material on the operating gas consumption at the constant surface area of the material [9]. Dependences of this kind are usually presented as peaked curves. The gravimetric and mass-spectral measurements were performed for a constant pressure of 100 Pa and a discharge current of 80 mA with variation of the linear gas flow velocity. Plasma action was exerted on samples with a width of 2 and 18 cm, and the reactor load ratio was 6 and 56%, respectively. Denote them as the low load ratio (LLR) and the high load ratio (HLR). The research results (Figs. 4–6) demonstrated that the dependences of all rates on the gas flow exhibit a common character for the LLR only. The linear velocity of the gas flow indicates the contact time of the chemically active plasma particles (CAPP) with the sample. The contact time τ_c is defined as $\tau_c = l/V$, where l is the sample length in the gas flow direction and V is the gas flow linear velocity. The data in the semilogarithmic scale are presented as dependences of the process rates on the contact time (Figs. 7 and 8). In this scale, the dependences obtained for samples with various geometrical area are generalized as unified peaked curves. The left-hand branches correspond to the situation when the contact time of the CAPP with the sample is less than the characteristic chemical reaction times; therefore, it substantially influences the rate of the studies processes. This



Fig. 5. Rate of the O₂ consumption (1) and formation of CO_2 (2), CO (3), H_2O (4), and H_2 (5) versus the gas consumption for the LLR of the reactor.



Fig. 7. Rate of the mass loss of the monofilament fabric versus the contact time of the gas with the sample.

influence is substantial until these times become equal or competitive processes begin to manifest themselves. For the HLR, the rates are beyond the limits of this interval in all studied ranges of operating gas consumption. It is interesting that the maximum positions for the formation rates of various gaseous products do not coincide. Most likely, the characteristic times of chemical reactions with formation of these products are different. In the range to the right from the maximum, the gain of the product of heterogeneous chemical reactions in the gas phase becomes a determining factor, which leads to a drop of



Fig. 6. Rate of the O₂ consumption (1) and formation of CO_2 (2), CO (3), H_2O (4), and H_2 (5) versus the gas consumption for the HLR of the reactor.



Fig. 8. Rate of the O₂ consumption (1) and formation of CO_2 (2), CO (3), H_2O (4), and H_2 (5) versus the contact time of the gas with the sample.

the generation rate and fluxes to the surface of the active plasma particles.

CONCLUSIONS

During the oxygen plasmochemical etching of fabrics of monofilament PETP fibers, the loading effect manifests itself in a wide range of the discharge parameters. As the treated material amount increases, the specific rates of etching, the consumption of oxygen from the gaseous phase and the formation of gaseous products of the fabric destruction decrease. However, all other conditions being equal, the oxygen plasma is more stable with respect to the loading effect than the air plasma; all the rates decrease relatively more slowly and the correlation between the destruction channels does not change. This can be associated with the following reasons: 1) the nonequilibrium O_2 plasma is a less complicated system with fewer feedback channels and 2) in the loading process, the changes in the gas phase composition with respect to the oxygen plasma reagent are lower than in the air plasma. One can suppose that, in the oxygen discharge, though the gain of the destruction products in the gas phase leads to a definite lowering of the generation rate and of the fluxes of active particle to the surface, the correlation of the fluxes remains. When the contact times of plasma with the sample are less than the characteristic times of chemical reactions, the rates of heterogeneous processes are determined by the contact time. The reciprocal influence of the heterogeneous and volume processes becomes appreciable only when the contact times of the plasma with the sample exceed the characteristic times of chemical reactions.

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ELECTRICAL PROCESSES IN ENGINEERING AND CHEMISTRY

Physicochemical Characterization and Thermal Behaviour of Two Tunisians Kaolins¹

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1. INTRODUCTION

Ceramic product depends on the nature and the properties of utilised raw material. The increase in temperature for singly fired ceramic clays exceed the energy threshold of the reactivity of mineral material and produces a series of reaction and transformations that lead to the formation of new phases and the disappearance of others [1]. For the some firing conditions the halloysite clay produced a higher bulk density than the kaolinite clay as well as finer mullite crystals. Mullite is formed in kaolinite clay at a lower temperature than in halloysite clay [2]. The kaolinite forms metakaolinite by heating from 550°C to 950°C, and mullite mainly forms above 1200°C [3].

The objective of this paper is to study the thermal transformation of two Tunisians kaolins chooses.

2. MATERIALS AND METHODS

Two samples are selected for this study: Kasserine clay (K) and Tabarka clay (T). We add a suffix "b" or "p" to indicate respectively if the clay is crude or purified.

Purification:

The clay fraction was purified by classical methods [4], repeated cation exchange with 1N NaCl solution, washing and sedimentation and dialysis. The fine clean sediment was freeze dried.

Chemical analysis:

The samples are attacked by a mixture of three acids (HCl, H_2SO_4 and HNO₃); all elements pass in solution only the silica that it measured out by gravimetric [5].

The chemical elements, as Al, Fe, Mg, Ca, Na and K are measured by atomic absorption.

X-ray diffraction:

Mineralogical analysis was performed by XRD, using a Philips diffractometer PW 1050/81, with the K $\alpha_{1, 2}$ radiation of the copper. In this method, oriented specimens are prepared on glass microscope slides. The slides have a density of 20 mg of samples and were successively given treatment of:

(i) Drying at 20°C

(ii) Heating for two hours an 500°C.

Infrared spectroscopy:

FT-IR spectra were recorded in the region 4000– 350 cm⁻¹ in an EQUINOX model 55 infrared Fourier transform spectrometer, using the KBr pellet technique (about 2 mg of sample and 200 mg of KBr were used in the preparation of the pellets).

Cation exchange capacity:

Clay is saturated first with other solutions. The excess of the reagent added is measured by volumetric method.

N_2 adsorption experiments:

The specific surface areas of the samples were determined by the corresponding nitrogen adsorption isotherms at 77 K, obtained from Micrometric Autosorb 2050 Analyser, after out degassing the samples at 120°C, with the residual pressure of 10–5 mmHg. The BET method was used for the corresponding calculations. Total pore volume (Vt) was determined at P/P0 = 0.98.

3. RESULTS AND DISCUSSION

3.1 Characterization of the two clays:

The centesimal compositions of raw and purified samples are given in Table 1. The following preliminary points may be noticed:

¹ The article is published in the original.



Fig. 1. XRD pattern of crude Tabarka clay.



Fig. 2. XRD pattern of crude Kasserine clay.



Fig. 3. XRD of oriented films of purified samples and heated at 500°C.

a) The loss on ignition of the Kasserine clay is very important (33.20%); it can be due to the presence of a supplementary water layer.

b) The (SiO_2/Al_2O_3) ratio is close to 1 for all samples. Therefore we can deduct that the two minerals are of types 1/1.

c) The (SiO_2/Al_2O_3) ratio of the Tabarka clay (1.15) is very close to the theoretical kaolinite 1.18 [6].

d) The amounts of SiO₂ (38.77%) and Al₂O₃ (37.20%) of purified Tabarka clay are nearly equal to those given by the literature for a kaolinite.

The XRD pattern of the Tabarka clay (Fig. 1) shows sharp peaks at d = 7.15, 4.45, 4.35, 4.17, 3.84 and 3.57 Å due to well crystallized kaolinite [7].

The XRD pattern of the Kasserine clay (Fig. 2) shows sharp peaks at d = 10, 4.48, 3.34 and 2.58 Å due to halloysite $4H_2O$ [8].

The diffractograms (Fig. 3) show that these two samples are respectively of kaolinite and halloysite that will be destroyed at 500°C. The confirmation of our results with those gotten by other authors [9] is returned in the following Table 2.

	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	ZnO	PF
K _b	35.12	28.90	0.19	0.63	0.28	1.29	0.15	0.24	33.20
K _p	45.95	28.52	0.17	0.08	0.12	0.08	0.14	0.025	24.69
T _b	44.36	38.77	0.50	0.33	0.08	0.11	0.02	0.107	15.66
T _p	46.03	37.20	0.46	0.36	0.08	0.05	0.04	0.19	15.59

Table 1. Chemical analysis of the samples

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The exam of IR spectra shows that (Figs. 4, 5):

a) IR spectra of raw and purified samples are identical; so no foulness associated to the two clays.

b) In the region between 3500 and 4000 cm⁻¹, the IR spectrum of the Tabarka clay (Fig. 4) shows thins and intense bands whereas the bands of the kasserine clay (Fig. 5) are larges and less intense. It proves that Tabarka clay is better crystallized than Kasserine clay.

c) Referring on results of IR spectroscopic analysis for a kaolinite, given by Vander Marel and Ben-tels Pacher in 1976, we deduce that Tabarka clay is a kaolinite well-crystallized (Table 3).

d) Figure 5 shows bands at 3698, 3625 1036 and 912 cm⁻¹ characterizes the clayey mineral of kaolin family [10]. The adsorption massif at 3468 cm⁻¹ and the band of deformation at 1640 cm⁻¹ (vibrations OH of the hydration water clay), show that the kasserine clay is a halloysite.

Figure 6 presents the DTA curves of the studied samples. The main changes pointed out by TG and DTA, during the heating of the samples are the following:

a) Lower to 200°C: a first endothermic pick that can be correlated with a pre-dehydration process, which takes place as a results of the reorganization in the octahedral layer, first occurring at the OH of the surface [11]. This explains the importance of the first loss of the Kasserine sample (Table 4) in relation to the one of the Tabarka sample.

b) 500–600°C: a second endothermic pick due to dehydroxylation of the clay. During this temperature kaolinite forms metakaolinite by dehydroxylation [12].

c) 976–1000°C: an exothermic pick that doesn't correspond to a weight loss but it indicates the transition of phase to high temperature of the amorphous product, due



Fig. 4. IR spectra of raw and purified Tabarka clay.

	Table 2.	Identification	of samples
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Minerals	Normal Glass	Glass heated at 500°C
Kaolinite	7.29 Å	Détruite
Halloysite	10 Å	Détruite

Table 3. IR bands (cm⁻¹) of Tabarka clay

	-
3695, 3660 and 3620	Al–OH of valence
940 and 913	Al–OH of deformation
1032	Si–O–Si of valence
1005	Si–O–Al of valence
695 and 539	Si–O–Al of deformation
	1

to the decomposition of the kaolinite. In well-crystallized samples the decomposition of kaolinite starts at higher temperature [13]. So the observation of these two picks of our samples permits us to conclude that Tabarka sample is better crystallized than Kasserine sample.

d) The calculation of losses in mass (Table 4) of kasserine clay and Tabarka clay shows that it is respectively a halloysite and a kaolinite [14].

Figure 7 presents the isotherms of adsorption-desorption of Kasserine clay and Tabarka clay.

The raw sample of kasserine has an important power of adsorption compared to the purified sample.



Fig. 5. IR spectra of raw and purified Kasserine clay.

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Fig. 6. DTA curves of crude and purified samples.



Fig. 7. Isotherms of adsorption-desorption of Kasserine clay and Tabarka clay.

The adsorption-desorption isotherms of Tabarka clay are confounded. This clay is not porous characteristic of kaolinite. Whereas the isotherms of desorption of the Kasserine clay present hysteretic buckles what indicates that this clay is porous.

The Kasserine clay presents the best power of adsorption of the two clays.

Specific surface values, determined from the isotherms of adsorption, of the two samples are represented in the following Table 5.

The specific surface is not sufficient for the characterization of clayey mineral. The specific surface of kaolinite is lower to $25 \text{ m}^2/\text{g}$ [15]. In our case the specific surface value of Tabarka clay (Table 5) its 24.5 m²/g corresponds to kaolinite.

The values of C.E.C of the raw and purified clays are nearly identical (Table 6), what confirm that these two samples don't contain any foulness.

According to the literature values [16] of the C.E.C we noted that:

a) The C.E.C of the Kasserine sample (40.11 méq/100g of clay charred), corresponds to Halloysite 4H₂O.

b) The value of the C.E.C of the Tabarka sample (3.15 méq/100gs of heated clay), corresponds to kaolinite.

3.2 Study of the thermal behaviour of the kaolinite of Tabarka and the halloysite of Kasserine:

The thermal analysis is realized by heating samples to different temperatures (100, 300, 500, 700, 1000 and 1200°C), during one hour. The heated samples are analyzed by different techniques (XRD, IR and specific surface analysis).

3.2.1 Study of the thermal Behavior by XRD: Figures 8, 9 present respectively the XRD patterns to different temperatures of the Tabarka and Kasserine samples.

The XRD patterns at 100°C (Fig. 9), shows a sharp peaks at d = 7.41, 4.41 and 3.59 Å characteristic of kaolinite, what explains the departure of water molecules of the halloysite. The kaolinite is destroyed to 550°C due to the formation of an amorphous dehydration product identified as metakaolinite after an endo-thermic reaction. At 1000°C, the structure of the two samples is completely changed what interpreted by the formation of crystalline product from the next amorphous intermediate phase results in a prominent exothermic reaction at 980°C [17]. The two difractograms obtained at 1200°C, show a sharp peaks at d = 5.41, 3.41, 2.89 and 2,70 Å relatives to a new phase that is the mullite.

The diffractogram of Tunisian mullite (Fig. 10) gotten by thermal treatment of the Tabarka clay is simulated to XRD pattern of a pure mullite (Fig. 11) but picks are less resolute that can be due to a bad crystallization.

Table 4.	Losses	in mass	s of sam	oles

Samples	1 ^{ist} loss (%) T < 200 °C	2 ^{sd} loss (%) 400 < T < 600°C
K _b	3.89	5.04
K _p	1.44	6.62
T _b	0.50	12.77
T _p	1.32	13.78

Weight Losses (Ross and Kerr, 1931)

Kaolinite	1–2%	13%
Halloysite	2–4%	6–14%

 Table 5.
 Specific surface of samples

Samples	Specific surface (m ² /g)
K _b	233.96
K _p	128.27
T _b	24.57
T _p	24.60

Table 6. C.E.C of samples

	samples	C.E.C (méq/100g of heated clay)
K _b		40.11
K _p		39.84
T _b		3.15
T _p		3.15
	$C \in C$ of some	clavey minerals (Kelley 1948)

E.C of some clayey minerals (Kelley, 1948)

Kaolinite	3–15
Halloysite 2H ₂ O	5–10
Halloysite 4H ₂ O	40–50



Fig. 8. XRD patterns of Tabarka samples to different temperatures.



Fig. 9. XRD patterns of Kasserine samples to different temperatures.

3.2.2 Study of the thermal Behavior by IR. Figures 11, 12 present respectively the IR spectera of Kassserine and Tabarka samples, obtained after thermal treatment. After the thermal treatment of samples, the transformation of kaolinite to metakaolinite is confirmed by the absence of detectable Al–O–H bands at 913 cm⁻¹. The reduction of 539 and 913 cm⁻¹ and the appearance of a new band at 786 cm⁻¹ can be connected with the change from octahedral coordination of Al³⁺ in kaolinite to tetrahedral coordination in metakaolinite [19]. The

characteristic bands of kaolinite have been disappeared after the thermal treatment over 500°C. a new band at $2850-3500 \text{ cm}^{-1}$ is observed in the sample treated at 700° C and is reduced as the treatment temperature is increased.

The specters of the two clay samples, heated to 1200°C, show the apparition of a new phase are similar to the mullite spectera (Fig. 13) observed using FTIR. This mullite is prepared from sol–gel process by the synthesis of the pure aluminosiloxane [20].



Fig. 10. XRD pattern of Tabarka clay heated at 1200°C and the diffractogram of pure mullite (M. F. de Souza and J. Yamamoto, 1999)[18].



Fig. 12. IR of Tabarka samples after thermal treatment.

3.2.3 Study of the thermal Behavior by specific surface. Figure 14 presents the adsorption–desorption isotherms of kasserine samples after thermal treatment, show a progressive diminution of the porosity until completely disappears at 1200°C.

The specific surfaces of two clays obtained after thermal treatment are represented in the following table 7.



Fig. 11. IR of kasserine samples after thermal treatment.



Transmitttance (arbitrary linear scale)

Fig. 13. Chemical homogeneity in mullite prepared from polymeric precursors can be observed using FTIR (Treadwell et al., 1996).

The specific surface of Kasserine clay (233.96 m^2/g to 20°C) remains very important until the temperature of 700°C, what reveals some catalytic applications to high temperature.

The specific surface of Tabarka clay according to the temperature (Fig. 16) remains constant until 700°C. One will note the extreme stability of the total surface



Fig. 14. Adsorption-desorption isotherms of Kasserine samples after thermal treatment.



Fig. 16. Evolution of the specific surface of Tabarka clay according to the temperature.

developed by this clay during the phase of the dehydroxylation. Therefore the dehydroxylation doesn't entail any modifications important of the texture of the kaolinite.



Fig. 15. Adsorption-desorption isotherms of Tabarka samples after thermal treatment.



Fig. 17. Evolution of the specific surface of Kasserine clay according to the temperature.

The representation of the evolution of the specific surface of Kasserine clay, according to the temperature (Fig. 17) show that:

Table 7. Specific surface of samples after thermal treatment

Temperature (°C)		20	100	300	500	700	1000	1200
Specific surface (m ² /g)	K	233.96	178.80	178.12	149.83	130.01	12.29	0.61
	Т	24.57	22.77	23.92	22.15	21.74	15.19	5.92

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a) A slightly decreases of the surface in the begin of the dehydroxylation.

b) The surface remains constant in the second stage of the deshydroxylation (100°C to 700°C). One will note the extreme stability of the total surface developed by kasserine sample during this phase.

c) An abrupt diminution at 700°C that is interpreted by a process of sintering.

4. CONCLUSION

The selected clays differ by their mineralogical properties. The Tabarka is a well-crystallized kaoli-nite. Whereas the Kasserine clay is a hydrated halloysite characterized by a important specific surface (233.96 m²/g). The evolution of specific surface according to the temperature of the Kasserine samples after thermal treatment shows an abrupt diminution at 700°C that are interpreted by a process of sintering. The thermal treatment of the two clays at 1200°C, shows the apparition of a new phase that is the mullite. This mullite is identical to mullite gotten by the process sol-gel from the synthesis of the pure aluminosiloxane.

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SUMMARY

The object of this work is to study the physicochemical proprieties and the thermal behaviour of two Tunisians kaolins. The two samples selected from Tabarka and Kasserine are tested by chemical analysis (CA), X-ray diffraction (XRD), differential thermal analysis (DTA), infrared spectroscopy (IR), cation exchange capacities (CEC) and specific areas (BET) in order to determine their chemical and mineralogical composition and structural differences. This study showed that the clay of Tabarka is a well crystallized kao-linite and the clay of Kasserine is a halloysite 4H₂0, containing amorphous alumina. The evolution of specific surface according to the temperature of the Kasserine samples after thermal treatment shows an abrupt diminution at 700°C that are interpreted by a process of sintering. The thermal treatment of the two clays at 1200°C, shows the apparition of a new phase that is the mullite. This mullite is identical to mullite gotten by the process sol-gel from the synthesis of the pure aluminosiloxane.

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ELECTRICAL PROCESSES IN ENGINEERING AND CHEMISTRY

Influence of Magnetic Field on Calcium Carbonate Precipitation in the Presence of Foreign Ions¹

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INTRODUCTION

Calcium carbonate precipitation has been the subject of numerous investigations because of its importance in several industrial processes. Its scale crystallization at the liquid/solid interface of flow systems induces important damage in the domestic and industrial installations using natural waters (pipe blocking, membrane clogging, efficiency decay of heaters or heat exchangers ...). The main reaction involved in the precipitation of CaCO₃ is governed by the following equilibrium called calcocarbonic equilibrium:

$$Ca^{2+} + 2HCO_3^{-} \iff CaCO_{3(s)} + CO_2 + H_2O \qquad (1)$$

Depending on the temperature, ions concentration, pH, and flow rate of the solution, equilibrium (1) can be shifted in the forward or backward direction. Three crystalline forms of $CaCO_3$ exist: calcite, which has a cubic shape; vaterite, which has a spherulite, hemispherical flowers, or lenses morphology; and aragonite, which is recognized as needles. Each $CaCO_3$ variety is stable depending on thermodynamic conditions.

Various methods are used to prevent scaling, for example water decarbonation using electrochemical processes, seeding or acid addition. However these chemicals are generally deleterious for human health and their use is forbidding in drinking water.

Thus, environmental protection and economic considerations are two strong motivations for developing various types of physical antiscale methods (ultrasonic, ultraviolet radiation, electric and magnetic treatment). Magnetic methods attract a special attention due to their ecological purity, safety, and simplicity. This technique was widely employed on the treatment of irrigation water [1], industrial water [2] and in numerous other cases.

Natural water contains particles charged in the form of positive and negative ions. Taking into account this fact, various studies related to the effectiveness of the magnetic field (MF) on the calcium carbonate precipitation in the presence of foreign ions were done. The effect of a static magnetic field on the precipitation of CaCO₃ was studied in the presence of Mg^{2+} , Fe^{2+} and SO_4^{2-} [3–5]. The found results showed that the MF affects the zeta potential, the pH, and the precipitation kinetics. The presence of Fe²⁺ maintains the zeta potential positive, however the presence of SO_4^{2-} make it negative. These effects SO_4^{2-} on the zeta potential are probably results from their specific adsorption on CaCO₃ surface. While the effect of Mg²⁺ is less clear. For Herzog et al. [6], it is the addition of particles of ferric hydroxide in the water which is responsible for the MF effect on CaCO₃ precipitation.

In a previously study [7], the effect of a magnetic treatment on a calcocarbonic water was largely tested. It was observed that the effectiveness of the magnetic treatment on the precipitation of calcium carbonate depends on various parameters such as pH of the solution, hardness of water, flow rate and time of treatment. The results indicated that the MF enhanced the precipitation of CaCO₃ in bulk-solution instead of heterogeneous one and decreases its solubility. It was advanced that the main magnetic effects concern the associations of ionic species which are present in the solution and which are involved in the nucleation process of CaCO₃ precipitation.

The properties of aqueous ionic solutions have been extensively researched in recent years since it has been shown that the presence of ions modifies the properties of water. In this reason, the application of a permanent MF on a more complex system remains very interesting. In this paper the experimental results on the effect of a MF on the precipitation process of calcium carbonate

¹ The article is published in the article.



Fig. 1. Effect of hardness of solution on (a) and (b) homogeneous presipitation of CaCO₃ for a various material pipe of treatment. (*1*: W PTFE, 2: Tygon, 3: PVC).

scale from calcocarbonic pure water containing Mg^{2+} , SO_4^{2-} or Na⁺/Cl⁻ are reported.

EXPERIMENTAL

The synthetic treated water was prepared by adding Mg^{2+} , SO_4^{2-} and Cl⁻/Na⁺ to a calcocarbonic pure water (water containing only Ca²⁺, CO₃²⁻ and HCO₃⁻ ions), prepared by dissolving 0.4 g.dm⁻¹ reagent grade CaCO₃ in deionized water, by bubbling carbon dioxide during a full day. The solutions, containing one of the foreign ions at the desired concentration, were prepared by dissolving Na₂SO₄, MgCl₂ or NaCl in pyre water and added to the calcocarbonic solution just before treatment. Three level of ionic strength (*IS*) are tested for each ion: 0.015, 0.0195 and 0.027 M, the reference solution is calcocarbonic pure water (*IS* = 0.012 M). The initial pH was adjusted at 7 and the temperature was maintained at 30°C.

The treatment of 0.50 dm³ of prepared water, through the permanent magnetic device, was applied in a pipe made of Tygon material. The magnetic device was described in details in the paper of Gabrielli *et al.* [8]: a series of 5 pairs of permanent magnets with north and south faces facing each other are associated alternately. The magnetic circuit of each pair was closed with a Ushaped iron yoke. The field strength was about 0.16 T in the air gap. The choice of Tygon is due to that this material gives the higher amount of CaCO₃ precipitated by homogeneous way [7, 9]. The total time of treatment $t_{\rm T}$ was maintained at 15 minutes and the flow rate was moderate in order to have a laminar regime $(0.74 \text{ dm}^3 \text{ min}^{-1})$, the precipitation test by the degassing method is for about 90 minutes. For every case of IS, two tests were made: treatment with circulation in the presence and absence of MF. All the experiments were replicated 3 times and average values were calculated (\sim 3%). After each test the tubing was thoroughly cleansed, first, by recirculating a low-concentration acid solution for about 0.5 h, after which deionised water was recirculated for 0.5 h. After each experimental series the tubing was replaced. The effect of MF on calcium carbonate precipitation from a pure calcocarbonic solution was, also, tested and three level of *IS* were chosen: 0.009, 0.012 and 0.015 M. In this part, three types of pipe material were tested: Tygon, PVC and W PTFE (White PTFE).

The experiment apparatus of magnetic treatment and of degassing technique employed in this study were described in previous article [7].

RESULTS AND DISCUSSION

1. Effect of hardness

As illustrated in Fig. 1, the total and the homogeneous precipitation ratio are increased, in the presence of MF, with increasing the water hardness and it's also influenced by the nature of the pipe material, especially for the total precipitation ratio. This effect could be attributed to the composition of the material. As reported by Parker and Ranney [10], Barcelona et al. [11] and by Curran and Tomson [12], the pipe could release solid particle on solution due to the erosion mechanism occurring at the polymer/water interface. The amount of these particles depends significantly on the nature of pipes. For these researchers, it was shown that Tygon leach substantial quantities of constituents and that PTFE do not appear to leach any constituents. These particles, in the step of degassing test, will support the nucleation of calcium carbonate, so, the amount of homogeneous precipitation increase with the number of constituents.

In presence of MF, this effect is amplified by the magnetohydrodynamic effect especially for the homogeneous amount of precipitation (Fig. 2). The most important effect was observed for the Tygon pipe. This result is in agreement with the results observed by Amire and



Fig. 2. Effect of hardness of solution on (a) total and (b) homogeneous precipitation of CaCO₃ for a various material pipe (WMF: With Magnetic Field, WoMF: Without Magnetic Field). (*1*: WPTFE, *2*: PVC, *3*: Tygon).

Dadkhah [13] who suggested that MF increased the amount of impurities leaded by the Tygon pipe in solution and

2. Efficiency of magnetic field in the presence of foreign ions

The results obtained in absence of magnetic field and in presence of foreign ions, on the induction time, total amount of precipitation and the homogeneous amount of precipitation are presented on Table.

The results presented in this table showed that NaCl slow down nucleation and decrease the rate of total precipitation. The more the quantity of this salt is added, the more this effect is accentuated until reaching an *IS* of 0.02 M after which NaCl loosed its effect. For the homogeneous precipitation, the addition of NaCl hasn't any influence.

For the sulfate, the application of treatment, haven't great effect on the total precipitation some either the IS (~50%) but show a higher effect on the homogeneous

precipitation. This amount decreased from 19.5%, 11% for 0.015 and 0.027 M, respectively.

The presence of Mg²⁺ in solution prolongs the induction period of CaCO₃, which also increased with increasing Mg²⁺ concentration as observed by Tai and Chien [14]. Pokrovsky [15] showed, also, that the induction period of CaCO₃ increases with increasing Mg²⁺/Ca²⁺ activity ratio in solution. The increase in t_{ind} is due to an increase in the crystal-solution interfacial tension at higher Mg²⁺/Ca²⁺ ratio and due to an increase in the activity of Mg²⁺ at lower Mg²⁺/Ca²⁺ region. In our study the t_{ind} passed from 10 min, in absence of Mg²⁺, to 13 min for Mg²⁺/Ca²⁺ = 0.25 and reach 26 min for Mg²⁺/Ca²⁺ = 1.25.

The presence of MF causes further changes in the determined parameters. This effect depends on the nature and the concentration of the foreign ions used. Fig. 3 showed that MF reduces the nucleation time of CaCO₃ some either the composition or the *IS* of treated solutions. Moreover, the degree of MF effect on t_{ind} is water composition-dependent. Indeed, with respect to reference solution (pure calcocarbonic water), the effect

Effect of foreign ions on t_{ind} , total and homogeneous precipitation ratio of CaCO₃

Ionic Strength/M	Salt	Induction time $(t_{ind})/min$	Total precipitation (TP)/%	Homogeneous precipitation (TH)/%
0.012	_	10	72.5	22.8
0.015	NaCl	12	55	21.2
	MgCl ₂	13	50	20.1
	Na_2SO_4	13	53.6	19.5
0.0195	NaCl	16	52.5	20.4
	MgCl ₂	20	35	17
	Na_2SO_4	16	47.5	15.7
0.027	NaCl	16	50	18.6
	MgCl ₂	26	17.5	13.3
	Na_2SO_4	17	44	11.1

of MF on t_{ind} is more pronounced in presence of foreign ions until an *IS* value about 0.02 M. Beyond this *IS* value, MF effect on t_{ind} become less important. Also, it should be noted that MF effect on nucleation time is more important in the presence of Mg²⁺ or SO₄²⁻ ions.

For the *TP* of calcium carbonate in the presence of foreign ions, Fig. 4 presents the obtained results versus the tests made without magnetic field. This curves showed that *TP* decrease in the case of NaCl and this reduce is more important for the higher *IS*. The opposite effect is observed in the case of magnesium. While, in the presence of sulfate, the effect of MF is almost constant whatever the *IS*.

In Fig. 5 is presented the effect of MF treatment on homogeneous precipitation. It's shown that MF treatment favoured the precipitation of calcium carbonate in the bulk of the solution by homogeneous process. The presence of foreign ions inhibits his effect and a contradictory effect is registered for higher *IS* (>0.024 M) in the presence of Mg²⁺ and SO₄²⁻ ions.

4. Effect of magnetic field on the morphology of CaCO₃ formed in the presence of foreign ions

In Fig. 6 are reported the X-ray diffraction patterns for the $CaCO_3$ precipitated by degassing test, in the bulk of solution, in presence of NaCl, Na_2SO_4 or $MgCl_2$ for treated and untreated solutions.

It was shown that in the presence of NaCl, MF don't influence on the morphology of CaCO₃ precipitate either the concentration of NaCl added. In presence of magnesium, with application of MF, the amount of formed aragonite was increased and the precipitation of vaterite and calcite were inhibited. When the *IS* is high (*IS* > 0.02), only aragonite was precipitated. For the sulfate, the pattern of the deposit from the treated water shows that MF inhibits the formation of calcite for the high *IS* and favoured aragonite in the other case.

In this paper, it has been proved that magnetic water treatment has effect on calcium carbonate crystallization by increasing the total precipitate amount and by favoured its formation in the bulk-solution instead of its incrustation on the walls. It was, also, proved that water composition and its IS has a noteworthy effect on $CaCO_3$ precipitation. Magnetic filed effectiveness is foreign ions-dependent, this effect is inhibiting with the presence of NaCl and encouraged in the presence of magnesium whereas the sulfate has no effect. These observations are not valid for the obtained results of homogeneous precipitate. The main difference is that the homogeneous precipitation is inhibited with IS. The morphology of CaCO₃ formed with MF is influenced by the nature of foreign ions, MF has as effect to favour the precipitation of vaterite in the case of sulfate and NaCl and the precipitation of aragonite in the presence of magnesium.

This effect is explained by the magnetically modified hydration of ions and solid surfaces and Lorentz force





Fig. 3. Effect of *MF* on induction time of CaCO₃ in presence of foreign ions. (*1*: NaCl, *2*: MgCl₂, *3*: Na₂SO₄).



Fig. 4. Effect of *MF* on total precipitation ratio of CaCO₃ in the presence of foreign ions (*1*: NaCl, *2*: MgCl₂, *3*: Na₂SO₄).



Fig. 5. Effect of MF on homogeneous precipitation ratio of CaCO₃ in the presence of foreign ions (*1*: NaCl, *2*: MgCl₂, *3*: Na₂SO₄).



effects on ions and dispersed particles. Which effect would prevail depends on the magnetic treatment regime and on the composition of the treated system [16].

Bush *et al.* [17] have assumed that the Lorenz forces exerted on charged species induce local convection movements in the liquid which could contribute to accelerate associations between ions or colloidal particles. According to these authors, magnetohydrodynamic (MHD) phenomena induce eddy currents which flattened the fluid velocity profile in the tube. This effect would result in a larger velocity gradient, along the walls. In addition, the streaming potential along the walls which is velocity dependent should increase with the magnetic field. This phenomenon, by changing the surface charge, could throw out of balance the water composition equilibrium in the vicinity of the tubing walls [17–19].

MF effects were also often explained in terms of magnetically induced changes in the hydration of ions or solid surfaces. According to Lungader Madsen [20-21] MF induces faster proton transfer from hydrogen carbonate to water, due to proton spin inversion in the field of diamagnetic salts. The increased formation of CO_3^{2-} ions would explain the beneficial effect of MF on the amount of precipitate. Another explanation proposed by Higashitani et al. [22] is related to the specific influence of MF on the hydration of CO_3^{2-} ions which could directly modify the polymorph phase equilibrium during the precipitation. The same phenomenon could also affect the dehydration process of the ionic pair associations and the hydrated calcium carbonate forms which act as precursors for the formation of the anhydrous forms which constitute the calcium carbonate precipitate.

CONCLUSION

Permanent magnetic treatment (0.16 T) of duration 15 min of calcocarbonic solution in the presence of Na₂SO₄, MgCl₂ or NaCl affects properties of CaCO₃ formed. It appears in changes of induction period, total and homogeneous precipitation ratio of calcium carbonate formed by degassing test of treated solution. The effects depended on the kind of the foreign ions present in the treated water. This effect is, also, influenced by the hardness of water and by the nature of the pipe material. Finally, MF influence the morphology of calcium carbonate precipitate by increasing the precipitation of vaterite and aragonite in the presence of magnesium and by suppressed the formation of calcite.

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SUMMARY

The study of magnetic effect on the precipitation of calcium carbonate was widely studied. The main objective was to prevent the mineral scales deposits on the walls of industrial or domestic equipments. Magnetic water treatment for scale prevention has been around and has been reported as being effective in many instances. This investigation focused on MF effect on CaCO₃ in presence of foreign ions. Because of their

abundance in natural waters Mg^{2+} , SO_4^{2-} , Na^+ and $Cl^$ were chosen for this study. It was shown that MF application reduces the induction time (tind) some either the water composition or the ionic strength (*IS*). With respect to reference solution, the effect of MF on tind is more pronounced in presence of foreign ions until *IS* = 0.02 M. Beyond this value, MF effect on tind become less important. Moreover, it was shown that MF effect on total and homogeneous precipitation ratios decreases with IS increasing. This inhibitory effect of magnetic treatment, with *IS*, is water compositiondependent. The presence of NaCl has the most effect on total precipitation whereas MgCl₂ and Na₂SO₄ inhibit the precipitation of calcium carbonate in bulk of the solution. ISSN 1068-3755, Surface Engineering and Applied Electrochemistry, 2009, Vol. 45, No. 1, pp. 63–70. © Allerton Press, Inc., 2009. Original Russian Text © E.G. Sprinchan, 2009, published in Elektronnaya Obrabotka Materialov, 2009, No. 1, pp. 73–80.

ELECTRICAL PROCESSING **OF BIOLOGICAL OBJECTS** AND FOOD PRODUCTS

Optimization of Technological Regimes for Obtaining Protein–Mineral Concentrated Products from Secondary Milk Raw Materials

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Abstract—The state of the matter and urgency of milk whey recovery have been analyzed. The well-founded need for various combinations of processes for the purpose of obtaining optimal conditions is shown. The material balance of the main elements of ash and protein is presented. Methods for optimizing the electrophysical processing of milk whey and the characteristics of major technological parameters have been determined. Optimal conditions and anodic liquid compositions, as well as the type of diaphragm, have been selected. The aims of the further investigations for the full and wasteless recovery of milk whey for obtaining high quality products have been preset.

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One of the major problems in the diary industry as indicated by the International Diary Federation is complete and wasteless milk processing [1], which has important ecological relevance, which consists of using traditional technological methods for processing diary products.

The processes of separating milk and producing cream, butter, cheese, and crude and milk protein according to the existing techniques result in the formation of byproducts, such as nonfat milk, buttermilk, and milk whey, which are known as "secondary milk raw material." In accordance with the scientific data, the production of 1 t of butter yields about 20 t of nonfat milk and 1.5 t of buttermilk, while the production of 1 t of cheese and curd yields up to 9 t of milk whey [2]. Milk whey contains valuable milk components, namely, proteins, carbohydrates, vitamins, and mineral substances, and actually contains no fat. Whey has the least amount of calories and its biological value is very high because the most valuable protein fraction of milk in is retained in milk whey, i.e., soluble whey proteins and almost all lactose (Table 1).

The very high biological and chemical absorption of oxygen (BOA and COA coefficients -5) by milk whey after it has penetrated the environment is disastrous for flora and fauna, as, once the primary milk products are obtained, not only proteins, but also the substances of their partial (peptides) and full (aminoacids) hydrolysis pass into the whey. This is why, regardless of the place¹ and type of production or the season, milk whey requires

additional and wasteless recovery to reach the closed cycle completion of milk processing. This problem has become urgent over the past 10-15 years due to the increase in the output volume of milk products all over the world [4].

A great number of methods for the milk whey recovery are known that allow one to obtain protein concentrates, which are used as various additives, including biologically active substances. Recently, the preparation of various infant formulas based on protein concentrates recovered from the milk whey have become of great demand. Maternal milk contains up to 60% of whey proteins and 40% of casein protein [5]. However, the recovery of protein fractions for this aim requires that a certain regime be maintained in order to preserve the protein nativity and a high degree of purity. In addition to infant formula, which is produced based on demineralized whey, a great deal of food and feed products are also produced abroad. Because of their emulsifiability, the use of whey proteins in the confectionary industry has led to the creation of new kinds of products, including pastelike products.

Table 1. Milk whey protein fraction content [3]

Protein fraction	Dry content, %	Isoelectric point (pH)	Denaturation temperature, °C	
Lactate albumines:				
β-lactoglobulines,	7-12	5.3	60–90	
α-lactalbumines	2–5	4.2-4.5	60-100	
Albumines	0.7–1.3	4.7	75–90	
Immunoglobulines	1.9–3.3	5.5-6.8	75–90	

¹ E. G. Sprinchan, Surf. Eng. Appl. Electrochem., 2009, no. 1, pp. 73-80.

N order	Specimens	Volume, 1	Protein quantity, g	Ca, g	P, g	Na, g	K, g	Chlorides, g
1	IMW supplied into CC	0.66	12.57	0.41	0.54	0.52	1.17	0.89
2	Mixture of PMC and DW, which left the CC as a foam	0.25	2.81	0.08	0.08	0.17	0.60	0.29
3	DW that remained in CC after the process completion	0.36	3.67	0.05	0.05	0.24	0.56	0.36
4*	PMC and DW total mixture, which left CC and remained in it	0.61	6.48	0.13	0.13	0.41	1.17	0.64
5	IMW supplied into AC	0.39	4.17	0.12	0.12	0.51	0.69	0.51
6	Whey that left the cell and remained in AC after recovery process	0.41	3.80	0.08	0.08	0.17	0.24	0.33
7*	IMW, supplied into both cells	1.05	16.74	0.49	0.49	0.78	1.92	1.29
8*	Whey that left the cells and remained in both cells	1.02	10.29	0.21	0.21	0.58	1.40	0.97
9*	Membrane depositon	0.03	6.46	0.28	0.28	0.20	0.51	0.31

Table 2. Changes in protein quantity and main mineral components caused by IMW electrophysical processing in cathode (CC) and anode (AC) cells (g in a given volume)

* Presented calculation data.

The development and improvement of methods for milk whey recovery can be combined in the following main directions: thermal, chemical, dialysis, electrodialvsis, ion-exchange, and membrane methods, which, in turn, can be divided into reverse osmosis, ultrafiltration, diafiltration, microfiltration, and nanofiltration. All of these methods have their own advantages and drawbacks [6]. The thermal and chemical methods cause, correspondingly, the denaturation (at temperatures over 50° C) and contamination of proteins with chemical reagents, which reduce the biological value of the products obtained and narrows their applicability [7]. The application of highly effective but expensive membrane methods (ultrafiltration) allows one to recover the maximal quantity of protein. However, the smaller the membrane pores, the more expensive their exploitation. Furthermore, these methods involve a recurrent action, which leads to a decrease in the effectiveness of recovery [8]. One of the advantages of ion-exchange methods is their fractionation of whey protein. However, the carriers are expensive materials, and certain long-term, extra procedures are necessary for to restore ion-exchangers [9]. The electrodialysis method for the recovery of milk protein involves regular membrane regeneration, which is fairly power consuming [10].

An analysis of state of the matter has allowed us to reach the conclusion that the most effective method of milk whey protein recovery is application of techniques based on a combination of two or more methods.

RESULTS AND DISCUSSION

The purpose of the accomplished investigations is to optimize the electrophysical method of milk whey recovery, which is based on the electroactivation of liquid media, which is aimed at the wasteless recovery of the milk whey and obtaining high quality products [11]. Previously, electrophysical and biochemical data were presented that describe and characterize this method [12, 13], which allows one to recover about 60% of the proteins contained by the initial milk whey (IMW) in the form of protein-mineral concentrate (PMC) and, thus, to produce deproteinized whey (DW), which contains a greater amount of IMW aminoacids; fairly high percentage of lactulose, which is inverted from lactose during the process; and residual lactose.

Based on the balance calculation of proteins and ion migration through the membrane (the data on the main ash elements is obtained with the Beckman analyzer), as well as the analysis of their influence on the protein concentrate formation, one can say that, in the process of protein recovery into PMC as a foam, ions of calcium are mainly involved that, at certain values of pH medium, bind the protein molecules and react with their activated disulfide bonds (Table 2). In this case, on the surface of the membrane, as viewed from the side of the cathode cell (CC), thick, yellowish protein sediment forms, which as the results indicate, is formed by the phosphorus-containing ions. As a result of a gradual protein deposition, the blockage of the separating diaphragm occurs and the resistance increases, provoking an increase in voltage, which is usually observed by the end of the process (Tables 5 and 6). According to calculations of the protein content, which varies with the IMW supply to both cells, on the surface of the membrane, there is a considerable deposition of protein up to 6.45 g, which is about 51.4% of the whey protein supplied to the cathode cell and 38.6% of protein supplied to the electrolyzer. This rather serious drawback determined the necessity for finding conditions for the process that would allow either the reduction or complete elimination of protein deposition on the membrane. For this purpose, an elec-

N order Time, min		IMW(1)	10% CaCl ₂ in DW(2)	5% CaCl ₂ in IMW(3)	1% CaCl ₂ in DstW(4)	1% CaCl ₂ in DW(5)	1% CaCl ₂ in DW(6)				
			Temperature <i>t</i> , °C								
IMW	0	10	18	10	10	8	9				
1	5	16	22	12	12	9	11				
2	10	21	25	16	18	14	14				
3	15	24	28	20	21	18	19				
4	20	27	30	24	24	20	22				
5	25	30	32	28	28	30	26				
6	30	34	34	33	30	31	30				
7	35	36	36	36	35	31	34				
8	40	38	36	37	38	34	36				
9	45	41	37	37	38	34	36				
10	50		40	38	42	41	39				
11	55			37	44						
12	60				46						

Table 3. Change in temperature with various anodic liquid solutions (canvas membrane, flowing regime in both cells, liquid consumption of 5 ml/min)

Note: numbers of variants are in parentheses.

Table 4. Temperature changing with various membranes and anodic liquid compositions

	Membrane type		Canvas		UFM	MK-40	MK-40	
N	Regime		Flui	d flowing 5 ml/	min	•	Stationary	
order	Anodic liquid composition	IMW(1)	1%CaCl ₂ in DstW(2)	1%CaCl ₂ in DW(3)	IMW(4)	2%CaCl ₂ in DstW(5)	2%CaCl ₂ in DstW(6)	
	Time, min Temperature t, °C							
IMW	0	10	10	9	10	15	6	
1	5	16	12	11	18	18	12	
2	10	21	18	14	23	23	16	
3	15	24	21	19	28	26	23	
4	20	27	24	22	33	28	26	
5	25	30	28	26	31	31	30	
6	30	34	30	30	30	33	34	
7	35	36	35	34	31	34	36	
8	40	38	38	36	34	36	38	
9	45	41	39	38	34	38		
10	50		42	39	33	39		
11	55		44		33	41		
12	60		46			42		

trolyzer with a diaphragm has been developed and patented that allows one to clean a blocked membrane [14]. tral analysis. These ions mainly stay in the DW and partially remain in the membrane sediment [12].

Ions of potassium and natrium take no part in forming a protein concentrate, which is confirmed by their absence on the summary PMC spectrogram, which in turn is obtained by means of electron-probe X-Ray specThus, the additional selective supply of calcium ions, which is performed for the purpose of optimizing the presented method, should not only cause an increase in the percentage of protein recovery in PMC, but also a

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Ν	N Time, $IMW(1)$ 1		10% CaCl ₂ in DW(2)	5%CaCl ₂ in IMW(3)	1% CaCl ₂ in DstW(4)	1% CaCl ₂ in DW(5)	1% CaCl ₂ in DW(6)				
order	min			Voltage U, V							
1	5	28	15	20	26	24	24				
2	10	26	18	20	26	22	24				
3	15	26	18	18	25	21	23				
4	20	26	18	20	23	23	24				
5	25	27	18	24	24	25	26				
6	30	27	20	26	23	24	25				
7	35	27	20	22	26	23	24				
8	40	28	21	20	26	24	25				
9	45	28	21	20	26	25	25				
10	50		22	20	26	28	26				
11	55			18	27						
12	60				30						

Table 5. Variations in voltage with different solutions of anodic liquid (canvas membrane and a fluid flowing regime and liquid consumption of 5 ml/min in both cells)

Table 6. Variations in voltage with different membranes and anodic liquid compositions

	Membrane type		Canvas		UFM	MK-40	MK-40			
	Regime		Fluid flowing 5 ml/min							
N order	Anodic liquid composition	IMW(1)	1%CaCl ₂ in DstW(2)	1%CaCl ₂ in DW(3)	IMW(4)	2%CaCl ₂ in DstW(5)	2%CaCl ₂ in DstW(6)			
	Time, min			Voltag	e <i>U</i> , V					
1	5	28	26	27	35	19	27			
2	10	26	26	24	30	16	24			
3	15	26	25	23	32	26	22			
4	20	26	23	24	33	15	20			
5	25	27	24	26	31	15	20			
6	30	27	23	25	30	15	20			
7	35	27	26	24	31	15	19			
8	40	28	26	25	34	16	19			
9	45	28	26	25	34	16	19			
10	50		26	26	33	16	19			
11	55		27			17				
12	60		30			17				

decrease in the voltage and, correspondingly, power consumption.

Optimization has developed in the following directions:

1) alteration of anion liquid composition for the purpose of increasing the

protein yield and conserving the quality of DW for its further recovery.

2) changing the type of membrane in order to reduce power consumption and perform a preset process.

Calcium chloride solutions of different concentrations were supplied into the anodic cell (AC). IMW, DW, and distilled water (DstW) were used as a solvent. Canvas, ultrafiltration, and ion-exchange cationic MK-40 membranes served as diaphragms. The latter allows the migration of only positive ions. The experiments were performed at a current density of 0.02 A/cm² and approximately similar fluid flows in both cells. It seems inexpedient to optimize the protein recovery into PMC with an increase in the supply speed of IMW to CC, since the dilution of the whey being recovered reduces the per-

N order	Anodic liquid composition	IMW(1)	10% CaCl ₂ in DW(2)	5%CaCl ₂ in IMW(3)	1% CaCl ₂ in DstW(4)	1% CaCl ₂ in DW(5)	1% CaCl ₂ in DW(6)					
	Time, min		Medium pH									
IMW	0	4.65	4.90	5.20	5.20	4.70	5.30					
1	5	5.40	5.35	5.65	5.70	6.00	6.30					
2	10	5.95	6.05	6.45	6.15	7.00	7.10					
3	15	6.25	6.30	6.95	6.55	8.40	7.65					
4	20	7.55	6.45	8.35	7.00	10.20	9.05					
5	25	9.43	6.60	10.85	7.40	12.15	11.20					
6	30	10.93	6.95	11.45	8.90	12.45	12.25					
7	35	11.10	7.15	11.45	11.80	12.60	12.75					
8	40	11.30	7.00	12.95	12.25	12.85	12.85					
9	45		7.00	12.15	12.35	13.10	12.90					
10	50			12.20	12.45	13.00	12.95					
11	55			12.25	12.55							

Table 7. Changes in pH of the medium with various compositions of anodic liquid membrane (canvas membrane and a fluid flowing regime with a liquid consumption of 5 ml/min in both cells)

centage of protein yield. It should be noted that the use of calcium chloride solutions in various solvents as an anion liquid (AL) prevents the deposition of protein on the surface of the membrane as viewed from the CC side, which is similar to how it is observed in the tests with IMW supplied in AC; furthermore, a more intensive foaming is observed.

The main characteristics of the optimization processes are given below. Temperature characteristics, regardless of the dependence on the anion liquid composition and diaphragm type, produce no effect on the protein yield (Tables 3 and 4). However, in the recovery process, preliminary and continuous IMW cooling is strongly recommended in order to avoid approaching the low temperature threshold of denaturation.

It should be noted that the minimal denaturation temperature for milk whey proteins is 55–60°C. In all of the investigated tests variants, the processing temperature was kept within this range, which directly influenced the final quality of the obtained product due to the elimination of thermal denaturation.

Changes in voltage indicate the role of calcium ions in both the processes of protein recovery and power-consumption decrease. Varying voltage at different ion concentrations in AL solutions and with a canvas membrane demonstrates the presence of energy carriers (Table 5).

The processes that characterize membrane resistance are presented in Table 6. The application of different types of membrane vividly accentuates the importance of using the ion-exchange membrane.

The deposition of protein on the surface of a diaphragm is not observed with a canvas membrane and different composition of anion liquid, particularly with $CaCl_2$ solution in DstW. A more intensive foaming occurs, almost until the full volume of the operation cell is filled. It is evident that the intense migration of calcium ions through the diaphragm causes the formation of PMC. A considerable decrease in voltage (Table 6, variant 5) and a substantial increase in the percentage of protein content in PMC (Table 10, variant 5) are observed with the substitution of a canvas membrane for an MK-40 ion-exchange membrane.

In case of a high calcium chloride concentration, a minor increase in the active acidity (Table 7, variant 2) occurs with a change in the pH medium, probably due to the high content of chlorine ions or possibly chlororganic compounds. This is undesirable with the given method and requires the selection of an optimal concentration of CaCl₂ solution (Table 7, variants 3 and 4). In almost all variants, after 25–30 min, a sharp increase in pH from neutral to strongly alkaline values is observed. This is registered in both the cases of various compositions of anion liquid and with different types of membrane. The application of deproteinized whey as anion liquid causes a sharp increase in the active acid meduium in CC, probably due to the migration of univalent ions from the AC, which enriches DW with potassium and natrium ions.

Based on the data in Tables 9 and 10, one can see that the application of an MK-40 ion-exchange membrane and CaCl₂ solution allow one to increase the percentage of the protein yield in PMC up to 70%, to obtain deproteinized whey that contains no chemical reagents, and to reduce power consumption and the duration of the process to 10–20 min (Table 10, variant 5).

The fairly high content of lactulose in DW reveals the presence of the reaction of lactose isomerization in lactulose during electrophysical processing, which creates favorable conditions for its further recovery up to the full inversion of the residual lactose and, hence, the creation of a technique for wasteless milk whey recovery.

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	Membrane type		Canvas		UFM	MK-40	MK-40				
	Regime		Fluid flowing 5 ml/min								
N order	Anodic liquid composition	IMW(1)	1%CaCl ₂ in DstW(2)	1%CaCl ₂ in DW(3)	IMW(4)	2%CaCl ₂ in DstW(5)	2%CaCl ₂ in DstW(6)				
	Time, min	Medium pH									
IMW	0	4.65	5.20	5.30	4.60	5.20	4.65				
1	5	5.40	5.70	6.30	5.00	6.50	7.05				
2	10	5.95	6.15	7.10	5.93	7.15					
3	15	6.25	6.55	7.65	6.38	7.50	10.45				
4	20	7.55	7.00	9.05	7.40	8.55					
5	25	9.43	7.40	11.20	9.15	9.40					
6	30	10.93	8.90	12.25	10.20	10.65	10.95				
7	35	11.10	11.80	12.75	10.78	11.25					
8	40	11.30	12.25	12.85	10.93	11.45					
9	45		12.35	12.90	11.00	11.85					
10	50		12.45	12.95	11.15	11.90					
11	55		12.55								

Table 8. Changes in pH of medium with different membranes and anodic liquid compositions

Table 9.	Variations in t	he amount of	protein in	PMC using	different	solutions of	of anodic	liquid	(canvas i	membrane	and a fl	luid
flowing r	egime with a l	iquid consum	ption of 5	ml/min in t	oth cells))		-				

N order	Anodic liquid composition	IMW(1)	10% CaCl ₂ in DW(2)	5%CaCl ₂ in IMW(3)	1% CaCl ₂ in DstW(4)	1% CaCl ₂ in DW(5)	1% CaCl ₂ in DW(6)						
	Time, min		Protein content, Q, %										
IMW	0	0	0	0	0	0	0						
1	5	36	41	27	27	36	39						
2	10	44	45	34	31	41	45						
3	15	49	57	43	36	53	52						
4	20	54	58	49	41	50	54						
5	25	59	70	50	43	51	53						
6	30	62	81	52	50	53	58						
7	35	59		53	45	43	56						
8	40	59		66	44	51	57						
9	45	59		53	52	59	57						
10	50			54	50	57	56						
11	55			56	44								

OPTIMIZATION OF TECHNOLOGICAL REGIMES FOR OBTAINING

	Membrane type		Canvas		UFM	MK-40	MK-40
	Regime		Stationary				
N order	Anodic liquid composition	IMW(1)	1%CaCl ₂ in DstW(2)	1%CaCl ₂ in DW(3)	IMW(4)	2%CaCl ₂ in DstW(5)	2%CaCl ₂ in DstW(6)
	Time, min						
IMW	0	0	0	0	0	0	0
1	5	36	27	39	39	55	40
2	10	44	31	45	43	59	
3	15	49	36	52	48	60	52
4	20	54	41	54	50	67	
5	25	59	43	53	54	64	
6	30	62	50	58	57	70	35
7	35	59	45	56	56	65	
8	40	59	44	57	52	69	
9	45	59	52	57	53	70	
10	50		50		52	70	
11	55		44			66	
12	60					68	

Table 10. Variations in amount of protein in PMC with different membranes and anodic liquid solutions

Thus, conditions were selected that allow one to obtain qualitative products, i.e., protein-mineral concentrate and deproteinized whey with a high lactulose content. The present investigations are another step in the chain of optimization by means of various parameters and a combination of processing conditions according to the presented method for the purpose of obtaining ecologically pure and high-quality consumer products, in both the food and pharmaceutical industries. The development of a continuous operation device as a separate unit of the technological line in PMC and lactulose obtaining is a later objective to achieve.

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EQUIPMENT AND INSTALLATIONS

Selection of Operating Fluid for Electrodischarge Submersible Installations

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Abstract—The technique and results of experimental studies of high-voltage discharge in aqueous electrolytes and water–oil emulsions with a view to determine their applicability as operating fluids for closed electrode systems in high-voltage electrodischarge submersible installations are presented.

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INTRODUCTION

Operating fluid is one of the basic elements of any electrodischarge submersible installation, whose stability and efficiency of operation, as well as technology as a whole, depend on this medium. Therefore, a strict control of stability of its parameters is required. For example, for ground-based installations, such as ones for dressing a casting, where water is used as an operating fluid, an increase in electric conductivity of water from 0.067 to 0.083 S/m leads to a decrease in the processing rate by a factor of 1.5 [1]. In the given example, the increase in electric conductivity of water takes place owing to dissolution of salts contained in the sand mix; for recovery of the initial electric conductivity in the liquid, ion exchange resins are used. In other cases, when the object under treatment does not change electric conductivity of the medium, the discharge itself contributes to its variation because of erosion of electrodes and formation of nitrates [2, 3].

As applied to electrodischarge submersible installations (EDSIs) for treatment of oil, gas, and water-supply wells, the problem of properties of the operating fluid is of primary importance [4, 5], since very often there is no possibility to ensure an operating fluid with optimum properties in a well for efficient and stable operation of an EDSI. Therefore, often one has to be restricted to process liquids available in a well at the time; for example, in the cementing period, an argillaceous cement slurry is used [6]; in the period of intensification of oil-well stimulation, natural and industrial water–oil emulsions (WOEs) are used [7].

The variety of operating fluids, the uncertainty of their actual properties in conditions of deep wells and high temperatures, and their variation due to intense dissolution of deposits and fluid influx from production formations—all of these hinder high technology. A crucial way out of this situation is placement of the electrode system of an EDSI filled with operating fluid with the required parameters into an impermeable, acoustically transparent enclosure [8].

SUBSTANTIATION AND FORMULATION OF THE PROBLEM

In this context, it is of current concern to select media with such electrophysical properties that ensure a stable and effective breakdown as well as low variability of these properties, at least in the course of several thousand discharges. These liquids must be available, inexpensive, and environmentally safe.

For solution of the specified problem, electrophysical studies were carried out earlier where we compared the influence of hydrostatic pressure and temperature in a well on discharge ignition voltage in aqueous electrolytes of different electric conductivity and in WOEs with different water content [9, 10]. The studies showed, in particular, that the discharge ignition dependence on hydrostatic pressure for WOEs (at water content from 30 to 50%) is less pronounced in comparison with that for aqueous electrolytes; in addition, the discharge ignition voltage for WOEs is lower than for aqueous electrolytes. This gave occasion to recommend application of WOEs as an operating fluid. However, the operating experience has shown that, in the course of time, a WOE changes its parameters relatively quickly, leading to a decrease in efficiency and stability of operation of an EDSI.

Thus, there appeared the necessity to study the physics of phenomena and the dynamics of change in all basic quantities characterizing electric discharge under the influence of hydrostatic pressure and electric discharges for aqueous electrolytes and WOEs used as an operating fluid in the electrode systems of EDSIs.



Fig. 1. Oscillograms of (1) current and (2) voltage at the prebreakdown stage of discharge for aqueous electrolytes.

RESEARCH TECHNIQUE

For solution of the formulated problems, studies were carried out with application of the technique described in [11]. This technique is based on registration of amplitude–time values of prebreakdown currents and voltages in the interelectrode gap (see Fig. 1).

It is known that the current passing through an aqueous interelectrode gap, at the stage of discharge formation, has characteristic regions. The first region begins from the moment of voltage application to the interelectrode gap; in the current oscillogram (curve 1), it is shown as a region with the duration t_{PL} and the amplitude $I_{\rm PL}(t)$. This is the so-called preleader stage of discharge, during which the current flows from the bare parts of an electrode, and a primary leader is formed on the electrode. The second region begins from the moment of first leader formation (discharge ignition); this is the leader stage with the duration $t_{\rm I}$ and the circuit current $I_{\rm I}(t)$. It is also known that these currents are provided by ionic conductivity of aqueous electrolytes. At the end of the leader stage, bridging of the interelectrode gap by the leader channel occurs, and the active stage of discharge begins (dashed line).

In accordance with the technique, studies were carried out on stick electrodes under multiple breakdown discharges with the following ranges of parameter variations: the charge voltage U_0 , from 15 to 30 kV; the capacitor bank capacitance *C*, from 0.25 to 2 μ F; the hydrostatic pressure $P_{\rm HS}$, from 0.1 to 50 MPa; the operating-fluid temperature *T*, from 293 to 369 K; the stick-electrode rounded radius $r_{\rm EL}$, from 0.5 to 2.5 mm; and the interelectrode gap length $l_{\rm IE}$, from 10 to 18 mm.

The operating fluids were an aqueous electrolyte with the electric conductivity σ_0 in the range from 0.06 to



Fig. 2. Oscillograms of current (1) and voltage (2) at the prebreakdown stage of discharge for HESs.

0.33 S/m and a hydrophobic-emulsion solution (HES), simulating a WOE, prepared according to [12].

For each set of initial data, the experimental series consisted of five experiments (according to the number of selected levels of hydrostatic pressure). For statistical analysis of results, 15 to 20 oscillograms (n_i) were recorded in each experiment.

Since, in contrast to technique [11], two independent parameters are present in the given experiments, i.e., the hydrostatic pressure $P_{\rm HS}$ and the number of preceding discharges ΣN , then it appeared necessary to study correlation dependences of the quantities ($I_{\rm PL}$, $t_{\rm PL}$, $I_{\rm L}$, $t_{\rm L}$) on the indicated parameters for each series.

This analysis is based on the property of correlationcoefficient sign identity for dependent quantities upon a change in direction of variation in an independent parameter. For example, with respect to the parameter $P_{\rm HS}$, the sequence of experiments was ordered both in the direction of an increase and in the direction of a decrease in the hydrostatic pressure, while for the parameter ΣN , variations are possible only in one direction, of an increase.

MAIN PART

Aqueous electrolytes. Some experimental data representing the general tendencies of discharge evolution in aqueous electrolytes are presented in Table 1.

Hydrophobic-emulsion solutions. The studies performed showed a qualitative difference in characteristics at the prebreakdown stage for HESs in comparison with aqueous electrolytes. Characteristic oscillograms of current and voltage at the prebreakdown stage of discharge are shown in Fig. 2.
Series no. 1. $U_0 = 22.5$ kV; $T = 293$ K; $\sigma_0 = 0.33$ S/m; $r_{EL} = 1.5$ mm; $l_{IE} = 13$ mm									
experiment number	1	2	3	4	5				
P _{HS} , MPa	0.1	10	20	37	50				
$\Sigma N(+n_i)$, pieces	18	33(+15)	55(+22)	75(+20)	91(+24)				
I _{PL} , A	250	225	250	250	250				
$t_{\rm PL}, \mu s$	6.5	5.1	17.4	30.61	37.6				
I _L , A	1477	983	989	897	753				
$t_{\rm L}, \mu s$, μs 4.9		4.4	4.8	5.3				
Series no. 2. $U_0 = 22.5 \text{ kV}$; $T = 293 \text{ K}$; $\sigma_0 = 0.33 \text{ S/m}$; $r_{\text{EL}} = 0.5 \text{ mm}$; $l_{\text{IE}} = 13 \text{ mm}$									
experiment number	1	2	3	4	5				
P _{HS} , MPa	P _{HS} , MPa 50		20	10	01				
$\Sigma N(+n_i)$, pieces	$CN(+n_i)$, pieces 21		59(+18)	74(+15)	102(+18)				
$I_{\rm PL}, {\rm A}$	рг, А 200		200	200	180				
$t_{\rm PL}, \mu s$	ls 3.55		1.42	1.15	1.16				
I _L , A	1000	994	894	1075	1442				
$t_{\rm L}, \mu { m s}$	4.8	4.9	5.8	4.9	5.1				

 Table 1. Experimental data for aqueous electrolytes

 Table 2. Experimental data for hydrophobic-emulsion solutions

Series no. 1. $U_0 = 30$ kV; $T = 293$ K; $r_{EL} = 1.5$ mm; $l_{IE} = 10$ mm									
experiment number	1	2	3	4	5				
P _{HS} , MPa	0.1	10	20	37	50				
$\Sigma N(+n_i)$, pieces	11	25(+14)	40(+15)	52(+12)	70(+18)				
I _{PB} , A	161.7	133.8	112	99.3	76.1				
<i>t</i> _{PB} , μs 30.7		28.5 37.9		32.4	49.1				
Series no. 2. $U_0 = 22.5$ kV; $T = 293$ K; $r_{EL} = 0.5$ mm; $l_{IE} = 13$ mm									
experiment number	1	2	3	4	5				
P _{HS} , MPa 50		37	20	10	0.1				
$\Sigma N(+n_i)$, pieces 10		22(+12)	22(+12) 38(+16)		63(+15)				
I _{PB} , A	Г _{РВ} , А 247		250	247	205.5				
$t_{\rm PB},\mu s$	33	32	31.8	40.4	52.7				

The distinction was that the region corresponding to the preleader stage for aqueous electrolytes was absent on the current oscillogram. For an HES, the current begins from zero and increases similar to the current of the leader stage for aqueous electrolytes; therefore, it was initially identified as the leader current, the more so that at the end of this stage the interelectrode gap may be bridged by the channel of through conductivity (active stage, shown by dash). A decrease in the test voltage down to a few kilovolts leads only to an increase in the processes time, with no change in the characteristic form of the oscillogram.

With a view to distinguish the characteristics of aqueous electrolytes, let us denote this current (maximal value) as I_{PB} , prebreakdown current, and the stage duration as t_{PB} , prebreakdown time. The pattern of variation

in voltage for HESs is similar to behavior of voltage for aqueous electrolytes at the stage of the leader process.

Some experimental data corresponding to general tendencies of discharge evolution in HESs are presented in Table 2.

RESULTS AND DISCUSSION

According to the technique, correlation coefficients for the given experimental arrays were computed (by means of the Excel program); they are shown in Tables 3 and 4.

On the basis of the data of Table 3, one can state that such quantities as $I_{\rm PL}$, $t_{\rm PL}$, and $I_{\rm L}$ have a unique dependence on hydrostatic pressure (the data in columns of $P_{\rm HS}$ shaded in black), since upon a change in direction of variation in $P_{\rm HS}$ (it increases in series no. 1 and decreases

Series no. 1				Series no.2							
	P _{HS}	$I_{\rm PL}$	t _{PL}	IL	t _L		P _{HS}	I _{PL}	$t_{\rm PL}$	IL	t _L
ΣΝ	0.99	0.4	0.97	-0.87	0.38	ΣΝ	-0.98	-0.77	-0.9	0.76	0.24
$I_{\rm PL}$	0.37	1	0.56	0.07	-0.07	I _{PL}	0.65	1	0.43	-0.95	0
$t_{\rm PL}$	0.98	0.56	1	-0.73	0.46	t _{PL}	0.96	0.43	1	-0.41	-0.48
$I_{\rm L}$	-0.85	0.07	-0.73	1	-0.21	IL	-0.64	-0.95	-0.41	1	-0.26
t _L	0.48	0.07	0.46	-0.21	1	t _L	-0.32	0	-0.48	-0.26	1

 Table 3. Correlation coefficients for the data of Table 1

in series no. 2) the correlation coefficients have not changed sign. Moreover, this dependence is significant, because the correlation coefficients have values (in absolute magnitude) close to one (0.98 for $t_{\rm PL}$ and -0.85 for $I_{\rm L}$). The plus sign preceding the correlation coefficient means that, at an increase in the parameter, the studied quantity increases; the minus sign means that it decreases. In this respect, one can state that an increase in hydrostatic pressure leads to an increase in the preleader time $t_{\rm PL}$ and to a decrease in the leader current $I_{\rm L}$ (maximal value), which is due to suppression of the leader system and a decrease in its degree of branching.

The dependence of the quantity I_{PL} on hydrostatic pressure becomes apparent too, although to a lesser extent. To all appearances, here we deal with the response to the well-known fact of an increase in electrolyte conductivity at an increase in hydrostatic pressure [13]. The result, being somewhat unusual to understand, is that the quantity t_L does not depend on hydrostatic pressure at all (since the coefficient has changed sign, the data in columns with P_{HS} are not marked).

As regard to the parameter ΣN , the quantities I_{PL} , t_{PL} , and I_L do not exhibit any dependence (the data in rows of ΣN without marking), since at constant direction of variation in ΣN (increase in series no. 1 and no. 2) the correlation coefficients have reversed sign. However, the quantity t_L exhibits a weak correlation with respect to the parameter ΣN (the data in rows of ΣN shaded in gray); as may be supposed, this is due to heating of the liquid in the course of increasing number of discharges.

On the basis of Table 4, it may be established that the quantities I_{PB} and t_{PB} do not exhibit a unique dependence on hydrostatic pressure (the data in columns of P_{HS} without marking), because upon a change in direction of variation in P_{HS} (it increases in series no. 1 and decreases in

Table 4. Correlation coefficients for the data of Table 2

	Series	s no. 1		Series no. 2				
	P _{HS}	I _{PB}	t _{PB}		P _{HS}	I _{PB}	t _{PB}	
ΣΝ	0.99	-0.99	0.81	ΣΝ	-0.99	-0.73	0.84	
$I_{\rm PB}$	-0.97	1	-0.78	$I_{\rm PB}$	0.66	1	-0.94	
$t_{\rm PB}$	0.78	-0.78	1	$t_{\rm PB}$	-0.79	-0.94	1	

series no. 2) the correlation coefficients have changed sign. With respect to the parameter ΣN , the quantities I_{PB} and t_{PB} exhibit a dependence (the data in rows of ΣN shaded in gray), since at constant direction of variation in ΣN (increase in series no. 1 and no. 2) the correlation coefficients have not changed sign; in addition, the dependence is significant, with coefficients up to -0.99 and 0.84, respectively.

The qualitative behavior is as follows: at an increase in number of discharges, the prebreakdown time t_{PB} increases and the prebreakdown current I_{PB} decreases.

The absence of any dependence of prebreakdown characteristics on hydrostatic pressure for HESs points to another physical picture of phenomena in the interelectrode gap as compared to aqueous electrolytes; in particular, there are no phase transformations of fluid (ebullition), being sensitive to external pressure, or availability of the leader system (ionization in the vapor–gas phase) in terms of the physics of breakdown.

Studies [14, 15] will help us to understand the processes taking place in a WOE under applied electric fields; the mechanism and law of the current flow through the interelectrode gap are specified in these papers.

WOEs are stable two-phase systems consisting of a base fluid—medium, being an oil product—and a phase distributed in it—small water drops (globules). Since the specific resistivity of an oil product is from 10^6 to 10⁹ Ohm m, and more conductive drops are disconnected in space, in totality the specific resistivity of an emulsion is high; therefore, upon application of a potential difference to the interelectrode gap, the initial electric current is very low. That is, initially, current carriers are almost absent in WOEs, whereas they are always present in aqueous electrolytes. After a certain period of time, determined mainly by the level of applied voltage, an electric current starts flowing through the interelectrode gap. This current is due to spatial motion of a great number of water globules, each of which carries a charge, which appears on them owing to the acting field. However, in the process of motion, globules collide with each other, coalesce, coagulate, and deposit on the bottom of a chamber during some time; they do not take part in current transport any more. Thus, if a direct-current voltage is applied to the interelectrode gap, then, over a period of time, the current grows at first and decreases afterwards, having a dome shape. The physical condition of the fluid is characterized by a continuous variation in globule concentration, its decrease, i.e., by variation in properties of the emulsion in time in the direction of a decrease in its electric conductivity.

In strong electric fields, the process of globule coalescence is more intense owing to high-power polarization of the globules. Coalesced and coagulated globules have no time to leave the interelectrode gap; they elongate and bridge the interelectrode gap, resulting in an electric breakdown.

The influence of a pulsed electric field on emulsion is similar to short-term action of a stationary field. After the pulse action has terminated, the system maintains its previous state; that is, pulse-to-pulse integration of the electric field action takes place.

The decrease in the current I_{PB} with increasing number of pulses (time of coagulation and deposition) and the increase in the time t_{PB} observed in our experiments result from integration of the state of globule concentration decrease to the extent of their complete settling out.

Thus, with respect to the phase state of a WOE placed into an electric field (direct-current, alternating-current, pulsed one), one can state that it necessarily changes in the direction of the emulsion breaking into oil and water constituents.

Moreover, in the given situation, two cases may occur: (a) the high-voltage electrode, being at the top, is washed by a dielectric liquid (dehydrated oil), which may cause overvoltage and insulation failure; (b) the high-voltage electrode is washed by strongly electroconductive deposited water, which will lead to breakdownfree discharges.

CONCLUSIONS

(i) The basic discharge characteristics in aqueous electrolytes have stable correlations with such a parameter as hydrostatic pressure; they do not depend on treatment time (in the studied range). This is due to internal physical interrelation of the processes; therefore, it is stable and allows predicting the behavior of some parameters of action with the use of empirical relations [16] with a view to exercise stable and high-performance modes of operation of EDSIs.

(ii) Discharge characteristics in WOEs depend both on time and intensity of electric field action and on total time of emulsion settling out, which does not allow predicting its state with a view to exercise stable and highperformance modes of operation of EDSIs.

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OPERATING EXPERIENCE

Simulation of the Process of Heating of Cylindrical Glass Fiber Plastics by Methods of Exposure to Radiation

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Abstract—The proposed model allows analyzing the process of heating of cylindrical glass fiber plastics KT-11-TOA with the application of energy of accelerated electrons. It is found that the model facilitates selection of the optimum temperature and cuts the running time of experiments.

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The application of energy of accelerated electrons for hardening of polymer composite materials makes it possible to intensify the hardening process significantly. There are complications in optimization of temperature conditions. One of the ways to solve the formulated technological problem is to construct a mathematical model of thermal processes in glass fiber plastics in the course of radiation hardening [1].

In this work, we studied the process of heating of glass fiber plastics KT-11-TOA+LBS-4 with a thickness from 0.5 to 10 mm by accelerated electrons.

The problem was formulated as follows. An infinite cylinder with the inner radius r_1 and the external radius r_2 revolves about its axis at the constant angular rate ω (Fig. 1). Outside of it, there is an electron-emitting source that irradiates it with a parallel beam of set width b, stimulating heating. The heat source power Q per unit length of the cylinder may be controlled by the electron energy E and the beam current I. Heated parts of the cylinder transfer heat to cold parts owing to the process of heat conduction.

For solution of the problem of temperature distribution in cylindrical glass fiber plastics, the heat conduction equation is used [2]

$$\rho c \left(\frac{\partial T}{\partial \tau} + \omega \frac{\partial T}{\partial \phi} \right)$$

$$= \frac{\partial}{\partial r} \left(\lambda \frac{\partial T}{\partial r} \right) + \frac{\lambda \partial T}{r \partial r} + \frac{1}{r^2} \frac{\partial}{\partial \phi} \left(\lambda \frac{\partial T}{\partial \phi} \right) + q,$$
(1)

where *T* is the temperature, K; τ is the heat conduction coefficient, W/m²; ρ is the density, kg/m²; *c* is the heat capacity, kJ/kg; *r* and φ are the radial and circumferential coordinates; and *q* is the heat released owing to electron irradiation.

For description of the process of cylinder heating by an electron beam, we have the third-order boundary conditions on the inner surface

$$\left. \lambda_r \frac{\partial T}{\partial r} \right|_{r=r_1} = \alpha_{k_1} (T_f - T_c), \tag{2}$$

and on the outer surface

$$-\lambda_r \frac{\partial T}{\partial r}\Big|_{r=r_2} = (\alpha_{k_2} + \alpha_r)(T_f - T_c), \qquad (3)$$

where T_f is the surface temperature; T_c is the temperature of the environment, K; α_{k_1} and α_{k_2} are the preassigned convection heat transfer coefficients; and α_r is the radiation coefficient.



Fig. 1. Diagram of the process of cylinder exposure to radiation by accelerated electrons.



Fig. 2. Construction of the finite-difference net.

Currently available methods for solution of boundary value problems may be classified with respect to various attributes [2].

The temperature distribution in the cylinder was determined by us using the method of separation of variables, on the hypothesis that the physical parameters and the heat conduction coefficients λ_{r} , λ_{ϕ} , and λ_{z} do not depend on the coordinates. The goal in solving the problem is evaluating the solutions obtained by other methods; therefore, we consider the given hypothesis justified.

The analytical solution of the given problem in the general case is presented in [3]; according to it, we obtain the following expression for distribution of the temperature T in the cylinder:

$$T(\tau, r, \phi) = T_1(\tau, r, \phi) + T_2(\tau, r, \phi) + T_3(\tau, r, \phi), \quad (4)$$

where $T_1(\tau, r, \phi)$ is the term depending on initial temperature, $T_2(\tau, r, \phi)$ is the term depending on the boundary conditions on the inner and outer surfaces of the cylinder, and $T_3(\tau, r, \phi)$ is the term describing the heat released by decelerated electrons.

The numerical solution is carried out by the method of finite differences (net–point methods). A range of continuous variation of the arguments is replaced with a computational net—a discrete set of points (nodes). Instead of a function of continuous arguments, we introduce functions of discrete arguments, i.e., network functions determined in network nodes. Partial derivatives appearing in the differential equation and boundary conditions are replaced (approximated) with differential correlations. As a result of this replacement, a boundary value problem with partial derivatives is reduced to a system of difference (algebraic) equations. For the cylinder, the finite-difference net looks as follows (Fig. 2):

$$i = 1, 2, ..., P + 1; h_{Z_1} = \frac{1}{P} \ln \frac{Z_1}{Z_0}; j = 1, 2, ..., N + 1;$$
$$h_{Z_2} = \frac{1}{N} \ln \frac{Z_2}{Z_1}; m = 1, 2, ..., M; h_{\varphi} = \frac{2r}{M}; k = 1, 2, ...;$$
$$h_x = \frac{\tau_k}{L},$$

where P and N are the partition numbers in the radial direction for the inner and outer cylinders, M is the partition number in the circumferential direction, and L is the number of time intervals.

It is known that the highest stability is found for an implicit difference scheme, where in transition from the time layer k to the time layer k + 1, discretization for space variables occurs for the layer k + 1. It looks as follows:

$$\frac{T_{i,m}^{k+1} - T_{i,m}^{k}}{h_{\tau}} + \omega \frac{T_{i,m}^{k+1} - T_{i,m-1}^{k+1}}{h_{\phi}} = \frac{\lambda_{r}^{(1)}}{e^{2zi}\rho_{1}c_{1}} \\
\times \left(\frac{T_{i+1,m}^{k+1} - 2T_{i,m}^{k+1} + T_{i-1,m}^{k+1}}{h_{z}^{(1)2}}\right) \\
+ \frac{T_{i,m+1}^{k+1} - 2T_{i,m}^{k+1} + T_{i,m-1}^{k+1}}{h_{\phi}^{2}}\right) + \frac{g_{i,m}}{\rho_{1}c_{1}}; \\
\frac{T_{j,m}^{k+1} - T_{j,m}^{k}}{R_{\tau}} + \omega \frac{T_{j,m}^{k+1} - T_{j,m-1}^{k+1}}{h_{\phi}} = \frac{1}{e^{2zi}\rho_{2}c_{2}} \\
\times \left(\lambda_{r}^{(2)} \frac{T_{ji+1,m}^{k+1} - 2T_{j,m}^{k+1} + T_{j-1,m}^{k+1}}{h_{z}^{(2)2}}\right) + \frac{g_{j,m}}{\rho_{2}c_{2}}.$$
(6)

Here, formula (5) refers to an arbor; formula (6), to a composite. Since the arbor is taken to be of an isotropic material, λ_r and λ_{ϕ} are equal for it.

At boundary node points, finite-difference correlations are presented as follows. On the bottom edge of the arbor or of the composite in the absence of an arbor,

$$T_{1,m}^{k+1} = \frac{T_c + T_{2m}^{k+1} a_{1,m} + \frac{q_1 m}{\rho c}}{1 + a_{1,m}},$$
(7)

where $a_{1,m} = \frac{\lambda_r}{\alpha_{k_1} h_z e^z}$.

Here, the variables T_c , ρ , c, q, λ_r , and h_z have indices (1) for the arbor and (2) for the composite. The quantity



Fig. 3. Temperature distribution in the rotating cylinder in the course of hardening of glass fiber plastics by accelerated electrons (result of numerical solution).

 $\exp(z)$ takes the values $\exp(z_0)$ for the arbor and $\exp(z_1)$ for the composite. The term *c q* is added with a view to impart more persistence to the scheme, i.e., ability to correspond to the energy conservation law.

On the top edge of the composite,

$$T_{N+1,m}^{k+1} = \frac{\frac{qN_1m}{2\rho_2c_2} + T_c^{(2)} + T_{N,m}^{k+1}a_{N+1,m}}{1 + a_{N+1,m}},$$
(8)

where $a_{N+1,m} = \frac{\lambda_z^2}{(\alpha_{k_2} + \alpha_r)h_{z_2}e^{z_2}}$.

Analysis of temperature fields in the glass fiber plastic cylinder hardened by accelerated electrons, conducted by the described techniques, has shown that the given model may be significantly simplified and reduced to a form convenient for engineering application.

The studies carried out for the above-considered numerical and analytical models, describing the process of temperature distribution in real cylinders due to irradiation of the latter with electrons, have shown that the terms of the differential equation depending on λ make an insignificant contribution to the process under consideration. This makes it possible to simplify the differential equation. If the cylinder is represented by a one-dimensional line, then the temperature balance at a point on this line is determined by heat input due to heating by electrons and heat dissipation from the external and bottom

surfaces. The temperature balance equation in the Langrangian coordinate system may be written in the form

$$\rho c \frac{dT}{d\tau} = q - \frac{(\alpha_{k1} + \alpha_{k2} + \alpha_{r})(T - T_c)}{r_2 - r_1}, \qquad (9)$$

where α_r is the radiation coefficient, which is determined by the Stefan–Boltzmann law and depends on the body temperature *T*, the temperature of the environment T_c , and the emissivity factor ε ; α_{k1} and α_{k2} are the preassigned convection heat transfer coefficients; and r_1 and r_2 are the radii of the inner and outer surfaces of the cylinder, respectively, mm.

Equation (9) is an ordinary first-order differential equation.

As time goes by, the process becomes independent of the number of cylinder revolution n. The formulas for cylinder temperature in such a quasistationary process have the form

$$T_{\rm st}^{\rm beg} = T_c + \frac{q \left[1 - \exp(-\gamma \psi)\right] \exp[-\gamma (2\pi - \psi)]}{\left[1 - \exp(-2\pi\gamma)\right]}.$$
 (10)

The numerical calculation was made for cylindrical glass fiber plastics with a thickness from 0.5 to 10 mm, with a step of 0.1 mm, with a time variation of 10 s per interval for the following initial data: b = 0.08 m; $\omega = 0.7 \text{ s}^{-1}$; $\lambda = 0.271$ W/(m K); c = 1.08 kJ/(kg K); $\rho = 1950$ kg/m²; $\varepsilon = 0.65$; $\alpha_{k1} = 40$ W/(m K); $\alpha_{k2} = 22$ W/(m K); E = 1.1 MeV; I = 7 mA; eps = 1×10^{-5} .

The following discretization parameters are taken: N = 15; M = 40; L = 100.

Figure 3 depicts the temperature distribution in the course of hardening of cylindrical glass fiber plastics by accelerated electrons.

The studies have shown that, in the course of hardening of cylindrical glass fiber plastics by accelerated electrons, the set temperature is maintained in the material to a thickness of 2 mm. As the thickness grows, the temperature decreases.

Thus, by means of the developed mathematical model, the temperature distribution in a composite depending on the thickness of glass fiber plastics is determined. This simplifies selection of the optimum temperature and cuts the running time of experiments.

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