

ELECTROCHEMICAL TECHNOLOGY OF FLUORINE REMOVAL FROM UNDERGROUND AND WASTE WATERS

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ABSTRACT

An improved method for removal of fluorine from ground water and of fluorine and chromium simultaneously from industrial waste waters is presented. The process consist of two stages, first iron(II) and calcium hydroxide solutions are added and the sediment is separated. In the second stage, after acidification, electrocoagulation using aluminium anode is applied, then, after further lowering of pH by an acid, the formed aluminium hydroxide with sorbed fluorine is removed by settling and filtration.

INTRODUCTION

A peculiarity of ion composition of the underground waters (which is actually similar for any region) is characterized by weak conductance, high percentage of hydrocarbonate ions and organic substances and predetermines the complex of technological methods for extraction of toxic components which simultaneously allow to maintain a salt content at the level of the utmost permissible concentrations (UPC).

Fluorine removal from the diluted solutions, to which the underground waters belong, up to UPC 0.7-1.5 mg/l presents a problem because of the defluorination process, based on formation of aluminofluorine complexes and their sorption on aluminium hydroxide with respect to pH and anion composition of a medium [1].

In the purification process of waters containing fluorine it is advisable to use the electrochemical method [1], that is easy in itself and enables to obtain the required quality of purification. However, great consumption of metallic aluminium, anion UPC in the purified water above the range and high energy consumption prevent the wide integration of this method.

The aim of the present work is to study the process of fluorine removal and to develop a technological solution of electrochemical defluorination of the underground waters, considering a reduction of specific consumption of (Al^{3+}) sorbent with maintaining a concentration of the major water anions within the UPC range for a further utilisation of the water in public and industrial water supply.

A method for purifying underground waters containing fluorine [1,2] is known, the essence of which lies in a preliminary acidification (usually by hydrochloric acid) of the water, in performing the electrolysis in an electrocoagulator with aluminium electrodes and a subsequent separation of a generated sediment of aluminium hydroxide. The pH value 6.0-6.1, up to which the acidification of the underground water is done, is estimated on the basis of the fact that in the electrolysis process there occurs alkalization of the fluorine-containing water being processed, up to pH 6.4-6.6. Within the same pH range is situated the isoelectric point of aluminium hydroxide and the most effective fluorine-ion sorption [1] takes place at this pH.

However, the water purified by this method fails to meet the requirements of the State Standard in respect of residual anion concentration (more than often it is the chloride ion), introduced with an acid.

RESULTS

Fluorine removal from ground water

A new defluorination technology suggested in the present paper provides for carrying out the water electrolysis with aluminium electrodes at the initial pH 8.3-8.8 after which an acid

is added up to pH 6.4-6.6 optimal to withdraw fluorine.

Experimental device for water defluorination consists of an electrocoagulator with aluminium electrodes made of D-16 alloy, the vessel for raw water, electroflotator with an insoluble anode made of titanium, coated with manganese oxides (to separate aluminium from the water being purified), a filtration unit and current rectifiers.

The fluorine ion concentration was defined by the express-method making use of the lanthan fluoride electrode and acetate buffer [1].

The study was carried out according to the suggested technology and parallel to the previously known process [1,2]. Several variants (points) of preliminary acidification were chosen: 0, 10, 20, 50, 70, 100 % of acid from the total volume introduced into the water being purified prior to electrolysis. In the purified water along-side with fluoride ions a residual chloride ion concentration was also determined: with respect to aluminium concentration its specific consumption was determined. Three parallel experiments were carried out at each of the points. The results are presented in Table 1.

It can be seen that with an increase of the fraction from the total volume of the acid introduced prior to electrolysis, the sorbent specific consumption grows, due to the fact that the remaining acid doesn't suffice to reaching the pH optimal value, necessary for the alumino-fluoride complexes sorption. In this case such indices as residual fluorine and chloride ion concentrations meet the requirements of the State Standards for drinking water.

In comparison with the known technologies of underground water defluorination [1,2], the one suggested here allows to reduce the sorbent specific consumption by 35-40 % on the average and simultaneously to maintain a residual anion concentration bellow UPC for drinking water (see Table 1).

The obtained effect can be explained by factors, realized only with soluble electrodes in hydrocarbonate media.

In the present variant during the electrocoagulation process

Table 1. Dependence of the specific sorbent (Al^{3+}) consumption on the acid volume, introduced prior to electrocoagulation

Acid volume %		pH after			Aluminium consumption, mg to 1 mg of the removed fluorine	Fluorine concentration in purified water, mg/l
		acid introduction	electrocoagulation	residual acid introduction		
prior	after					
electrocoagulation	electrocoagulation					
0	100	8.5	9.2	6.40	12.4	1.00
		8.5	9.05	6.45	14.2	1.29
		8.5	9.04	6.47	15.0	1.20
10	90	7.5	8.60	6.53	15.3	1.10
		7.5	8.53	6.50	14.8	1.20
		7.5	8.67	6.45	14.3	1.10
20	80	7.35	8.47	6.47	14.7	1.46
		7.35	8.45	6.58	15.5	1.20
		7.35	8.50	6.61	15.6	1.17
50	50	6.81	8.33	6.70	15.7	1.00
		6.81	8.20	6.71	16.8	1.15
		6.81	8.26	6.73	17.0	1.10
70	30	6.56	7.91	6.93	19.2	1.03
		6.56	8.00	7.05	20.7	1.10
		6.56	7.93	7.01	19.8	1.20
100	0	6.41	7.11	7.11	23.9	1.17
		6.41	7.23	7.23	24.1	1.13
		6.41	7.30	7.30	25.1	1.20

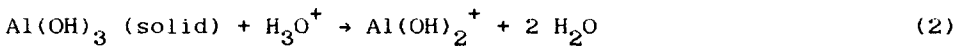
pH of the underground water 8.5; initial fluorine concentration in water 7.5 mg/l; chloride ion concentration in purified water, including chloride ions being in it prior to defluorination 300 mg/l

ina weak alkaline medium (at pH over 7.0) the electrogenerated ions of aluminium are hydrolyzed with a solid phase formation according to equation:



In this case the higher pH value of the water before electrolysis, which is connected with the amphoterism of aluminium hydroxide and the higher the pH value of water, the quicker occurs the solid phase formation, that is of aluminium hydroxide [3].

In the process carried out by the known method[1] the hydrogen ions of the introduced acid neutralized the hydrocarbonate ions, however the generated CO_2 remains in solution. At further stages of electrolysis the formation of aluminium hydroxide is affected by the previously introduced hydrogen ions, shifting reaction (1) to the right and inhibiting the solid phase formation. On the other hand, at pH less than 7.0 [3] as a result of anodic dissolution of aluminium and hydrolysis reaction of aluminium ions the solution is alkalinized at the expense of solid phase dissolution according to the equation:



and the molecules of dissolved CO_2 change back to hydrocarbonate ions, thus largely increasing the pH final value in comparison with the offered variant and increasing the sorbent specific consumption due to the fact that the sorption process of aluminium fluoride complexes occurs in a non-optimal pH region.

The other factor that explains the effect of the offered technology is a hydrocarbonate ion sorption on the electrogenerated sorbent which increases with pH growth.

The sorbent excessive consumption, using the known defluorination method [1], can be avoided by means of pH correction in the purified water at a stage of fluorine sorption up to 6.4-6.45. However, in this case an excess of salt in water being purified grows up to 25 % (a residual concentration of

chloride ions in purified water, including those remaining in it prior to defluorination, is about 400 mg/l).

It was found that for the case of lowering the fluorine concentration according to the offered technology from 7.5 - 8.7 up to 1.0 - 1.2 mg/l by the hydrolysis of aluminium ions, obtained from the anodic dissolution of metals, the generated hydroxy compounds of aluminium sorb about 2.0 mmol/l of hydrocarbonate ions.

It should be noted the above effect takes place when a strong acid is used for acidification (hydrochloric, sulphuric, nitric etc.). For practical use it is advisable prior to electrolysis to introduce hydrochloric acid in amount of 10-20 % of total required volume in order to have chloride ions in water which are supposed to be depassivators [1].

Fluorine removal from waste waters

Removal of fluorine and fluorine together with chromium from industrial waste waters is an urgent problem nowadays. The aim of the work was to develop a purification technology to be applied to weakly mineralized fluorine and chromium containing waters, that would allow to maintain the residual concentration of components in purified water within the UPC range.

Fluorine and chromium containing technological waters from electronic industry were subjected to purification (fluorine concentration 50 mg/l; chromium 10 mg/l). For the given type of solutions a low level of mineralization is characteristic ($\kappa = 0.3 - 0.4 \cdot 10 \text{ Ohm}^{-1} \text{ cm}^{-1}$). It is known from the literature[4], that fluorine can be effectively removed at the first stage at the ratio $\text{Ca}^{2+} : \text{F}^- = 5 : 1$ ((mmol/l). For coagulation of thin dispersion sediments of calcium fluoride the coagulants (hydroxides of iron (II) and (III), in particular) are used [5-7]. However, the literature presents incompletely:

- a) the values of optimal dose of the coagulant;
- b) the effect of anions, introduced with the coagulat (chlorides, sulphates), on the deposition process of calcium fluoride and

hydroxide sediments;

c) the application of flocculants to accelerate their deposition.

At the first stage the experimental methods consisted of modeling the above water composition, the subsequent deposition by calcium (II) salts, the coagulation by iron (II or III) hydroxides and determination of the residual content of fluorine and chromium.

Large effect on the efficiency of calcium fluoride deposition and, hence, fluorine removal is produced by counter ion (chloride or sulphate ion). The analysis of experimental data shows that sulphates, as well as their mixtures with chlorides at a ratio of $[\text{Cl}^-] : [\text{SO}_4^{2-}] = 1:1$ and higher produces a stronger coagulation effect on the sediment of calcium fluoride, than the chlorides alone.

It was found experimentally that at fluorine contents up to 50 mg/l the optimal ratio of the coagulant (iron salts) to the component being removed (fluorine) makes 1 - 0.9 : 1 (mmol/l). Further increase improves insignificantly the removal effect but increases anion content in water.

The activating influence on the anion flocculants coagulation process of alkyl sulphates is found at 0.5 - 2.0 mg/l.

Accordingly to the above scheme the process of fluorine removal from waste waters was studied in a wide range of initial concentrations (from 17 to 163 mg/l) and coagulant dose variations (from 0 to 260 mg/l with iron(II)) at ratio of introduced calcium to fluorine 5 : 1.

Experimental data show that the fluorine removal process over the whole range of concentrations proceeds efficiently at previously found optimal amounts of introduced coagulant and depositor.

It was found experimentally that the process of fluorine removal should not be performed immediately after the iron salts introduction; a sediment should be separated and then a tertiary treatment should be carried out, using the aluminium ions, because without the intermediate step a sharp increase (about 3 times) of aluminium consumption occurs. This is a result of adsorption

ability decrease of aluminium hydroxide, caused by the inseparated sediment blocking the sorbent surface and a subsequent deterioration of the alumino fluoride complexes removal.

EXPERIMENTAL

Waste waters containing no chromium but 8-14 mg/l of fluorine and with pH 11.3- 12.2 were used for experiments. They were subjected to purification by aluminium hydroxide and subsequent separation of the sediment. In purified water the residual concentration of fluoride chloride, sulphate, aluminium, iron and calcium were determined.

In the process of study it was necessary to compare the efficiency of aluminium hydroxide application, obtained as a result of aluminium sulphate hydrolysis and electrochemical dissolution of the aluminium anode under current; the effect of the initial pH value before the electrocoagulation on the purification process and residual contents of the main anions (chlorides, sulphates); and also the possibility of using electroflotation for separation of aluminium hydroxide sediment with sorbed alumino fluoride complexes.

It was found that [1] maximum combining of fluorine into the complex occurs within the pH range of 6.35 - 6.65. As it was shown above, pH of the water after the first stage makes 11.3...12.2.

Electrogenerated sorbent (electrocoagulation process) was obtained in the apparatus with electrodes made of D-16 aluminium, the interelectrode space of which was not exceeding 4 mm; the sorbent quantity varied with respect to the flowrate of water.

Comparative investigations on application of aluminium hydroxide, electrogenerated and obtained by salt hydrolysis, showed that the use of electrogenerated sorbent is more efficient by about 15 % (as to its consumption) due to its higher adsorption ability.

Besides, it was experimentally proved that a residual salt content (total content of chloride and sulphate ions in UPC measurement) after the chemical coagulation is by 15 - 20 % higher

than that after the electrical coagulation, which can be explained by peculiarities of running the electrochemical reactions in alkaline media [3].

It should be taken into account that as the experiments showed a part of fluorine (30 - 40 % of the total quantity) after the first stage is found to be in the form of calcium fluoride, and therefore the role of aluminium hydroxide is not only to combine fluoride ions into a complex, but also to deposit calcium fluoride. That is why in the process of defluorination after the first stage it is necessary to determine the fluoride ion and to add the sorbent in a ratio of 10:1 up to 15:1 (in respect to aluminium) [1].

A comparative study was carried out on the removal of aluminium hydroxide sediment by settling and electroflotation. The experiments were performed in an electroflotator with an insoluble anode (titanium, coated by manganese oxides), anode of stainless steel and grid anode (grid of stainless steel). The current density and electroflotation duration varied. A residual aluminium and iron content was controlled.

A comparison of the experimental data showed that the electroflotation was more efficient at the energy specific consumption of 0.5 - 1.0 kWh/m. Than the settling (sediment separation) time was reduced by 7 - 10 times with essentially smaller volume of the sediment; in case of the insoluble anodes, an after-removal of iron(II,III) hydroxides, that remain after the first stage of defluorination, is necessary from concentrations of 5 - 7 mg/l to UPC.

CONCLUSION

The technological scheme of the waste water defluorination is as follows:

1st Stage: the addition of iron salt solution at a ratio of fluorine to iron(II) 1 : 0.9 - 1.0; the addition of lime milk ($\text{Ca}^{2+} : \text{F}^- = 5 - 3 : 1$), the addition of anion type flocculant; settling for 15 min. The final pH value is 11.3 - 12.2.

2nd Stage: acidification by hydrochloric acid up to pH 10.0 - 10.5; electrocoagulation with aluminium electrodes; subsequent acidification by hydrochloric (sulphuric) acid solution up to pH 6.4 - 6.6; sediment separation; settling for 60 min or electroflotation for 5 min; filtration by filter-press or sand filter.

The offered technological scheme allows to purify the technological waste waters from fluorine and chromium to UPC and not to exceed the State Standards on the introduced anions and cations.

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