Wastewater Purification from Inorganic Fluorine Compounds

M. L. BELIKOV and E. P. LOKSHIN

*Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,
Kola Science Centre of the Russian Academy of Sciences,
Ul. Fersmana 26A, Apatity184209 (Russia)*

E-mail: belikov@chemy.kolasc.net.ru

Abstract

Basing on model solutions, the conditions have been determined for purifying wastewater containing 10 mg/L of fluorine in the form of AlF_6^{3-} and/or FeF_6^{3-} complex anions, by means of cerium compounds. For real wastewaters of the enterprises of the Kola region (Apatite JSC and Lovozero Mining-Concentrating Combine) optimum modes have been determined for the purification from fluorine impurities using titanium compounds up to the standard content of fluorine and sulphate ion established for potable water reservoirs.

Key words: fluorine containing wastewater, purification, cerium compounds, titanium

INTRODUCTION

There are several hydrogeochemical provinces in the territory of Russia whose underground waters are characterized by an increased content of fluorine [1–7]. The excess content of fluorine is inherent in the waters of the Moscow artesian freshwater basin [2], the Leningrad [3], Nizhniy Novgorod [4] and the Vologda [5] Regions, Mordovia (including its capital, the Saransk city) [6], Khakassia [7]. In many cases the subsoil waters contain fluorine in the form of FeF_6^{3-} complex. A similar picture is observed for many countries of Asia, Africa, America where fluorine content in superficial and subsoil waters amounts up to 3 and 35 mg/L, respectively [8–12].

Wastewaters with increased content of fluorine in the form of stable inorganic complexes are formed in the manufacture of metal aluminium [13], in the processing of apatite and phosphorite concentrates into mineral fertilizers [14, 15], in the process of etching titanium alloys and special steel. Industrial wastewaters formed are polluted with fluorine in the form of complex anions SiF_6^{2-}, AlF_6^{3-}, and FeF_6^{3-}.

According to the recommendations of the World Health Organization, the permissible content of fluorine in potable water ranges within 0.1–0.5 mg/L. At a lower content of fluorine there is a risk of teeth caries, whereas dental fluorosis develops at fluorine content >1.5 mg/L and pathological skeleton transformations begin at fluorine content of 6 mg/L [16].

The content of fluorine in fish industry reservoirs higher than 0.7 mg/L results in benthos destruction and, as consequence, in disappearance of some fish species.

A variety of methods for wastewater treatment from inorganic fluorine compounds were offered. However, all of them or are either inapplicable for purifying large-scale volumes of wastewater (10^6–10^7 m^3/year), or they do not provide the efficiency for purification. Moreover, the use of these methods often results in a secondary pollution of treated wastewater to an unacceptable extent with the components of reagents used as well as in the formation of solid waste products whose burial requires for creation of special ranges.

At low concentration in an aqueous solution (10 mg/L as recalculated for fluorine) fluorine-

containing complex anions can be arranged according to the following sequence of the hydrolytic stability: $SiF_6^{2-} < FeF_6^{3-} \approx TiF_6^{2-} < ZrF_6^{2-} < AlF_6^{3-}$ [17]. The authors of [18] demonstrated the possibility for purification of wastewater containing up to 10 mg/L of fluorine in the form of F^- ion and complex anion SiF_6^{2-}, with the use of titanium sulphate compounds [17]. In this case the recovery of titanium sulphate compounds from sediment and the isolation of fluorine compounds those could further find practical application is provided [19]. However, it follows from the hydrolytic stability order listed above that this method is unsuitable for purifying the wastewater containing fluorine in the form of AlF_6^{3-} and FeF_6^{3-}.

The purpose of this work consisted in the development of methods for wastewater purification from fluorine impurities these are present in the form of stable inorganic complexes AlF_6^{3-} and FeF_6^{3-} as well as in verifying the approach developed earlier [18, 19] based on the use of titanium compounds, for the purification of real wastewaters from ore dressing enterprises of the Kola industrial region.

EXPERIMENTAL

The investigation was carried out with the use of model solutions and real wastewaters from the enterprises of the Kola industrial region. To fluorine-containing solutions was entered a preset amount of a reagent. The preset value of pH was maintained by adding NaOH concentrated solution. After stirring the sediment formed was separated via sedimentation or centrifugation. The level of fluorine removal was estimated from the residual fluorine content in the solution determined by means of ionometric method using an ionometer I-160 with Volta 3000 fluorine selective electrode. The measurement was carried out at pH 8, which provided completeness for the hydrolysis of fluorine containing complexes [17].

For a number of experiments we additionally determined the amount of fluorine passed into the sediment. For this purpose the sediments were processed with NaOH solution (pH 12), the solid and liquid phases were separated by means of centrifugation and then the

content of fluorine in the solution obtained was determined using an ionometric method. No discrepancy in the balance of fluorine was observed.

RESULTS AND DISCUSSION

Studies on defluoridation of aqueous solutions containing fluorine in the form of FeF_6^{3-} and AlF_6^{3-}

The experiments were carried out with the use of model solutions containing 10 mg/L of fluorine in the form of complex compounds such as $(NH_4)_3FeF_6$ or $(NH_4)_3AlF_6$. The chosen value of the fluorine content was caused by the fact that the total content of fluorine in various anionic forms does not usually exceed 10 mg/L both for the wastewater of enterprises and subsoil water from artesian wells contaminated with fluorine. In the studies of methods for wastewater purification from the impurities of fluorine presenting in the form of stable inorganic complexes, the main part of the results is obtained for the most hydrolytically stable complex such as AlF_6^{3-}.

The purification of solutions from fluorine is possible provided that the fluorine complex with a precipitating sorbent formed is hydrolytically much more stable, than the fluorine complex presenting in the solution. Moreover, it is necessary that the water solubility of the anew formed complex be low enough.

At the initial stage we have investigated the possibility to use water-soluble compounds of cerium (IV) for the purification from fluorine. The choice of cerium (IV) cation for binding fluorine as a constituent of FeF_6^{3-} and AlF_6^{3-} anions is based on the following reasons:

(i) It has been demonstrated earlier [17] that in subacid media (pH 5–5.6) such anions as FeF_6^{3-} и AlF_6^{3-} at low concentration are hydrolyzed to a considerable extent;

(ii) we have found no data concerning the value of water solubility for CeF_4, however this value should be, to all appearance, comparable to the solubility of ThF_4, equal to $2 \cdot 10^{-5}$ mass % [20];

(iii) The solubility product value for $Ce(OH)_4$ is equal to $2 \cdot 10^{-48}$ [21], therefore the solubility of $Ce(OH)_4$ amounts to $2.0 \cdot 10^{-5}$ mg/L.

We have hypothesized that fluorine is either precipitated in the form of low-soluble

TABLE 1

Purification of solutions of fluorine impurities entered in the form of Na_3AlF_6 using calcium compounds

Compound	Ca^{2+} consumption, g/L	Molar ratio Ca^{2+}/F^-	pH	Residual fluorine (F^-) content, mg/L
$CaCl_2$	0	0	5.65	15.0
	0.144	4. 6	6.10	12.0
	0.580	18.3	6.20	9.0
$Ca(OH)_2$	0.220	6.8	12.00	10.5
	0.430	13.7	12.23	8.4
	0.650	20.5	12.45	7.2

CeF_4, or adsorbed by cerium (IV) hydroxide formed due to the hydrolysis $Ce(SO_4)_2$ at $pH \geq 2.7$ [22]. In this case one could achieve a negligible secondary pollution of wastewater with Ce^{4+} ion.

It has been demonstrated earlier [23] that at the content of fluorine ≥ 10 mg/L, a part of fluorine from the solutions containing fluoride ion F^- should be preliminary precipitated in the form of CaF_2 with using $Ca(OH)_2$ or $CaCl_2$ in order to reduce the consumption of rare-earth salts as well as to decrease the secondary contamination of the solution with the anion of a salt used for sedimentation,

From the data of Table 1 one can see that fluorine presenting in the solution in the form of Na_3AlF_6 is more difficult to precipitate by calcium compounds, and its content can be reduced only down to ≈ 7 mg/L. It is connected with the fact that under increase in $CaCl_2$ concentration in the solution there is an increase in the secondary contamination of the solution with chlorine and calcium, whereas the increase in concentration $Ca(OH)_2$ is limited by its water solubility value equal to 1.6 g/L.

We used $Ce(SO_4)_2 \cdot 4H_2O$ as a water-soluble cerium (IV) compound. The technique for the investigation of fluorine sedimentation efficiency is similar to that described earlier in [17].

In order to study the effect of solution pH at fixed $Ce(SO_4)_2 \cdot 4H_2O$ consumption on the efficiency of fluorine sedimentation, a solution of Na_3AlF_6 was placed into four glasses 250 mL in capacity, to each of them was added 100 mg of $Ce(SO_4)_2 \cdot 4H_2O$ and then a reaction was run at the solution pH value of 4, 5, 6 or 7, respectively. For adjusting the acidity value NaOH was used. After 60 min passed, the residual content of fluorine was determined.

Data concerning the sedimentation of fluorine present in the solution in the form of Na_3AlF_6 depending on solution pH are tabulated below (the molar ratio $Ce^{4+} : F^- = 1.88$):

pH	Fluorine content in purified solution, mg/L
3.0	3.8
3.5	3.9
4.0	3.9
5.0	4.0
6.0	4.2
7.0	7.0

One can see that for pH value ranging within 3−6 the efficiency of fluorine sedimentation changes insignificantly, but at pH 7 the efficiency of fluorine sedimentation is reduced in an abrupt manner, which indicates a considerable increase in the hydrolysis level for cerium compound precipitated. At pH 3−5 one can observe the formation of fine-dispersed sediment with a low sedimentation rate, whereas at pH 6−7 a much coarser with a high sedimentation rate is formed. In this connection the further experiments were carried out at pH value of 5.5−6, which provided a high enough efficiency of fluorine sorption with a plausible sedimentation rate.

We have investigated the kinetics of fluorine binding with cerium (IV) in Na_3AlF_6 solution (Table 2). For this purpose to 1000 mL of Na_3AlF_6 solution containing 10 mg/L F^-, was added 1400 mg of $Ce(SO_4)_2 \cdot 4H_2O$. The solution was stirred maintaining the acidity of the solution to be within the range of pH 5.5−6.0 by adding NaOH, and then we measured the residual content of fluorine with a periodical sampling. The data obtained concerning the residual fluorine content are somewhat underes-

TABLE 2

Fluorine content in the solution depending on the time interaction between AlF_6^{3-} and $Ce(SO_4)_2 \cdot 4H_2O$ (molar ratio $Ce^{4+} : F^- = 5.65$)

Interaction time, min	pH of determination	Fluorine content in purified solution, mg/L
5	5.6	2.2
10	6.0	1.80
15	6.0	1.20
20	6.0	1.10
60	5.80	1.05

Fig. 1. IR spectrum of the sediment formed due to $Ce(SO_4)_2 \cdot 4H_2O$ hydrolysis (interpretation according to[24]).

timated (see Table 2) since the measurements were carried out at pH 5.5−6.0 (the authors of [17] demonstrated that the hydrolysis of AlF_6^{3-} completes at pH 7.7, whereas the measurements at pH 6 result in a relative error of ~30 %). Nevertheless, one can see that the process of sorption completes, in the main, approximately within 15 min.

Table 3 demonstrates the data concerning the influence of cerium (IV) consumption upon the efficiency of purification for the solutions containing 10 mg/L fluorine in the form of $(NH_4)_3FeF_6$ or Na_3AlF_6.

As one would expect from the comparative analysis of the data for hydrolytic stability of AlF_6^{3-} and FeF_6^{3-} anions, the purification of the solution containing fluorine in the form of AlF_6^{3-} proceeds in a somewhat more difficult manner as compared to the purification of the solution containing fluorine in the form of FeF_6^{3-}.

The reduction of fluorine content down to the level regulated for water reservoirs of drinking purposes (1.5 mg/L) is achieved at the consumption of $Ce(SO_4)_2 \cdot 4H_2O$ amounting to 1200 and 1400 mg/L for wastewater contain-
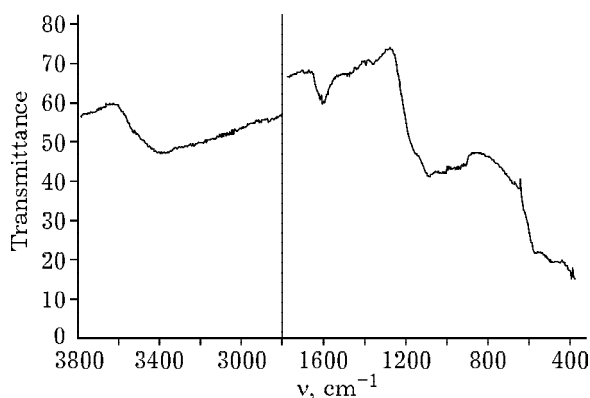
ing 10 mg/L fluorine in the form of FeF_6^{3-} and AlF_6^{3-}, respectively. As the consumption of $Ce(SO_4)_2 \cdot 4H_2O$ increased, a more profound fluorine separation from the solution is attained.

The data presented in Table 3 allow one to conclude that the main part of fluorine (~80 %) is precipitated rather readily, whereas in order to reduce its content down to <2 mg/L a significant consumption of a precipitating agent is required. Judging by the molar ratio $Ce^{4+} : F^-$, fluorine is precipitated by no means in the form of fluoride CeF_4.

According to IR spectroscopy, the fluorine-containing sediment represents basic cerium (IV) sulphate (Fig. 1). On the one hand, this fact determines the decrease in the secondary contamination level for the solution with sulphate ion which level at the residual fluorine content <1.5 mg/L reached is equal to 285 and 330 mg/L for the solutions containing FeF_6^{3-} and AlF_6^{3-}, respectively. These values meet the standards concerning the content of sulphate ion for water reservoirs of drinking purpose (500 mg/L).

On the other hand, the fluorine-containing sediment represents by no means hydroxide, but basic cerium (IV) sulphate, therefore due

TABLE 3

Sedimentation level for fluorine in the form of $(NH_4)_3FeF_6$ или Na_3AlF_6 depending on $Ce(SO_4)_2 \cdot 4H_2O$ consumption (the solution acidity during defluorination process corresponds to pH ~ 5.5−6.0)

Reagent consumption, mg/L	Molar ratio $Ce^{4+} : F^-$	Fluorine content in purified solution*, mg/L
800	3.76	1.75/2.00
1200	5.65	1.30/1.70
1400	6.69	1.25/1.35
1600	7.53	0.65/1.00

*The first and the second values stand for the use of $(NH_4)_3FeF_6$ and Na_2AlF_6, respectively.

to $Ce(SO_4)_2 \cdot 4H_2O$ hydrolysis there is the formation of only two rather than four hydroxyl groups falling on each cerium atom those could be replaced by F^- anion. In this connection, in order to study the possibility for a more efficient utilization of cerium in the process of fluorine sedimentation we have carried out experiments with the participation of Ce(III) water-soluble salts whose hydrolysis results in the formation of three hydroxyl groups falling on each Ce(III) atom.

To Na_3AlF_6 solutions containing 10 mg/L F^-, was added 0.705 g/L of $Ce_2(SO_4)_3 \cdot 8H_2O$. A preset pH value was maintained with the use of Na_2CO_3. Data concerning the effect of pH value on the purification from fluorine (at the molar ratio $Ce^{3+} : F^- = 3.76$, interaction time of 120 min, the temperature of 18.5 °C) are presented below:

pH	Fluorine content in the solution purified, mg/L
4.0	2.90
5.0	2.90
6.0	1.30
7.0	1.42

From the comparative analysis of the above listed results and the data of Table 3 it follows that the efficiency of purification with the use of cerium (III) is almost in 1.5 times higher than in other cases at the identical values of pH and molar consumption of cerium (the residual content of fluorine decreases from 2 to 1.3 mg/L).
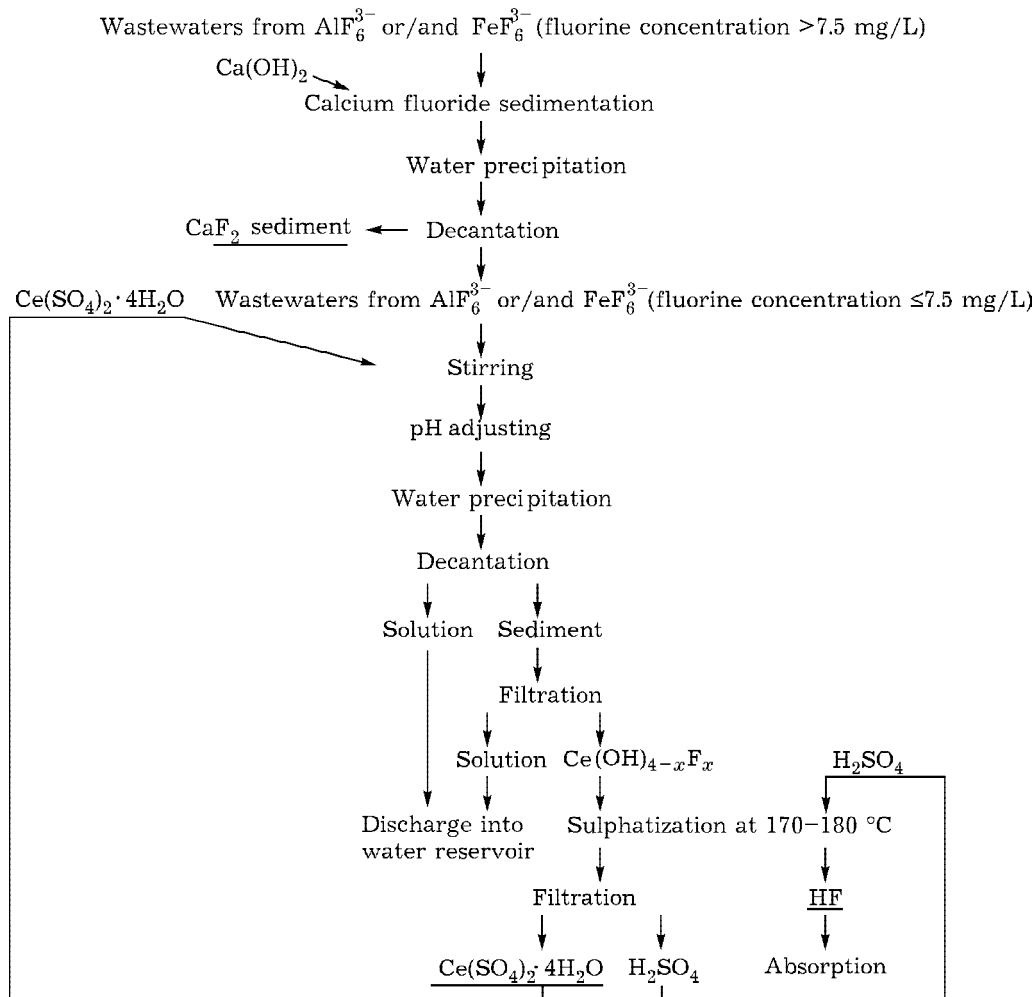

Fig. 2. Schematic diagram for the purification of wastewater containing fluorine in the form of AlF_6^{3-} or/and FeF_6^{3-} anions to meet the standards established for water reservoirs of drinking purpose.

With the use of cerium (III) and pH < 5 a fine-disperse sediment is also formed. At pH 5.8 coarse flakes are formed those precipitate almost completely within 15 min (the solution layer height being of 0.4 m). A fine-disperse fraction remaining in the solution precipitates during 15–18 h. The maximum efficiency of fluorine extraction from solutions is attained at pH 6. In this case the residual content of fluorine and sulphate ion (285 mg/L) meets the standards established for water reservoirs of drinking purpose.

Figure 2 presents a schematic diagram for the purification of wastewater containing fluorine in the form of AlF_6^{3-} or/and FeF_6^{3-} anions that provides the regeneration of $Ce(SO_4)_2 \cdot 4H_2O$, the isolation of a fluorine-containing product excluding the increased secondary contamination of wastewater with sulphate ion. A variant which provides the use of $Ce_2(SO_4)_3$ or $CeCl_3$ and somewhat differs in the regeneration of cerium compound used for fluorine sedimentation is also possible. The use of $CeCl_3$ allows one to meet the standards established for water reservoirs of drinking purpose with respect to the content of both fluorine and chloride ion.

The residual content of cerium was determined using a ICPS-9000 Shimadzu plasma emission spectrometer. It has been revealed that this value depends on pH of the solution and sedimentation time, amounting to 0.010–0.012 mg/L, or $(0.7–0.86) \cdot 10^{-7}$ mol/L under the conditions optimal for the purification from fluorine (pH 5.5–6.0).

The maximum permissible concentration in water for cerium and other lanthanides is not established in Russia. The authors of [25] demonstrated that at the concentration values $<10^{-6}$ mol/L lanthanides do not influence the process of hemolysis. From this it follows that the secondary contamination of water by cerium, to all appearance, is of no hazard.

Purifying the Kola regional mining enterprises wastewaters from fluorine impurities

For the experiments we used aqueous solutions such as wastewaters from the concentrating factory ANOF-II of the Apatite JSC and the Karnasurt mine of the Lovozero MCC. Table 4 presents data concerning the content of fluorine and some impurities those could influence the removal of fluorine.

The content of aluminium and iron impurities appeared low enough; therefore we investigated the possibility for purifying these wastewaters by means of titanium compounds.

From the data presented in Table 5 one can conclude that the use of titanium compounds is rather efficient: the residual content of fluorine and a sulphate ion in water does not exceed the standards set-up for water of drinking purpose. It has been established that the process temperature (4–21 °C) exerts no effect on the results of purification. The sedimentation rate value for a reagent containing fluorine amounted to 0.026–0.03 m/h, and attempts to increase it by entering a coagulant (polyacrylamide) appeared unavailing. However, after 18 h the final content of fluorine in the solution with polyacrylamide is lower than fluorine content in the solution without polyacrylamide.

The content of fluorine could be lowered to meet the standard established for water reservoirs of fish industry purpose; however, in this case the secondary contamination with sulphate ion would increase.

Experiments on the regeneration of a precipitating sorbent were carried out. The fluorine-containing sediment isolated from the so-

TABLE 4

Content of some impurities in wastewaters from the enterprises of Apatite JSC (ANOF-II) and Lovozero MCC (the Karnasurt mine)

Enterprise	pH	Impurity content, mg/L					
		F	Fe	Al	CaO	SiO_2	P_2O_5
Apatite JSC	8.90	8.4	<0.5	<1.0	20	7	n/d
Lovozero MCC	7.86	11	<1.0	1.2	n/d	n/d	16

Note. n/d – not determined.

TABLE 5

Efficiency of fluorine removal from waste waters from the ANOF-II Apatite JSC and the Karnasurt mine of Lovozero MCC (initial content of fluorine being of 8.4 and 11 mg/L, respectively, room temperature) depending on the consumption of $TiOSO_4 \cdot 2H_2O$

$TiOSO_4 \cdot 2H_2O$ consumption, mg/L	SO_4^{2-} content in purified solution, mg/L	Final fluorine content, mg/L
	ANOF-II	
640	313	1.3
800	392	1.1
1200	588	0.8
1400	686	0.5
	Karnasurt mine	
640	313	1.6
800	392	1.5
1200	588	0.9
1400	686	0.8

lution was treated with NaOH or Na_2CO_3 solution under permanent stirring. Fluorine therewith quantitatively passes into the solution and titanium oxohydroxide is formed. The solution of NaF could be used as raw material for the manufacture of fluorine-containing products. Titanium oxohydroxide separated from NaF solution was dried; then it was mixed with a stoichiometrical amount of sulphuric acid (93 %), which was determined according to equation $TiO_2 + H_2SO_4 \rightarrow TiOSO_4 \cdot H_2O$. Further the mixture was heated up to the temperature of $150\ ^{\circ}C$ and held under these conditions for 4 h. A fragile cake well soluble in water or in 5 % H_2S0_4 solution was obtained. The level of titanium extraction into sulphate solution in searching experiments amounted to 90 %. The solution of $TiOSO_4 \cdot H_2O$ obtained is suitable for using as a precipitating sorbent.

CONCLUSIONS

1. The possibility is established and the conditions are determined for purification of wastewaters containing 10 mg/L of fluorine in the form of complex AlF_6^{3-} and/or FeF_6^{3-} anions with the use of cerium (IV) sulphate up to the values meeting the standards in the content of fluorine for drinking water reservoirs.

Fluorine removal down to a level meeting the standards set-up for water reservoirs of fish industry purposes is observed to be possible; however, the secondary contamination of wastewaters with sulphate ion exceeds a permissible value.

2. The use of cerium (III) compounds for the purification from fluorine is considered to be more efficient in comparison with the use of cerium (IV) compounds. The optimum acidity of the solution providing both efficient wastewater purification from fluorine, and minimal secondary contamination of wastewaters with cerium cations, corresponds to pH $\approx$ 6.

3. The use of cerium (III) chloride (simple lanthanide tetrachlorides are unknown [26]) allows one perform the purification of wastewater containing fluorine even in the form of complex anions such as AlF_6^{3-} and/or FeF_6^{3-}, up to meeting the standards established for water reservoirs of fish industry purpose.

4. The possibility is established as well as optimum modes are determined for purifying wastewater of the enterprises of the Kola region (Apatite JSC, Lovozero MCC) to remove fluorine impurities using titanium compounds up to meeting the standards concerning the content of fluorine and sulphate ion established for drinking water reservoirs.

The potentiality is demonstrated for processing fluorine-containing sediments formed with the regeneration of a titanium compound used for the sorption as well as the isolation of a fluorine-containing product.

REFERENCES

1 V. V. Semenova, L. V. Vorobyeva, P. G. Romashov et al., III Mezhdunar. Konf. "Gorod v Zapolyarye i Okruzhayushchaya Sreda" (Proceedings), Syktyvkar, 2003, p. 391.

2 I. A. Klimenko, V. A. Polyakov, L. G. Sokolovskiy, *Pityevaya Voda*, 2 (2005) 14.

3 A. A. Shtolts, S. A. Gorbanev, *Vestn. SPbGMA*, 3 (2005) 192.

4 Yu. V. Gerasimov, Mezhdunar. Nauch.-Prom. Forum "Velikiye Reki 2003" (Thesises), Nizhniy Novgorod, 2003, p. 274.

5 T. I. Figurina, N. V. Chezhina, R. S. Meshalkin, Nauch.-Prakt. Konf. "Sovremennye Tekhnologii, Metody Ochistki i Obezzarazhivaniya Pityevykh i Stochnykh Vod" (Proceedings), Cherepovets, 2003, p. 12.

6 L. I. Kashina, E. P. Yanin, Institute of Geochemistry and Analytical Chemistry of RAS (Treatises), Moscow, 2003, issue 24, p. 157.

7 O. A. Atyaksheva, I. S. Shvabenland, 8 Mezhdunar, Nauch. Ssk.-Konf. Studentov i Molodykh Uchenykh, Abakan, 2004, vol. 2, p. 40.

8 S. S. Tripathy, J.-L. Bersillon, K. Gopal, *Separ. Purif. Technol*, 50 (2006) 310.

9 C. Reimann, K. Bjorvatn, B. Frengstad et al., *Sci. Total Environ.: An Int. J. Scientific Res. into the Environ. and Its Relationship with Man*, 311 (2003) 65.

10 Wang Jun-yi, Li Bo-ling, Yu Jiang et al., *Chin. J. Endemiol.*, 24 (2005) 420.

11 M. Tahaikt, I. Achary, M. A. Menkouchi Sahli et al., *Desalination: Int. J. Sci. Technol. Water Desalting*, 167 (2004) 357.

12 Wang Zhen-yu, Wang Jin-sheng, Teng Yan-guo et al., *Hydrogeol. and Eng. Geology*, 31 (2004) 42.

13 K. V. Shipilova, II Vseros. Nauch.-Prakt. Konf. (Proceedings), Novokuznetsk, 2006, p. 184.

14 G. A. Selevtsova, T. A. Dbyltrth, 39 Mezhdunar. Nauch Konf. "Agroekologicheskaya Effektivnost' Primeneniya Sredstv Khimizatsii v Sovremennykh Tekhnologiyakh Vozdelyvaniya Selskokhozyaystvennykh Kultur" (Proceedings), Moscow, 2005, p. 321.

15 V. K. Bishimbaev, Zh. K. Bakhov, A. U. Isaeva, Zh. Ospanova, *Uzb. Biol. Zh.*, 4 (2004) 13.

16 A. V. Jamode, V. S. Sapkal, V. S. Jamode, *J. Ind. Inst. Sci.*, 84 (2004) 163.

17 E. P. Lokshin, M. L. Belikov, *Zh. Prikl. Khim.*, 81 (2008) 177.

18 E. P. Lokshin, M. L. Belikov, *Ibid.*, 76 (2003) 1505.

19 RU Pat. No. 2228911, 2004.

20 A. N. Kirgintsev, L. N. Trushnikova, V. G. Lavrentyeva, Rastvorimost' Neorganicheskikh Veshchestv v Vode (Handbook), Moscow−Leningrad, 1972.

21 I. M. Korenman, Zh. Obshch. Khim., 25 (1955) 1859.

22 I. M. Kolthof, E. B. Sendel, Kolichestvenny Analiz, Goskhimizdat, Mosow−Leningrad, 1948.

23 E. P. Lokshin, M. L. Belikov, Mezhdunar. Konf. "Kompleksnaya Pererabotka Netraditsionnogo Titano-redko-metallnogo i Alyumosilikatnogo Syrya: Sovremennoye Sostoyaniye i Perspektivy (Proceedings), Apatity, 2006, p. 138.

24 R. A. Nyguist, R. O. Kogel, Infrared Spectra of Inorganic Compounds, Acad. press, New York etc., 1971, 495 pp.

25 X. Yang, X. Liu, B. Chen et al., Proc. of the First Sino-Dutch Workshop on the Environmental Behavior and Ecotoxicology of Rare Earth Elements, Beijing, 1996. The Netherlands Organisation for Applied Sciences: Netherlands, 1997, p. 205.

26 D. Brown, Halides of the Lanthanides and Actinides, Wiley, NY, 1968.