Electrolytic alloying of iron-chromium during deposition of coatings from a sulfate-chloride electrolyte

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Abstract. The paper presents the results of studies of the process of electroreduction of alloy iron-chromium from a sulfate-chloride electrolyte, influence of electrolyte composition and electrolysis (acidity, electrolyte temperature and cathode current density) on the process kinetics, the output of the alloy current efficiency and physico-mechanical properties of the coatings (microhardness, morphology). There were determined such parameters as the optimal ratio of concentrations of electrolyte components – 150 g/l of iron chloride (2) and 50 g/l of chromium sulfate (3) and modes of electrical recovery of metals – current density 40 A/dm²; the temperature of the electrolyte is 50°C, the acidity of the solution is 0.5 pH units, which contribute to obtaining a high-quality coating with high tribological characteristics. Assumptions are made about the mechanism of the alloy formation by electrolysis from a mixed electrolyte.

1. Introduction
Currently, when repairing cars, the cost of spare parts is more than 50% of all costs. Restoration of worn parts can significantly reduce these costs, reduce the cost of repair and maintenance of machines, free up significant production capacity of the industry that manufactures spare parts and save metal used for these purposes.

As evidenced by the practice of renovation of machinery and equipment, the most cost-effective way to restore worn-out machine parts is galvanic metal build-up and, first of all, iron plating. Electrolytic iron, due to the high productivity of the process and the possibility of obtaining a coating with pre-defined physical and mechanical properties, is becoming increasingly common in the repair industry. However, the coating of electrolytic iron is inferior to chrome due to its insufficient microhardness and wear resistance. At the same time, iron plating allows the restoration of parts from environmentally friendly electrolytes in comparison with the use of toxic electrolytes based on hexavalent chromium compounds for chrome plating.

Iron-based alloys are a promising compromise between high deposition rate of electrolytic iron and wear-resistant chromium coating. Moreover, electrolytic alloys, in contrast to alloys obtained by metallurgical methods, have fine-grained properties and phase stability [1]. However, when selecting components for the deposition of a future alloy, it is necessary to take into account that the joint deposition and crystallization of two or more metals with the formation of alloys is possible in cases where their equilibrium potentials differ slightly from each other [2, 3].

The most widespread in the practice of repair production are ferric chloride electrolytes, from which coatings with high physical and mechanical properties and current output are deposited. At the same
time, solutions of iron (2), chromium (3) and other metal chlorides have the property of unstable composition due to rapid oxidizability, aggravated by the use of high temperature during electrolysis. Sulfate electrolytes are largely devoid of these disadvantages, but their widespread industrial use is hindered by the relatively low productivity of the deposition process.

In our opinion, the use of mixed sulfate-chloride electrolytes is a compromise solution to the problem of applying a high-quality coating that has reliable operational properties and high process productivity. The analysis of the literature data on the compositions of mixed electrolytes used to produce the iron-chromium alloy [4] shows that the kinetics of the Fe-Cr alloy deposition process, the effect of various additives and modes of co-deposition of metals in the alloy are insufficiently studied.

The purpose of our research was to search for and optimize the composition of mixed sulfate-chloride electrolyte, electrolysis modes, and identify the mechanism of deposition of high-quality iron-chromium alloy coatings that meet the operational requirements of the surface to be restored.

2. Materials and methods

To study the deposition process of the iron-chromium coating, a sulfate-chloride electrolyte was prepared by mixing solutions of chromium sulfate and iron chloride in various proportions. The ferric chloride solution prepared by known methods [4], a solution of chromium sulfate – by dissolving a solid of hydrated chromium sulfate (3) in acidified water followed by bringing the acidity of the electrolyte to a predetermined pH by using 1 n HCl solution. The content of Fe$^{2+}$, Fe$^{3+}$, and Cr$^{3+}$ cations in the electrolyte was monitored by potentiometric titration according to the approved method [5]. For the preparation of electrolytes, reagents of the "H" and "HCH" qualification were used.

Coatings were applied at direct current to cylindrical samples made of steel 20 with a surface area of 0.001 m$^2$. Before electrolysis, the samples were degreased with Viennese lime, and then anodically etched in a 30% aqueous solution of sulfuric acid, followed by washing in running water for 20 seconds.

To power the electrolyzer, a DC source was used, a VU-42/70A rectifier with a two-half-period current rectification circuit. In the studies, the current density was changed using the RNT voltage regulator. The current in the circuit was measured by an ammeter M–104 CL. 0.5. the temperature of the electrolyte was changed from 30 to 50°C, and the acidity – from 0.2 to 1.2 pH units.

Heating and temperature control of the electrolyte was carried out in a thermostat with an accuracy of 0.1°C using a thermorelet. The working volume in the cell was 2 liters. The acidity (pH) of the electrolyte was controlled using a pH meter Smart Sensor model AS218 with a measurement accuracy of 0.01 units. calibrated with standard buffer solutions.

To ensure a strong adhesion of the galvanic Deposit to the sample surface, the cathodic current density at the beginning of the electrodeposition process was gradually increased from 2 A/dm$^2$ to the set value for 10 minutes. The deposition time of the coating was 1 hour, taking into account the "acceleration".

The current yield of the metal was determined by gravimetric method. The value of the electrochemical equivalent of deposition of the iron-chromium alloy (at a chromium concentration in the coating of 18 %) is 0.971 g/A·h [6]. Samples were weighed before and after coating on a VLR–200 scale with an accuracy of 0.01 mg. The deposition rate of the iron-chromium alloy was determined by measuring the coating thickness with a micrometer MK 0-25 mm (GOST 6507-60) by the diameter of the sample in its middle part before and after deposition. When calculating the speed of the process from the deposition time, taking into account the loss of sample thickness during etching, the time to enter the operating mode was not taken into account.

The morphology of the coating was studied using a metallographic microscope (MMU–3) with magnification multiplicity of 250, 620, 990, with information output to a personal computer and image processing by S-EYE software version 1.6.0.11. the microhardness of the coating was measured on a PMT-3 microhardness meter with an indenter load of 100 g (1H), followed by measuring the size of the print diagonal and calculating the microhardness using a well-known method [5].

Polarization studies were performed in galvanostatic mode on a P5848 potentiostat in an electrochemical cell YASE–2 with platinum indicator and auxiliary electrodes and a silver-chloride
reference electrode. The current sweep time was 750 s, the potential of the working electrode was measured with an electronic multivoltmeter with an accuracy of 0.01 mV and a fixation frequency of 1 Hz, with constant transfer of information to a personal computer. Registration of multi-voltmeter readings was performed by the software "UT61C_D" V3.03.

3. The study of the structure of the modified lead-tin-base bronze

At the first stage of research, it was necessary to select the composition and concentration of the base electrolyte. According to the analysis of the literature data, all previously studied electrolytes used ferrous iron chloride or sulfate and trivalent chromium chloride or sulfate to produce the Fe-Cr alloy. Our research on the stability of electrolytes of different compositions to oxidation and their electrical conductivity allowed us to conclude that a mixed sulfate (chromium) – chloride (iron) electrolyte is the most effective and stable in quality composition. To determine the quantitative ratio of the components, their concentrations were varied widely: FeCl₂ – 50–200 kg/m³, Cr₂(SO₄)₃ – 10–100 kg/m³. Moreover, in all electrolytes, one of the components was always present in the predominant amount: it could be either a sulfate compound or a chloride one. Based on our research (resistance to oxidation, to the formation of colloidal precipitation, electrical conductivity of solutions), we adopted a mixed sulfate-chloride electrolyte with a predominant concentration of ferrous iron (FeCl₂) as the basis. To determine the optimal quantitative ratio of Fe(2):Cr(3) components in a mixed electrolyte, polarization studies were conducted to assess the effect of the component concentration, acid balance, and electrolyte temperature on the reduction potentials of chromium (3) and iron (2) ions in pure and mixed electrolytes (figures 1, 2, and 3).

Figure 1 shows the dependences of the electrode potential on the current density obtained in chromium sulfate electrolytes with a chromium sulfate concentration of 25-100 g/l and an interval between the studied concentrations of 25 g/l (curves 1-4, respectively); in iron chloride electrolytes with iron chloride concentrations of 100-200 g/l and an interval of 50 g/l (curves 5-7, respectively), as well as in a mixed electrolyte of the composition: 150 g/l FeCl₂ and 50 g/l Cr₂(SO₄)₃ (curve 8). Studies were performed at a temperature of 40°C and pH=0.6.

Analysis of figure 1 shows that the potential of the chromium electrode (curves 1-4) has shifted to the negative region relative to its equilibrium value (φ (for Cr³⁺) = – (0.35±0.45) mV, while in a highly acidic environment the equilibrium potential of the platinum electrode for chromium \( \Delta \phi_{\text{eq}} \) (Cr³+/Cr) = 50 mV) and practically does not depend on either the concentration of the metal cation or the current density. A simple calculation shows that the electrode was polarized by the value \( \Delta \phi_{\text{pol}} \) (for Cr³⁺) = 85±95 mV.

The potential of the electrode for iron (curves 5-7) turned out to be more positive in comparison with its equilibrium value (φ (for Fe²⁺) = -(220±260) mV, and in a strongly acidic medium \( \Delta \phi_{\text{eq}} \) (for Fe²⁺/Fe) = -320 mV), and there are noticeable potential fluctuations both depending on the concentration of the Fe²⁺ ion and when the current density changes. The electrode polarization for iron \( \Delta \phi_{\text{pol}} \) (for Fe²⁺) was – (60±100) mV, bringing it closer in value to the opposite sign of the polarization for chromium, which indicates the presence of a common factor of displacement of metal potentials from their equilibrium values. With the combined presence of iron and chromium ions in a mixed electrolyte (curve 8), the potential of the electrode is further shifted to the positive range, indicating their mutual influence and participation in the electrolysis process, and at the same time practically does not react to changes in the current density.

From our point of view, the common factor of electrode polarization in strongly acidic electrolytes of chromium and iron plating is the discharge of hydrogen ions (H3O⁺) combined with metal cations. We believe that the behavior of the electrode in the chromium electrolyte is due not only to the step discharge of the chromium cation Cr³⁺ and its intermediate hydrate (due to hydrolysis) compounds together with the hydrated hydrogen ion H3O⁺, but also to the preferences for the H3O⁺ cation under these conditions (due to the low hydrogen overvoltage on platinum). The following process scheme is possible:

\[
\begin{align*}
\text{Cr}^{3+} + \text{H}_2\text{O}^+ + \text{e}^- &= \text{Cr(OH)}^{2+} + \text{H}_2; \\
\text{Cr(OH)}^{2+} + \text{H}_3\text{O}^+ + \text{e}^- &= \text{Cr(OH)}_2^+ + \text{H}_2; \text{Cr(OH)}_2^+ + \text{H}_3\text{O}^+ + \text{e}^- &= \text{Cr} + \text{H}_2 + 3\text{OH}^-.
\end{align*}
\] 

(1)
As can be seen (curves 1-4), at low current densities (2-30 A/dm²), the release of hydrogen at the cathode from the chromium electrolyte prevails with a slight fluctuation in the concentration of Cr³⁺, and subsequently, the chromium surface is also deposited on the chromium surface for the same reason of low hydrogen overvoltage on chromium.

At the same time, during electrolysis from a strongly acidic iron electrolyte (curves 5-7), even with a step discharge of Fe²⁺ and its hydroxo compounds together with H₂O⁺, metal wins in their competition (due to the high overvoltage of hydrogen on the deposited iron after a current density of 10 A/dm²). The scheme of the process is already different: Fe²⁺ + H₂O⁺ + ē = Fe(OH)⁺ + H₂;

\[ 2\text{Fe(OH)}^\cdot + ē = \text{Fe} \cdot \text{Fe(OH)}^\cdot; \text{Fe} \cdot \text{Fe(OH)}^\cdot + ē = 2\text{Fe} + \text{OH}^- \].  

(2)

A shift to the region of more positive values of the electrode potential in a mixed electrolyte (figure 1, curve 8) indicates the formation of associative hydrolysis complexes of iron and chromium with a solvent in their joint presence according to the scheme:

\[ \text{Fe}^2^+ + \text{Cr}^3^+ + 8\text{H}_2\text{O} \leftrightarrow \text{Fe}[\text{Cr(OH)}]_4^+ + 4\text{H}_2\text{O}^+. \]

(3)

![Figure 1](image1.png)

**Figure 1.** Effect of component concentration at tel=40°C and pH=0.6 on the value of the potential of the platinum electrode depending on the cathode current density in the chromium sulfate electrolyte (curves 1-4); in the iron chloride electrolyte (curves 5-7) and in the mixed sulfate–chloride electrolyte (curve 8) at concentrations (g/l): 1) Cr₂(SO₄)₃–100; 2) Cr₂(SO₄)₃–75; 3) Cr₂(SO₄)₃–50; 4) Cr₂(SO₄)₃–25; 5) FeCl₂–150; 6) FeCl₂–100; 7)

![Figure 2](image2.png)

**Figure 2.** Changes in the potential of the platinum cathode in the ferric chloride electrolyte (curve 1), the chromating sulfate electrolyte (curve 2), and the mixed chloride-sulfate electrolyte (curve 3) at pH=0.4 on the polarization of the platinum cathode: curve 1 – t=30°C, curve 2 – t=50°C.

![Figure 3](image3.png)

**Figure 3.** Influence of the cathode current density and temperature of the sulfate-chloride electrolyte (composition, g/l: 150 FeCl₂ and 50 Cr₂(SO₄)₃) at pH=0.4 on the polarization of the platinum cathode: curve 1 – t=30°C, curve 2 – t=50°C.

It is likely that the activation energy of the reduction of metal ions from hydrate complexes decreases, which facilitates the process of their joint discharge. However, testing the stability of the mixed electrolyte over time showed that the concentration of iron salt in it should not be increased to 200 g/l due to an increase in the viscosity of the highly concentrated solution and the formation of an even denser cathode film on the electrode surface, which slows down the ion discharge process [6].

To prove our opinion about the mechanism of mutual influence of iron, chromium and hydrogen ions on the electrolysis process, figure 2 shows the dependence of the cathode potential of the platinum electrode on the current density at the electrolyte temperature of 40°C and the acidity of the solution of 0.8 units. pH in pure electrolytes with concentrations (g/l): FeCl₂ – 150 (curve 1), Cr₂(SO₄)₃ – 50 (curve 2) and in mixed electrolyte 150 FeCl₂ + 50 Cr₂(SO₄)₃ (curve 3).
As follows from figure 2, the increase in the polarization of the electrode in the iron electrolyte with an increase in pH to 0.8 units. (curve 1) leads to a significant dependence of the discharge potential on the current density. The reason lies in the increased hydrolysis of iron cation in a less acidic environment and an increase in the concentration of iron hydroxide ions according to the Le Chatelier principle in the reaction:

\[ \text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}^+ + \text{H}_3\text{O}^+ \]  

(4)

This requires more energy to restore the metal from the oxygen-containing ion, which means that the dependence of the potential on the current density is increased.

The offset potential of the polarized cathode in a mixed electrolyte with increasing pH in the zone of more negative values compared to strongly acidic electrolyte (curve 3 in figure 2 compared to curve 8 in figure 1) brings it closer to the equilibrium value of the potential discharge of pure chromium, which facilitates a joint recovery of Cr and Fe, and the independence of polarization on current density suggests the idea of forming a more stable associative complexes of iron and chromium with the participation of not only solvent, but also anions, particularly chloride anion Cl\(^-\), which compacts the adsorption layer on the surface of the electrode and increases its concentration polarization. In this case, the joint discharge of iron (2) and chromium (3) cations is facilitated, in our opinion, at higher operating current densities (50-80 A/dm\(^2\)). The following process scheme is possible:

\[ \text{Fe}[\text{Cr(OH)}_4]^+ + e^- = \text{Fe}[\text{Cr(OH)}_4]_\text{ads} + \text{H}_2\text{O}^+ \]
\[ \text{Fe} \cdot \text{Cr(OH)} + \text{H}_3\text{O}^+ + e^- = \text{Fe} \cdot \text{Cr(OH)}_2 + 2\text{H}_2\text{O} \]
\[ \text{Fe} \cdot \text{Cr(OH)}_3 + \text{H}_2\text{O}^+ + e^- = \text{Fe} \cdot \text{Cr(OH)}_2 + 2\text{H}_2\text{O} + \text{Fe} \cdot \text{Cr} + 4\text{H}_2\text{O}. \]  

(5)

This step-by-step mechanism for the formation of the cathode film and the discharge of Fe and Cr cations from it increases the speed of the process, increases the quality of higher-thickness wear-resistant coatings that provide high tribological reliability of the restored parts and meet production requirements for wear surfaces.

In General, the analysis of the research results presented in figures 1 and 2 allows us to conclude that it is advisable to mix iron and chrome electrolytes in a ratio of 3:1 or 150 g/l FeCl\(_2\) : 50 g/l Cr\(_2\)(SO\(_4\))\(_3\).

It was also of interest to find out the effect of the electrolyte temperature on the mechanism of the electrolysis process at the optimal ratio of component concentrations in it.

As a result of studies of the effect of the cathode current density and temperature of the sulfate-chloride electrolyte on the polarization of the electrode when coating with Fe-Cr alloy, it was found (figure 3) that with increasing temperature, the potential of the electrode shifts to more negative values, increasing its concentration polarization. At the same time, an increase in the current density over 20 A/dm\(^2\) with an increase in temperature to 50°C stabilizes the potential of the electrode, indicating that the maximum discharge current has been reached. From our point of view, the observed effect is that the temperature rise, on the one hand, strengthens the hydrolysis of metal cations according to reactions described by equations (3) and (5), and on the other accelerates the diffusion of cathode film, its rebuilding as a result of partial loss of adsorbed ions and solvent molecules, and hence, the relative loosening of the film, thereby producing a positive effect on the process of extraction of metals iron and chromium in the alloy.

Note that the increase in temperature to a lesser extent than the acidity of the electrolyte affects the polarization of the electrode (for comparison, curve 8 in figure 1 at pH=0.6, curve 3 in figure 2 at pH=0.8, and curves 1-2 in figure 3 at pH=0.4).

In support of the above, the dependences of the current yield of the alloy (figure 4) and the deposition rate (figure 5) on the acidity and temperature of the mixed electrolyte at a constant current density were studied. The alloy was deposited from a mixed electrolyte with an optimal concentration of components (FeCl\(_2\):Cr\(_2\)(SO\(_4\))\(_3\)=150:50) at a cathode current density of 40 A/dm\(^2\) and electrolyte temperatures of 30, 40 and 50°C.

Figure 4 shows that, regardless of temperature, the current output of metals increases with decreasing acidity of the solution (curves 1, 2, 3). The maximum current output effect (78 %) for a given current density is achieved in the deposition range pH=0.9–1.04 and t= 40°C (curve 2). It also corresponds to a high deposition rate of 0.25 mm/h (figure 5 curve 2). However, the appearance and quality of the coating at the initial acidity of the solution of 0.9 units with a subsequent increase in pH during electrolysis do not meet the specified properties. The explanation for this lies in the features of the mechanism of co-
reduction of Fe$^{2+}$, Cr$^{3+}$, and H$_3$O$^+$ cations depending on the acid-base balance in the electrolyte.

In our opinion, when the concentration of hydrogen cations is insufficient (pH≥0.8–0.9), the near-cathode layer is alkalinized by the reactions described by equations (1) and (2), colloidal iron and chromium hydroxides are formed with an intermediate degree of oxidation and their incomplete reduction from the film by hydrated electrons. Ingress of oxygen-containing components into the coating worsens the structure and properties of the sediment. When the temperature drops to 30°C (figure 4, curve 1), the current output becomes unstable even at lower pH values (0.4 – 0.9 units), varying in the range of 18-45 %. The same situation is observed with the deposition rate (figure 5, curve 1), which varies in the range of 0.12 – 0.24 mm/h, which confirms the assumption of incomplete reduction of iron and chromium cations in the entire pH range above 0.4 units. from cold electrolyte.

When the temperature rises to 50°C, the situation improves (figure 4, curve 3) both in terms of current output and sediment quality in the pH=0.4÷0.8 range. Under these conditions, the deposition rate of metals gradually increases from 0.15 to 0.28 mm/h (figure 5, curve 3). With a further decrease in acidity, the process becomes unstable again. The most stable in terms of current efficiency and deposition rate is the electrolysis process at temperatures of 40 and 50°C in the pH range of 0.6-0.8.

![Figure 4. Dependence of the current output of the Fe-Cr alloy from a sulfate-chloride electrolyte with component concentrations (g/l) FeCl$_2$ – 150; Cr$_2$(SO$_4$)$_3$ – 50 and current density 40 A/dm$^2$ on the pH of the beginning of deposition and the temperature of the electrolyte: 1 – t=30°C; 2 – t=40°C; 3 – t=50°C.](image)

![Figure 5. Dependence of the deposition rate of Fe-Cr alloy from a mixed electrolyte (150:50) at a current density of 40 A/dm$^2$ on the pH of the deposition start and temperature: 1 – t=30°C; 2 – t=40°C; 3 – t=50°C.](image)

![Figure 6. Dependence of the microhardness of the coating on the pH of the beginning of deposition and the temperature of the electrolyte: curve 1 – t=40°C; curve 2 – t=50°C.](image)

The dependences of the alloy deposition rate and current output on the pH and temperature of the electrolyte described in figures 4 and 5 during electrodeposition on steel (ST20) electrodes indicate the extreme complexity of the mutual influence of ions on the kinetics of their recovery and correlation with polarization studies (figures 1–3). The discharge potentials of iron and chromium cations converge under certain conditions, providing their mutual support during recovery (see equations 4). At the same time, intermediate iron complexes formed under mild conditions accelerate the reduction of chromium (3) and its crystallization in a structure favorable to iron atoms, ensuring the formation of the alloy as an intermetallic compound or solid solution, which prevents the appearance of defects in the crystal lattice.

Physical studies of the microhardness and surface morphology of deposited metals from the FeCl$_2$–Cr$_2$(SO$_4$)$_3$ mixed electrolyte were performed with an optimal concentration ratio (g/l) of 150:50 at a current density of 40 A/dm$^2$, depending on the acidity and temperature of the electrolyte. The research results are shown in figures 6 and 7.

Studies of the microhardness of coatings depending on the modes of electrolysis indicate that the surface formation is inhomogeneous when the acidity of the medium changes and when the electrolyte is heated (figure 6, curves 1 and 2). The most solid precipitation (900-1010 kg/mm$^2$) was obtained in the lower pH range (0.4–0.5) at Dk=40 A/dm$^2$ and te=40-43°C (curve 1) and at te=50-52°C (880-920
kg/mm²), curve 2. Increase the pH of the electrolyte to 0.6 units, dramatically reduces the hardness of the coating at both temperatures, remaining stable at 40°C up to pH=0.8 (820 kg/mm²) and rising in the same pH range to the initial value of 900 kg/mm² at 50°C. Further reduction of acidity to pH=0.9 and higher reduces the microhardness of the precipitate in an electrolyte with a temperature of 40°C to 500 kg/mm² and actually destroys the coating at a temperature of 50°C. Such changes in the microhardness of coatings indicate that the acidity of the electrolyte significantly affects the structure of the coating, shifting the equilibrium of the metal reduction process in the direction of iron, then in the direction of chromium. The choice of the electrolysis mode in favor of the hot electrolyte (t=50°C) becomes quite obvious with an initial precipitation acidity of 0.8 units. pH and warm electrolyte (t=40°C) with an initial precipitation acidity of 0.5 pH units.

Studies of the morphology of coatings obtained from a mixed sulfate-chloride electrolyte at a current density of 40 A/dm², depending on pH and temperature, allowed us to see both cracked and uncracked coatings with fewer or more globules on the surface to be coated (figure 7, a, b, c, d).

The results obtained are in good agreement and are a real confirmation of our earlier assumptions about the mechanism of joint electrical recovery of iron and chromium metals into an alloy. For example, figure 7a provides an understanding of the high microhardness of the surface in a cold electrolyte at low current densities due to the formation of fine-crystalline Fe-Cr cellular complexes in the form of solid solutions with a predominance of iron or chromium in them, and therefore the presence of interfaces between these complexes.

4. Conclusion

The article proposes a mechanism for the joint reduction of iron and chromium cations to an alloy by an electrolytic method from a mixed sulfate-chloride electrolyte. It defines optimal ratios of component concentrations (150 g/l iron chloride FeCl₂ and 50 g/l chromium sulfate Cr₂(SO₄)₃) and modes of electrical recovery of metals (current density 40 A/dm²; pH of the electrolyte at the beginning of deposition 0.8 and 0.5; temperature 40±2°C, which contribute to obtaining a high-quality coating with high current output (49% and 42%, respectively), deposition rate (0.18 and 0.12 mm/h, respectively), microhardness of the sediment (820 and 1010 kg/mm², respectively).

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