Fluoride Ion Removal from Liquid Media by Precipitation-flotation

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The presence of fluoride ion in some technological aqueous systems in low concentrations, but higher than the safety limit, imposed the study of separation methods that fulfill the national requirements concerning the water quality. In case of plants, where hydrofluoric acid (HF) is used in pickling tanks (e.g. special steels), the current fluoride ion removing method is the precipitation of CaF_2 followed by decantation. This method does not provide a residual fluoride concentration imposed by the national regulations of 5 $mg\cdot L^{-1}$. The subject of the present contribution is the optimization of this method. It points out the research results regarding the removal of F^- ion by precipitation using technical calcium hydroxide as precipitating reagent. The DAF technique – flotation in the presence of a collector and a flocculent - was used to separate the precipitate from the system. The optimum separation parameters were established and the precipitate-collector interaction mechanism was studied in order to efficiently conduct the process. The proposed solution reaches separation efficiencies nearly to 99%.

Keywords: fluoride removal, precipitate-flotation, technical calcium hydroxide

Waste management has become an important issue in the industry as a result of stringent environmental regulations. Among other pollutants, hydrofluoric acid is used extensively in steel manufactures as pickling agent. Besides the natural geological sources for fluoride enrichment in groundwater, various industries are also contributing to a great extent to fluoride pollution [1]. The industries, which discharge wastewaters containing high fluoride concentrations, include glass and ceramic fabrication, semiconductors manufacturing, electroplating, coal fired power stations, brick and iron works, and aluminum smelters [2]·.

Numerous studies regarding the decrease of fluoride concentration have been undertaken over the years using various methods for wastewater treatment. Adsorption on hydroxyapatite 4.54 $mg\cdot g^{-1}$ adsorption capacity [3], metallurgical grade alumina 12.57 $mg\cdot g^{-1}$ [4] , alum impregnated activated alumina 40.68 $mg\cdot g^{-1}$[5], calcium oxide-modified activated 101.01 $mg\cdot g^{-1}$ [6], aluminium hydroxide impregnated lime stone 84.03 $mg\cdot g^{-1}$ [7], nano-geothite 59 $mg\cdot g^{-1}$ [8], Al–Ce hybrid adsorbent 91.4 $mg\cdot g^{-1}$ [9], Fe–Al–Ce trimetal oxide 178 $mg\cdot g^{-1}$ [10], Fe–Al mixed hydroxide 91.7 $mg\cdot g^{-1}$ [11] are mentioned in the literature. Other applied methods were precipitation with alum sludge [12] and calcium [13], ion exchange [14]; adsorption-electrodialysis [15], reverse osmosis [16], nanofiltration [17] and electro coagulation [18], which have been used to remove fluoride from water with good yields. Among those methods, precipitation is the most convenient, effective, and cheap, especially for industrial applications. Precipitation processes are governed by the resulted salt solubility [17].

The most common method of treatment is the precipitation of calcium fluoride using calcium from either lime or calcium chloride. The existing fundamental problem using lime arises from the low solubility of the CaF_2 (solubility product of CaF_2 is theoretically $K_{spCaF_2} = 3.9 \cdot 10^{-11}$ at 25°C). The relatively high solubility of the calcium fluoride does not allow a complete removal of fluoride. An additional difficulty with lime precipitation is the poor settling characteristics of the precipitate. Lime and calcium salts precipitation of fluoride can practically reduce the residual fluoride concentration to 10 – 15 $mg\cdot L^{-1}$ or even lower but not below the 5 $mg\cdot L^{-1}$ legal limit stipulated by the Romanian legislation. The lime-based fluoride removal can be improved by using an improved variant of ion flotation, part of the adsorptive bubble separation methods.

This paper presents a systematic study for fluoride ion removal from model aqueous media using technical calcium hydroxide, based on principles and characteristics of precipitation and flotation aiming to increase the separation efficiency. The selection of precipitating reagent takes into account its application in both precipitation and pH adjustment of the water from the treatment plants belonging to the special steel industry. Therefore the use of this reagent to decrease the fluoride concentration under the safety limit (5 $mg\cdot L^{-1}$) in such treatment plants by applying combined precipitation-flotation method do not require additional costs.

Experimental part

Materials an methods

- NaF Carlo ERBA (Italy) p.a., 10.53 . 10^{-3}M stock solution of fluoride. Standard solutions with varying NaF concentration were prepared by appropriate dilution of the stock solution. Distillated water was used for preparing the solutions.

-$Ca(OH)_2$ 10% solution was prepared from technical calcium hydroxide powdered (with 90.5% CaO + MgO total; 71.4% CaO + MgO active; 0.8% MgO; 4.2% CO_2 ; 0.3% SO_3);

- NaOL Fluka (Hungary) p.a., 2.5 . 10^{-2} M solution, as collector agent;
- FR2510 (Henkel) anionic flocculent polyacrylamide type, aqueous solution 0.2% concentration;
- H_2SO_4 (1.5M) for *p*H adjustment.
- Kruss K11 tensiometer;
- pH-meter type Orion 420A+;
- A dissolved air flotation unit (DAF) with the cell dimensions: h = 30 cm, Φ = 4.5 cm;

-UV-Vis spectrophotometer SPECORD 205;

-FTIR Spectrometer, ABB MB3000 Series;

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-Thermal Analysis Unit (TG/DTG/DTA/DSC) Netzsch TG 449C STA Jupiter.

A determined volume of solution with fluoride content was treated under stirring with different quantities of technical calcium hydroxide solution 10% on a shaker at a low constant stirring rate in a given time. The precipitating reagent is used in excess for a quantitative precipitation reaction, in order to reduce the solubility of the precipitate as much as possible. The sample was treated with a collector NaOL and then with a flocculent FR2510, after the CaF_2 precipitation with technical calcium hydroxide $Ca(OH)_2$.

The flotation process was carried out in a dissolved-air-flotation apparatus [19]. Water saturated with air in the saturator and kept under pressure of $4 \cdot 10^5$ $N \cdot m^{-2}$ was introduced to the cell base. Fine air bubbles were generated for an appropriate solid/liquid separation, when releasing water to the atmospheric pressure.

The software program Excel was used for processing experimental data, perform calculations and graphs and the reproducibility of separation was estimated by Student's method.

Collector selection

The fluoride ion removal imposed chemical and hydrodynamic conditions for separation of solid particle loaded with pollutant from aqueous medium. The hydrodynamic parameters are adjusted by the homogenous size of the air bubbles and the rate of gaseous flux for a better mass transfer on the top of column from liquid.

In flotation process the collector is a surface-active substance with long linear chain carbon atoms used in order to decrease surface tension of aqueous phase, favouring foaming and interaction with the colligend (ion) by polar functional group forming insoluble sublate, which was concentrated into the foam.

In precipitate flotation, the colligend is precipitated with a reagent, other than the collector. An adequate collector is introduced in system to increase hydrophoby of the precipitate and a flocculent in mass ratio ($m_{flocculent} : m_{pollutant}$) 1 : 100 is used to increase the particle size.

For this reason in selection of collector, it is necessary to know the surface-active tension and is reactivity towards the precipitated colligend.

Collector selection in precipitate flotation must take into consideration the zeta potential of precipitate, CaF_2 in this case, as compatibility and favoring factor for the precipitate-collector interaction.

In this paper sodium oleate (NaOL), a common anionic surfactant agent was used. The importance of oleate solution chemistry in the flotation process results from the fact that the oleic acid in aqueous solution undergoes hydrolysis and forms complex species which exhibit markedly different solubility and surface active characteristics .

Oleic acid ($C_{17}H_{33}COOH$) is a weakly acid insoluble compound in aqueous solution with $pK_a = 4.2$, which forms highly soluble salts with monovalent alkali metal ions such as sodium or potassium. These soluble salts, under appropriate solution *p*H conditions can undergo a series of hydrolysis reactions yielding to complex oleate species. The species that have been considered are oleate ion (R^-), oleic acid (RH) ,acid-soap (R_2H^-), acid - soap salt (R_2HNa) and oleate dimer (R_2^{2-}) [20].

Surface properties were verified by drawing NaOL surface tension isotherms of oleic acid solutions of different concentrations.

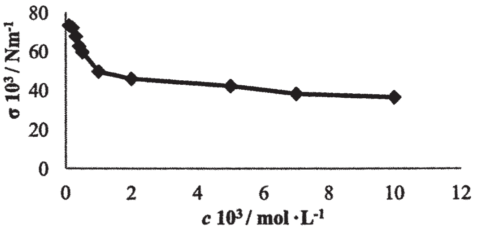

Fig. 1. NaOL surface tension isotherm (18°C)

The surface activity of sodium oleate solution could be assessed by the descending allure of surface tension isotherm showed in figure 1.

Literature information's regarding the CaF_2 zeta potential (ζ) shows that it has positive values for a *p*H values up to 10.5 . For *p*H values high than 10.5 its sign reverses. Thereby the use of an anionic collector and the optimum *p*H range for flotation can be anticipated.

Results and discussions

The influencing factors under various conditions (*p*H, stirring rate, contact time, molar ratio, initial fluoride concentration, etc.) were studied in order to establish the optimal F^- separation parameters.

pH effect

The aqueous solution *p*H has an important role, which influences the precipitation of CaF_2. Therefore the precipitation of fluoride as CaF_2 was examined at various *p*H values ranging from 7.5 to 12.3. The results were presented in figure 2. The *p*H of the investigated solutions is controlled by adding calcium hydroxide technical solution.

The fluoride ions separation efficiency increased with pH and for the decanted effluents the maximum is approximately 99% at *p*H = 10.44, which is nearby the *p*H value corresponding to the CaF_2 ζ sign changing. One can observe that the separation efficiency over 90% is obtained beginning with the 10.5 *p*H.

An explanation would be the presence of M^{2+} (M = Ca, Mg) ions in the diffuse layer due to the excess of the precipitating reagent, that surrounds the solid precipitate particles, such as the oleate anion reacts efficiently at *p*H = 10.44 (fig. 2).

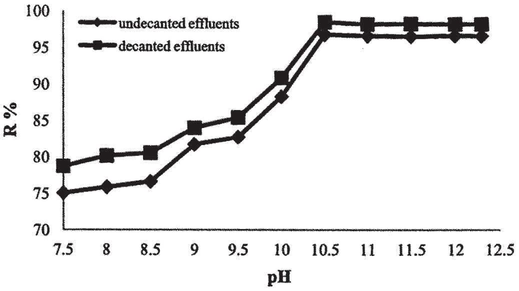

Fig. 2. R % = f (*p*H), $c_{iF^-} = 200$ $mg \cdot L^{-1}$, stirring rate = 200 rpm., stirring time = 20 min., $c_{F^-} : c_{Ca^{2+}} : c_{NaOL} = 2 : 1 : 10^{-1}$, mass ratio ($m_{flocc} : m_{F^-}$)= 1 : 100, $V_{sample} : V_{water} = 3 : 1$, p = $4 \cdot 10^5$ $N \cdot m^{-2}$, flotation time = 5 min

Stirring time influence

In order to establish the optimal stirring time, 9 similar model solutions were prepared and only the contact time (t) of mixed reagents was changed (6; 9; 12; 15; 18; 20; 24; 27 and 30 min.). Each sample was flotated after the determined reacting time (fig. 3).

The experimental results plotted in figure 3 point out that a stirring time higher than 20 min is not necessary

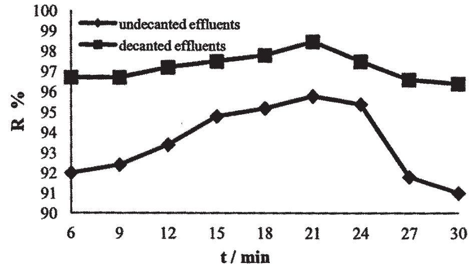

Fig. 3. R % = f (t), $c_{iF^-} = 200$ mg·L^{-1}, stirring rate = 200 rpm., pH = 10.44, $c_{F^-} : c_{Ca^{2+}} : c_{NaOL} = 2 : 1 : 10^{-1}$,mass ratio ($m_{flocc} : m_{F^-}$) = 1 : 100, $V_{sample} : V_{water} = 3 : 1$, p = 4·10^5 N·m^{-2}, flotation time = 5 min

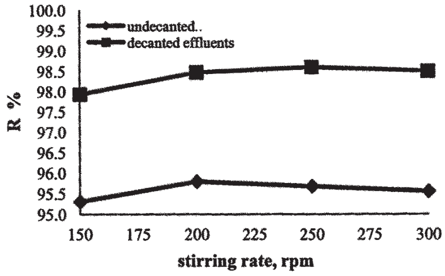

Fig. 4. R % = f (stirring rate), $c_{iF^-} = 200$ mg·L^{-1}, stirring time = 20 min., pH = 10.44, $c_{F^-} : c_{Ca^{2+}} : c_{NaOL} = 2 : 1 : 10^{-1}$,mass ratio ($m_{flocc} : m_{F^-}$) = 1 : 100, $V_{sample} : V_{water} = 3 : 1$, p = 4·10^5 N·m^{-2}, flotation time = 5 min

because the maximum separation efficiency is reached for timescales up to this value.

Stirring rate

In order to observe that parameter impact on the separation process four identical samples were prepared at different stirring rates (150; 200; 250 and 300rpm.) for 20 min. After the sampling, the aqueous systems were flotated and more effluents resulted. Figure 4 shows the experimental results for all the effluents.

Experimental results plotted in figure 4 shows that the optimum stirring rate is 200 rpm.

Reagents concentration

The collector concentration influence on the separation efficiency was studied with respect to the following conditions: $c_{iF} = 200$mg·L^{-1}, stirring rate = 200rpm., stirring time = 20 min, optimum pH = 10.44 and different $c_{F^-} : c_{Ca^{2+}} : c_{NaOL}$ molar ratios.

In the precipitation phase, the separation efficiency dependence on the precipitating reagent concentration (excess) for different molar ratio ($c_{F^-} : c_{Ca^{2+}} : c_{NaOL}$) was studied (table 1).

One can observe that the separation efficiencies are high ($95.28 \le R\ \% \le 99.42$) in the case of precipitating reagent excess ($2 : 1 \le c_{F^-} : c_{Ca^{2+}} \le 2 : 10$) in the decanted effluents at pH = 10.44, but a large excess of technical calcium hydroxide should be avoided.

In the case of small consumption of collector (10^{-3}M) and in the undecanted effluents, the separation yields ($90.13 \le R\ \% \le 93.87$) are lower.

The results presented in table I shows that the best separation efficiency ($98.47 < R\ \% \le 98.50$, where 3.01 mg·L^{-1} $< c_{fdF^-} \le 3.06$ mg·L^{-1}) was obtained for a molar ratio range $2 : 1 : 10^{-1} < c_{F^-} : c_{Ca^{2+}} : c_{NaOL} \le 2 : 1.25 : 10^{-1}$ for the decanted effluents by correlation between the precipitating reagent excess and the collector consumption.

Fluoride ion initial concentration

In order to establish the fluoride ion initial concentrations, different concentrations of those ions in the studied model solutions ranging from 10 mg·L^{-1} to 1000 mg·L^{-1} and mimicking the real water samples from the special steel factory have been proposed. Its influence on the separation efficiency by flotation experiments in the presence of the selected collector (NaOL) was studied. The fluoride ion initial concentrations were: c_{iF^-} = 10; 50; 100; 200; 500 and 1000 mg·L^{-1}, respectively. Those solutions were mixed with technical calcium hydroxide for 20 min with a stirring rate of 200 rpm resulting the first effluents from the studied systems, which were subject to the flotation (fig.5).

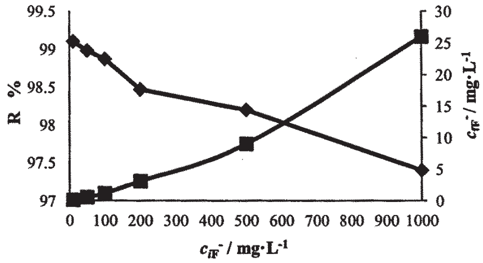

Fig.5. R % = f (C_{iF^-}), stirring rate = 200 rpm, stirring time = 20 min., pH = 10.44, $c_{F^-} : c_{Ca^{2+}} : c_{NaOL} = 2 : 1 : 10^{-1}$, mass ratio ($m_{flocc} : m_{F^-}$) = 1 : 100, $V_{sample} : V_{water} = 3 : 1$, p = 4·10^5 N·m^{-2}, flotation time = 5 min

Table 1

R % = f ($c_{F^-} : c_{Ca^{2+}} : c_{NaOL}$)

Molar ratio $c_{F^-} : c_{Ca^{2+}} : c_{NaOL}$	c_{fF^-} mg·L^{-1}		**R_{ud} %**	**R_d %**
	$c_{f\,ud}$	$c_{f\,d}$		
2:10:1	4.38	2.15	97.81	98.93
2:10:10^{-1}	3.26	1.96	98.37	99.02
2:10:10^{-2}	5.5	3.21	97.25	98.40
2:10:10^{-3}	12.26	5.28	93.87	97.36
2:5:1	3.14	1.54	98.43	99.23
2:5:10^{-1}	6.42	2.09	96.79	98.96
2:5:10^{-2}	7.48	2.81	96.26	98.60
2:5:10^{-3}	17.2	5.84	91.40	97.08
1:2.5:1	3.5	1.68	98.25	99.16
1:2.5:10^{-1}	8.91	2.85	95.55	98.58
1:2.5:10^{-2}	9.88	4.28	95.06	97.86
1: 2.5:10^{-3}	16.52	8.64	91.74	95.68
2:1.25:1	3.72	1.79	98.14	99.11
2:1.25:10^{-1}	7.22	3.01	96.39	98.50
2:1.25:10^{-2}	10.28	4.32	94.86	97.84
2:1.25:10^{-3}	19.41	9.16	90.30	95.42
2:1:1	3.69	1.83	98.16	99.09
2:1:10^{-1}	7.24	3.06	96.38	98.47
2:1:10^{-2}	10.58	4.74	94.71	97.63
2:1:10^{-3}	19.74	9.44	90.13	95.28

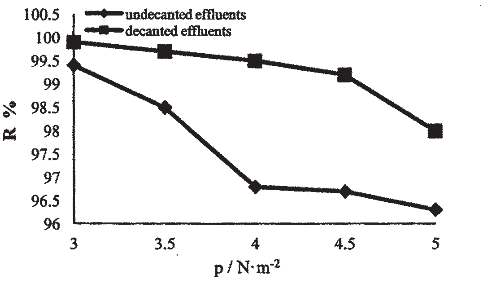

Fig.6. R % = f (p), $C_{i\,F^-}$ = 200 mg·L^{-1}, stirring rate = 200 rpm, stirring time = 20 min., *p*H = 10.44, $c_{F^-} : c_{Ca^{2+}} : c_{NaOL}$ = 2 : 1 : 10^{-1}, mass ratio ($m_{flocc} : m_{F^-}$) = 1 : 100, $V_{sample} : V_{water}$ = 3 : 1, flotation time = 5 min

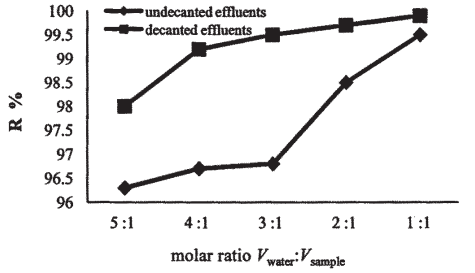

Fig. 7. R % = f (V_{sample}:V_{water}), $c_{i\,F^-}$ = 200 mg·L^{-1}, stirring rate = 200 rpm, stirring time = 20 min, *p*H = 10.44, $c_{F^-} : c_{Ca^{2+}} : c_{NaOL}$ = 2 : 1 : 10^{-1}, mass ratio ($m_{flocc} : m_{F^-}$) = 1 : 100, p = 4’”10^5 N·m^{-2}, flotation time = 5 min

The separation efficiency depending on the fluoride ion initial concentration has varied between 97.4 and 99.1 for the decanted effluents. So that, the fluoride concentrations can be used in the range of 10 - 200 mg·L^{-1} to obtain an effluent containing less than 5 mg·L^{-1}.

The interference of NO_3^- and Cl^- ions on separation efficiency

Studies were also achieved to establish the NO_3^- and Cl^- ions interference on the fluoride ion separation efficiency. The influence of different concentrations of nitrate ions (10, 20, 50, 100 mg·L^{-1} NO_3^-), chlorine ions (10, 20, 50, 100 mg·L^{-1} Cl^-) and of the similar concentrations for both ions, respectively, were studied using the previously determined optimal separation parameters.

The obtained experimental results indicate that the fluoride separation efficiency is not influenced by the presence of NO_3^- and Cl^- ions in the aqueous solutions.

Pressure in pressure vat

After establishing *p*H flotation, the sample was introduced in a flotation cell and the gas bubbles were generated by expansion of pressurized water. For this reason was necessary the study of pressure influence on the separation efficiency R %. Flotation experiments were performed at in a pressure vat (5·10^5; 4.5·10^5; 4.0·10^5; 3.5·10^5; 3.0·10^5 N·m^{-2}) and invariable dilution rate established in another experimental and theoretical studies (V_{sample} : V_{water} = 3 : 1) figure 6.

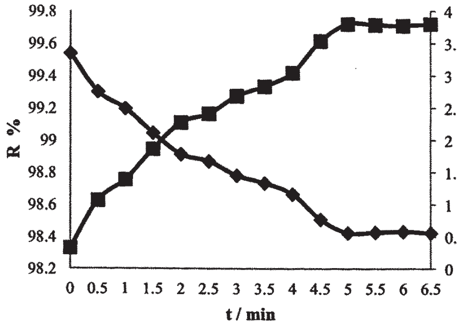

Fig. 8. Separation equilibrium

From figure 6 can be observed that the optimal value of the pressure corresponds to 4·10^{5}N·m^{-2}.

Dilution ratios V_{sample}: V_{water}

Flotation experiments were done to constant pressure (4 . 10^5 N·m^{-2}) and different dilution ratios V_{sample} : V_{water} (5 : 1; 4 : 1; 3 : 1; 2 : 1 and 1 : 1). The figure 7 shows fluoride separation efficiency correspondent with all the experimental ratios.

It will use the economically dilution ratio V_{sample}: V_{water} = 3 : 1.

Flotation separation equilibrium

Study of flotation separation equilibrium performed at optimal parameters (table 2) has in view separation efficiency fate depending on time.

The curve *R % = f(t)* represented in figure 8 shows a growth of flotation separation efficiency during the time, when, after only about 5 min , the separation equilibrium state is reached.

Optimum separation parameters

In order to obtain maximum separation efficiency the optimum separation parameters were established (table 2) based on the studied influencing factors.

Separation reproducibility

Reproducibility of separation is a research stage, which validates the optimal confidence interval of the obtained results, expressed by c_{fF^-}. For this purpose determinations were performed on five identical samples for each three solutions with different initial F$^-$ concentrations like c_{iF^-} = 200 mg·L^{-1}, 100 mg·L^{-1} respectively 50 mg·L^{-1}. The obtained results (c_{fF^-}) were processed by Student’s method (table 3).

The process flow sheet

The process flow sheet showed in figure 9 was proposed for an efficient separation of fluoride ions in respect with the selected optimal parameters.

Collector - precipitate interaction

The study of collector-precipitate interaction, which was established in the process of the fluoride ion separation by precipitate flotation from aqueous systems, represents an

Table 2
OPTIMUM SEPARATION PARAMETERS

Separation parameters	
Stirring rate, rpm.	200
Stirring time, min.	20
pH flotation	10.44
Molar ratio $c_{F^-} : c_{Ca^{2+}} : c_{NaOL}$	2 : 1 : 10^{-1}
F$^-$ concentration, mg·L^{-1}	10 - 500
Dilution ratio V_{sample} : V_{water}	3 : 1
Equilibrium pressure in pressure recipient, Nm^{-2}	4.0 · 10^5
Flotation time, min.	5

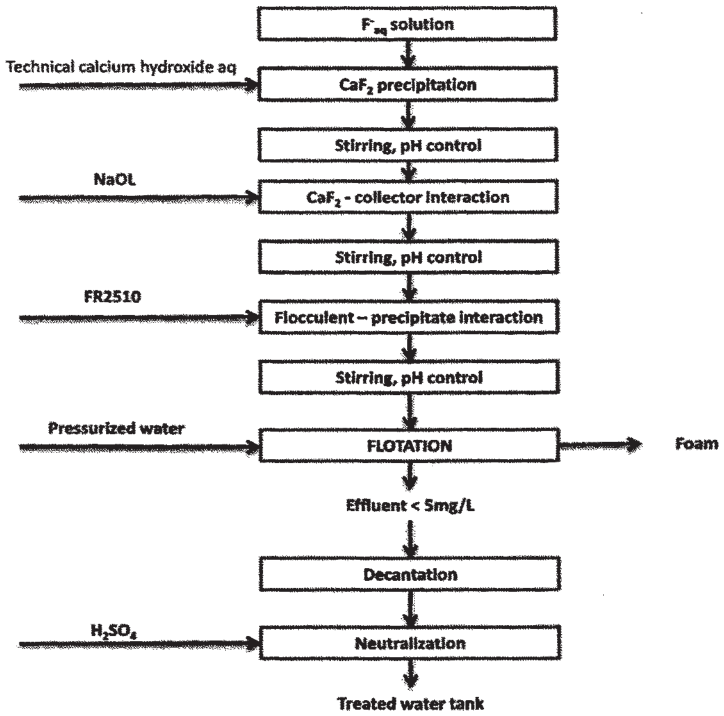

Fig 9. The process flow sheet for the CaF_2 precipitation-flotation.

Table 3
F^- SEPARATION REPRODUCIBILITY

Sample no.	Separated sample characteristics	c_{fF}^- mg·L^{-1}	Statistical probability
1	ci_F^-=200 mg·L^{-1} Stirring rate, 200 rpm Stirring time, 20 min pH =10.44 $c_F^- : c_{Ca}^{2+} : c_{NaOL} = 2:2.5:10^{-1}$ Mass ratio ($m_{flocc}:m_F^-$) = 1:100 $V_{sample}:V_{water} = 3:1$	3.05	$\bar{x}$=3.05 $S_{\bar{x}}$= 0.0226 P = 95 % c_{fF}^- = 3.05 ± 0.0583 P = 99 % c_{fF}^- = 3.05 ± 0.0914
2		2.98	
3		3.06	
4		3.03	
5		3.12	
1	ci_F^-=100 mg·L^{-1} Stirring rate, 200 rpm Stirring time, 20 min pH = 10.44 $c_F^- : c_{Ca}^{2+} : c_{NaOL} = 2:2.5:10^{-1}$ Mass ratio ($m_{flocc}:m_F^-$) = 1:100 $V_{sample}:V_{water} = 3:1$	1.12	$\bar{x}$=1.15 $S_{\bar{x}}$ =0.0216 P = 95 % c_{fF}^- = 1.15± 0.0555 P = 99 % c_{fF}^- = 1.15 ± 0.0870
2		1.13	
3		1.21	
4		1.18	
5		1.09	
1	ci_F^-=50 mg·L^{-1} Stirring rate, 200 rpm Stirring time, 20 min pH =10.44 $c_F^- : c_{Ca}^{2+} : c_{NaOL} = 2:2.5:10^{-1}$ Mass ratio ($m_{flocc}:m_F^-$) = 1:100 $V_{sample}:V_{water} = 3:1$	0.53	$\bar{x}$=0.53 $S_{\bar{x}}$=0.0191 P = 95 % c_{fF}^- = 0.53 ± 0.0492 P = 99 % c_{fF}^- = 0.53 ± 0.0771
2		0.48	
3		0.51	
4		0.56	
5		0.59	

important stage in our research. The insoluble species (sublate) concentrated in froth at optimum separation parameters was investigated by physicochemical methods (FT-IR and thermal analyses). The same investigations were achieved for the free collector (NaOL), CaF_2 p.a., obtained CaF_2 by precipitation and technical calcium hydroxide for comparison with sublate.

FT-IR spectra were plotted in 200 - 4000cm^{-1} region (table 4).

The information obtained from FT-IR analysis has revealed the formation of CaF_2. This presumption is sustained by the specific $n_{Ca\text{-}F}$ band present in CaF_2 obtained precipitate and sublate.

The examination of derivatogrames performed in 20 - 550°C range (fig. 10) for CaF_2 p.a- 1, NaOL -2, technical calcium

Table 4
CHARACTERISTIC FT-IR BANDS of NaOL, CaF_2 (p.a.), CaF_2 (pp), CaOL (pp.) AND SUBLATE(PF)

Sample	Characteristic bands assigned, cm^{-1}				
	ν_{OH_2}	$\nu_{C=O}$	$\delta_{Ca\text{-}O\text{-}H}$	$\nu_{Ca\text{-}O}$	$\nu_{Ca\text{-}F}$
Literature[21]	3700-3500	1660 - 1701	1430 - 1414	332	280
NaOL	-	1560, 1701	-	-	-
CaF_2 p.a.	-	-	-	-	287
CaF_2 pp.	3645	-	1436	-	241, 312
CaOL pp.	3647, 3777	1560	1429	312, 375	-
Sublate (PF)	3152, 3643	-	1448	417, 451	241, 312

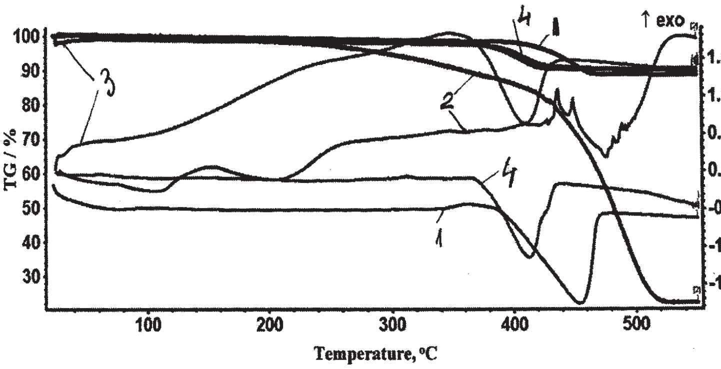

Fig 10. Thermal analysis: 1-CaF_2 p.a , 2-NaOL, 3- tehnical $Ca(OH)_2$, 4-sublate

hydroxide -3 and sublate - 4 indicate: (*i*) DTG curves for CaF_2 p.a and sublate have similar allure; (*ii*) similar mass losses (CaF_2 p.a 88.44%, technical calcium hydroxide 71.91% and sublate 90.34%). The technical calcium hydroxide excess used for CaF_2 precipitate does not have any significant impact on the sublate formation.

Conclusions

Flotation is a complex separation process, whose achievement depends on physico-chemical properties of the system, of the hydrodynamic factors, and interface mass-transfer, correlated with the species structure.

Precipitate flotation is a separation process with main advantages like: high efficiencies ($R\ \% \geq 99\%$), rapidity, availability, affordability, low cost, the capacity to remove inorganic species (fluoride ion in this case) and possibly isolated species recovery.

The present work established the optimum separation conditions (according to table II) for fluoride ion removal from aqueous systems by applying chemical precipitation as CaF_2 using as precipitation reagent the technical calcium hydroxide combined with DAF technique.

The high separation efficiencies ($R\ \% = 98.5$) of the proposed separation process provides the possibility of rapidly decreasing fluoride concentrations bellow the safety limits ($c_{fF^-} = 3.06 \pm 0.09$).

Excessive use of technical $Ca(OH)_2$ is not justified because it does not influence the interaction and the consumption of reagents in excess generate large amounts of sludge.

The proposed method uses a common and cheap precipitation reagent (technical calcium hydroxide) and represents a very attractive choice for water treatment in special steel manufactures being economic-effective affordable and involving low costs.

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