Abstract—The paper has investigated regularities of water defluorination by methods of galvanocoagulation and electrocoagulation. It has been shown that electrocoagulation ensures more effective defluorination of water than galvanocoagulation. It has been proposed to use the methods in question for removal of fluorides from concentrates being formed in defluorination of water by reverse osmosis.

INTRODUCTION

At present the method of reverse osmosis (RO) is widely used for water defluorination [1–3], which is related to high efficiency and economy. In addition, it features certain universality since it makes it possible to purify water containing organic, inorganic, and biological pollutants. Drawbacks of RO include the formation of concentration of salts subject to utilization.

Papers [3–6] demonstrate that for purification of solutions having an increased content of fluorides, which are concentrates obtained after RO it is expedient to use methods of galvanocoagulation (GC) and electrocoagulation (EC).

The GC method is based on dissolution of aluminum and iron in the field of short-circuited galvanic aluminum element—coke at varying contact of components of the galvanic couple. Owing to the difference of electric potentials aluminum (iron) is polarized anodically and goes to the solution in the form of ions without superposition of current from an external source. In this case coke in the galvanic couple is polarized cathodically [4]. However, despite incontestable saving using this method it is impossible to achieve defluorination of water having an increased content of fluorides to the required norm in drinking water.

Behind the EC method lies dissolution of the anode under the effect of the field of permanent electric current with the formation of active hydroxide sediments [4]. Intensity of the electrocoagulation process in great measure is determined by the rate of the electrode reaction, i.e. current intensity across corresponding electrodes. In this case, it is important to take account of factors superimposed by the medium being treated (the composition and concentration of water impurities, the pH, etc.). Drawbacks of this method should include high energy capacity [3].

The objective of the present paper is determination of main regularities of the GC and EC processes in defluorination of solutions imitating concentrates after purification of water of fluorides by reverse osmosis.

EXPERIMENTAL

Investigations were carried out in a laboratory galvanocoagulator comprising of a vertical polymer cylindrical housing of 1.1 dm³ with a charge from the blend of crushed aluminum chips (wastes of production) and coke. The initial water was fed to the upper part of the galvanocoagulator. Mixing was brought about by air sparging coming to the lower part of the galvanocoagulator.

The galvanocoagulator had a similar design. It distinguished from he galvanocoagulator only by the fact that the internal surface of the polymer housing accommodated a cylindrical cathode made of sheet stainless steel and separated from aluminum chips with polymer netting. In the center of the housing there located a graphite positively charged bar in contact with aluminum chips, which were anodically dissolved. The perma-
ent electric current in the unit was created by means of a laboratory power unit Electronics Home Tools 30V6A. The experiments were carried out in flowing mode selecting samples (by 100 cm$^3$) every 10 min.

Sodium fluoride, qualification “chemically pure”, was used as model solutions. When investigating the influence of chlorides on the processes of water defluorination the solution of sodium chloride (“chemically pure”) was added to the initial solution of fluorides. Ions of F$^-$ were analyzed by means of a fluoride-selective electrode ELIS-131F, while Cl$^-$ by titrating nitrogen–acid mercury in the presence of an indicator diphenylcarbazone [7].

RESULTS AND DISCUSSION

A substantial factor of regulating the efficiency of the GC process is the ratio between polyelements of the galvanic couple since they determined the amount of Al$^{3+}$ ions in the water being purified and the value of its pH. Initially we found out that at galvanocoagulational defluorination it is expedient to use the ration Al : coke — 2 : 1. In this case the most intensive rise of the degree of defluorination is observed in the first 20 min of the process. The finite value (pH$_{\text{con}}$) of solutions after the experiment was conducted for 10 min increased compared with initial values (pH$_{\text{ini}}$ 6.6–7) by more than a unity. This is related, first of all, with alkalization of the solution in the near cathode region, secondly, with the specificity of anodic dissolution of aluminum ruling out the formation of H$^+$ [4]. Further increase of GC time insufficiently affected its characteristics.

GC was carried out for different values of the pH$_{\text{ini}}$ of solutions with the initial concentration of the mixture of fluorides (C$_{F_{\text{ini}}}$) and chlorides (C$_{Cl_{\text{ini}}}$) respectively 29.9 and 253.6 mg/dm$^3$. Obtained data are given in Fig. 1.

![Fig. 1. Impact of the initial pH on the degree of removal (R) of fluorides (1) and the value of the finite (2) of purified solutions.](image)

From Fig. 1, curve 1 one can see that the efficiency of GC turned to be rather sensitive to the change of the pH of the medium. The highest degree of defluorination (74.6%) was observed at pH$_{\text{ini}}$ 3 and its further increase led to the gradual decrease of the degree of defluorination. It may be explained by chemical dissolution of aluminum in an acid medium and an increase of the pH$_{\text{con}}$ in the course of GC. In the given case depending on the content of Al$^{3+}$ ions their monomeric and dimeric hydroxocomplexes of the type [Al(H$_2$O)$_5$OH]$^{2+}$ and [Al$_2$(H$_2$O)$_8$]$^{4+}$ with which actively interact fluorides; at pH ~5 aluminum hydroxide starts to precipitate [8].

An increase of the pH$_{\text{ini}}$ of solutions from 3 to 7 results in an increase of the pH$_{\text{con}}$ from 6.7 to 7.6 (see Fig. 1, curve 2). In this case the ratio C$_{\text{OH}^-}$ : C$_{\text{Al}^{3+}}$ increases, which is conducive to the release of hydroxocomplexes [Al$_4$(H$_2$O)$_2$(OH)$_6$]$^{6+}$ as a result of hydrolytic polycondensation of which cyclic structures of hexanucleate aluminum hydroxocomplexes are formed in the form of hydargillate. The larger are aluminum