Mass Transfer in a Layer of Aluminized Glass-Fiber Material in the Treatment of Chrome-Containing Wastewater

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Abstract. It is possible to use column-type devices with the loading of composite material - thin glass fibres partially coated with an aluminium layer (AGFM) to purify low-concentrated wastewater on plating plant containing chromium compounds. The main physical characteristics of this material are given. For the mass transfer research, current-potential curves obtained by reducing the chromium forms Cr(VI) to trivalent on a thin copper yarn placed in a layer of aluminum-removed fiberglass were studied. Dependence of effective mass-transfer coefficient on solution flow rate is obtained. Taking into account the ionic strength of the solution, the diffusion coefficient of the reducing anion Cr(VI) was calculated, which allowed to move to the criterion equations of the form $Nu = f(Pr, Re)$. Coefficients are found in the criteria mass-transfer equation at different degrees of filling of the filter volume with a AGFM material.

1. Introduction
Waste water containing toxic, carcinogenic compounds of hexavalent chromium is formed in many galvanic processes of metal surface treatment (chroming, aluminium oxidation, electrochemical polishing, etching and passivating alloys), with up to 90% of the waste volume being low-concentration solutions from washing baths with Cr(VI) content of up to 200 mg/l [1, 2].

There are enough known methods for cleaning such effluents from heavy metal ions, for example: reagent method, biological method, electro-coagulation, reverse osmosis, sorption, extraction, etc. [3-6]. One of the methods is galvano-coagulating, which involves the galvano-chemical dissolution of aluminum or iron anodes due to the potential difference that occurs when the anodes come in contact with coke or copper [7-12]. The advantage of this method is the possibility of using different metal-containing wastes of production: swarf, filings, scrap, etc [13].

One such potential material is waste of special production, which is a combined aluminized glass-fiber material (AGFM), described in [14]. The material is thin glass threads coated throughout the length with a layer of aluminium, in two forms of packaging: strands of "horse tail" type 0.5…1 m long and bundles of 4…5 cm wrapped with paper.

2. AGFM properties and problem statement
The appearance of the material is shown in figure 1. Research of the physical characteristics of AGFM have shown (table 1) that the aluminum layer is not solid and covers the fiber only about one third of
the perimeter of its section, but is fairly evenly distributed over the length of the fibers, figure 2. According to the composition of impurities, aluminium can be classified as A95 or Al 99.94.

![Figure 1. Aluminized glass-fiber material.](image1)

![Figure 2. Photos of AGFM fibers with a scanning electron microscope: 1– fiberglass, 2 – aluminium.](image2)

| Characteristic                        | Unit       | Value  |
|---------------------------------------|------------|--------|
| Fiber density                         | g/cm³      | 2.48   |
| Total specific surface                | 1/cm       | 964.2  |
| Glass fiber diameter                  | µm         | 30     |
| Specific surface of glass fibers      | 1/cm       | 460.2  |
| Mass average aluminium content        | %          | 22     |
| Average thickness of the aluminium   | µm         | 15     |
| Average specific surface area of aluminium | 1/cm   | 504    |
| Fiber density                         | g/cm³      | 2.48   |

When analyzing the data from table 1, it can be expected that the large specific surface area and the presence of a rigid "framework" of glass fibres will result in a high mass-transfer coefficient, stability in the change of aluminium content, occurring over the course of operation of the apparatus, as well as high efficiency of the cementation process of copper and practically complete dissolution of aluminium in the cleaning process.

The cleaning technique involves a column type apparatus into which a mixture of AGFM and particulate depolarizing material is charged, which is less electronegative than aluminum (copper, graphite or coke) [15, 16]. The aluminium is oxidized and transferred to the solution. If, in addition to Cr(VI), copper ions are also contained in wastewater, it is more rational to use only AGFM. In this case, the processes of cementing copper crystals on AGFM and reducing occur simultaneously.

The purpose of the work was to evaluate the physical properties and mass transfer parameters of this material in relation to the conditions of its use as a load of column-type galvano-coagulating devices.

3. Mass transfer in the fiber layer

3.1. Methodology and research results

The study of mass transfer processes was carried out in a 13.15 cm³ flow cylindrical vinyl plastic cell. The determination of the mass-transfer coefficient $\beta_{\text{eff}}$ in the AGFM layer was carried out according to the method adopted for studying fibrous carbon-graphite materials, i.e. by the dependence of the value
of the limit current density \( i_{\text{lim}} \) on the linear flow rate of the solution \( w \). For this purpose copper thread with a diameter of 50 µm was placed in a cell with a layer of glass fibres, from which aluminium was previously removed by etching [17].

The mass-transfer coefficient was studied at three degrees of filling the cell volume with glass fiber – 5%, 10%, 20% (bigger values are not possible due to reaching the maximum elasticity of the fibers), as well as in the absence of glass fiber in the cell.

Limit current was determined by the height of a polarographic wave of Cr(VI) to Cr(III) on the reduction curves received in the potentiodynamic conditions (a complex of potentiostate and a potentiometer). Working solution composition: \( \text{Na}_2\text{SO}_4 – 500 \text{ mg/l}, \text{Cr(VI)} – 200 \text{ mg/l}, \text{pH} = 1.0 \). The flow rate was within 0.00114 … 0.0721 cm/s, or 2.3 … 137 volume/h.

3.2. **Mass-transfer coefficient**

The hydrodynamic mode of movement of the liquid flowing around the thread is formed by features of the fibrous layer structure. The mass-transfer coefficient \( \beta \) to such a thread is determined by the formula:

\[
\beta = \frac{i_{\text{lim}}}{zFC_0}
\]  

(1)

where \( z \) is the number of electrons involved in the reaction; \( F \) is the Faraday number; \( C_0 \) is the ion concentration at the cell inlet.

Since part of the surface of the copper thread is not reactive due to glass fiber shielding, and it is difficult to determine the refined surface value, it makes sense to talk about the effective mass-transfer coefficient \( \beta_{\text{eff}} \). The results are shown in figure 3 as a dependence of the mass-transfer coefficient \( \beta_{\text{eff}} \) on the linear rate flow \( w \) at four degrees of cell filling.

Similarity theory for mass transfer indicates that there is a relationship between the similarity criteria of a species:

\[
Nu = A \cdot Pr^m \cdot Re^n
\]  

(2)

where \( Nu \) is the Nusselt criterion; \( Pr \) is the Prandtl criterion; \( Re \) is the Reynolds criterion; \( m, n, A \) are experimental coefficients.

From this relation follows an equation linking \( \beta_{\text{eff}} \) and \( w \):

\[
\beta_{\text{eff}} = B \cdot w^n
\]  

(3)

where \( B \) is the empirical coefficient.

The least-squares method using a computer algebra system determined the coefficients \( B \) and \( n \) (table 2) for all four dependencies (lines 1-4 in figure 3).

| Degree of volume filling with fiber (%) | Porosity \( \varepsilon \) (fractions) | \( B \cdot 10^3 \) | \( n \) |
|---------------------------------------|-------------------------------------|-----------------|-----|
| Fiber free                            | 1                                   | 11.9            | 0.22|
| 5                                     | 0.95                                | 9.45            | 0.23|
| 10                                    | 0.9                                 | 13.2            | 0.33|
| 20                                    | 0.8                                 | 34.7            | 0.54|

The change of a tilt angle of straight lines (an exponent \( n \)) it is connected with the fact that at identical speeds to increase in filling degree of volume with fibre there is a change of hydrodynamic nature of a stream. Follows from the date of the table 2 that the parameters of the equation (3) depend on porosity of a layer.
For the approximating dependence of coefficient $B$ on layer porosity the power function, for coefficient $n$ – the linear function was chosen. When determining regression coefficient data of the first line of table 2 were excluded, i.e. in the absence of fibers in a cell. In figure 4 the received lines of the approximating functions for $B$ and $n$ are shown.

Figure 3. The dependence of the mass-transfer coefficient $\beta_{\text{eff}}$ (copper thread in the glass fiber layer) on the linear rate flow $w$ (cm/s): 1 – in absence of fibers, and with various degrees (%) of volume filling: 2 – 5, 3 – 10, 4 – 20.

Thus, empirical coefficients were calculated using the least-squares method in the following equation linking porosity, flow rate, and mass-transfer coefficient:

$$\beta_{\text{eff}} = 6.17 \cdot w^{2.467-2.371\epsilon} \cdot \epsilon^{-7.67}$$  (4)

where $\epsilon$ is the layer porosity.

The approximation average error of coefficients $B$ and $n$ was 3.1%, the average error for $\beta_{\text{eff}}$ was 5.1%.

3.3. Diffusion coefficient of dichromate ion

Diffusion coefficient $D$ for the reducible form of chromium $\text{Cr}_2\text{O}_7^{2-}$ was calculated using [18]:

$$D = 8.96 \cdot 10^{-9} T \frac{\lambda}{z}$$  (5)

where $T$ is the absolute temperature; $\lambda$ is the equivalent ionic conductance: $\lambda = u \cdot F$; $u$ is the electric mobility of the ion; $z$ is the ion charge.

We accept anion mobility $\text{Cr}_2\text{O}_7^{2-}$ at $t = 18^\circ\text{C}$ and infinite dilution equal to $4.7 \text{ m}^2/(\text{V} \cdot \text{s})$ [19], determine the diffusion coefficient at infinite dilution: $D_0 = 0.94 \cdot 10^{-9} \text{ m}^2/\text{s}$. The temperature dependence of the diffusion coefficient is determined by the Arrhenius formula:

$$D = k \cdot \exp \left( -\frac{A}{RT} \right)$$  (6)

where $k$ is a constant; $A$ is the activation energy; $R$ is the Boltzmann constant.
We take activation energy value \( A = 15 \text{ kJ/mol} \), which is characteristic of viscous flow of liquid [18], then by the known value \( D_0 \) at \( t = 18^\circ \text{C} \) we determine value \( k \) and obtain:

\[
D_0 = 2.97 \cdot 10^{-7} \cdot \exp \left( \frac{1805.1}{T} \right).
\]  

(7)

For dilute electrolyte solutions with increasing concentration, the main effect in reducing the diffusion coefficient is to increase interionic interactions, which can be expressed by applying the first Fick's law [18]:

\[
D = D_0 \cdot \left( 1 + \frac{\partial \ln \gamma}{\partial \ln C} \right)
\]

(8)

where \( \gamma \) is the activity coefficient; \( C \) is the concentration of electrolyte.

Expressing coefficient of activity \( \gamma \) as a function of ionic strength \( I \) on the known formula of the second approximation of Debye-Hückel (parameter \( a = 0.49 \cdot 10^{-9} \) m), and \( I \) – through concentration of \( C \) for a double-charged ion, and replacing differentials with finite differences, it is possible to calculate the value of expression \( \left( 1 + \frac{\partial \ln \gamma}{\partial \ln C} \right) \) depending on ionic strength. Thus, the necessary data were calculated for graphs of the dependence of the anion diffusion coefficient \( \text{Cr}_2\text{O}_7^{2-} \) on the ionic strength of the solution at different temperature conditions.

Calculated taking into account the ionic equilibria of the Cr(VI) forms and the \( \text{K}^+ \) and \( \text{Na}^+ \) cations, the solution ionic strength used in experiments to determine the mass-transfer coefficient was \( 0.0572 \) mol/l. The diffusion coefficient under these conditions is equal \( D_0 = 5.54 \cdot 10^{10} \cdot 0.733 = 4.061 \cdot 10^{-10} \text{ m}^2/\text{s} \).

3.4. Criteria dependences

The calculated diffusion coefficient allowed us to propose a relationship between the Nusselt, Prandtl, and Reynolds criteria for three degrees of filling the cell volume with fibers during the mass transfer of the anion \( \text{Cr}_2\text{O}_7^{2-} \) in the AGFM layer. The value of the Reynolds criterion was determined by the formula taking into account the specific surface of fibrous materials [20]:

\[
Re = \frac{4w_r}{a \cdot \nu}
\]

(9)

where \( w_r \) is the actual flow rate, taking into account the porosity; \( a \) is the specific surface area of the fibers per unit volume (96420 m\(^{-1}\)); \( \nu \) is the kinematic viscosity of the solution.

The Nusselt diffusion criterion characterizing mass transfer at the phase boundary was determined taking into account the equivalent diameter \( l \), expressed in terms of the value of \( Re \), i.e. \( l = Re \cdot \nu / w_r \).

In criterion dependence, equation (2), coefficient \( m \) is taken equal to \( 1/3 = 0.333 \). The remaining coefficients \( A \) and \( n \) were selected by the least squares method, as shown in table 3.

As mentioned above, due to the blocking part of the surface part of the copper thread by the fibres, the mass-transfer coefficients \( \beta_{eff} \) calculated by the equation (1) are underestimated compared to the true ones. It should be expected that the decrease in the apparent mass-transfer coefficient compared to the true one will also increase with the increase in the volume filling rate. The same phenomenon of screening a part of the fiber surface occurs in real devices, so in practice the Cr(VI) reduction process will be adequately expressed by criterion dependencies with coefficients from the table 3.
Table 3. Values of coefficients A and n in equation (2) at different degrees of filling the volume with fibers (porosity).

| Degree of filling (%) | Porosity ε (fractions) | Range of values Re | A     | n    | Average error (%) |
|-----------------------|------------------------|--------------------|-------|------|--------------------|
| 5                     | 0.95                   | 0.00316...0.32     | 6.465 | 0.223| 2.02               |
| 10                    | 0.9                    | 0.00316...0.1      | 4.898 | 0.319| 1.87               |
| 20                    | 0.8                    | 0.001...0.016      | 7.448 | 0.575| 11.8               |

3.5. Practical application

Based on the conducted experiments and established criteria dependencies, the optimal design and operating parameters of the column-type apparatus with a capacity of 5 cubic meters per hour for cleaning washing chrome-containing wastewater were determined. The device is undergoing pilot tests at a machine-building plant in Vologda (Russia).

4. Conclusion

Based on the totality of the data presented in this work, we can draw the following conclusions:

1. The physical and hydrodynamic characteristics of AGFM allow it to be used for the neutralization of chromium-containing wastewater by galvano-coagulation.
2. The refined dependence of the diffusion coefficient of the dichromat anion on the ionic strength of the solution is established.
3. The dependencies of the mass-transfer coefficient on the flow velocity are found in various degrees of filling the volume of the treatment devices.
4. The coefficients in the mass-transfer equation that connects the Reynolds, Prandtl and Nusselt criteria, which allow the engineering of the column-type apparatus for galvano-coagulation cleaning of chrome-containing wastewater, are determined.

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