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Development of an integrated electro-coagulation–flotation for semiconductor wastewater treatment

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ABSTRACT

In this study, an electro-coagulation–flotation process was used as a polishing treatment of semiconductor wastewater after precipitation. Batch mode experiments were undertaken using aluminium sheets as anode and stainless steel as cathode. Experiments on a synthetic solution showed that coupling electro-coagulation with electro-flotation in the same cell is efficient for simultaneous defluoridation and clarification. This combination was carried out by proper electrode arrangement and material choice. The performance is ascribed to the combined effect of anodically created coagulants and hydrogen micro-bubbles evolving on the cathode. The effects of the main parameters: electrode nature and arrangement, treatment time, current intensity, initial pH, initial concentration, type and concentration of supporting electrolytes were studied. Defluoridation efficiency may reach 90% corresponding to residual fluoride of 4.61 mg/L, while, turbidity removal efficiency may reach about 85% which corresponds to a residual turbidity of 3.09 NTU. The obtained final concentrations comply with national hazardous waste regulations.

Keywords: Semiconductor wastewater; Fluoride; Turbidity; Electro-coagulation–flotation; Integrated process

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1. Introduction

In semiconductor-manufacturing plants, a large quantity of hydrofluoric acid (HF) is currently used for wafer etching and quartz-cleaning operations [1]. It has been found that acid fluoride-containing wastewater contributes to 40% of hazardous waste produced from the semiconductor manufacturer [2]. Fluoride concentrations, up to 3,500 mg/L, are found in this type of wastewater [1]. Fluoride ions originated from two sources; spent HF baths and waste rinse water. The direct discharge of such solutions may represent a huge threat for the environment. Environmental authorities limit fluoride discharge levels to 15 mg/L [3,4]. Most commonly, fluoride ions are removed by forming calcium fluoride (CaF_2) after adding lime [1]. Neutralization can be described according to the following reaction:

$$Ca(OH)_2 + 2\,HF \leftrightarrow CaF_2 + 2\,H_2O \qquad (1)$$

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In spite of its cheapness, lime precipitation is insufficient to meet environmental requirements. Fluoride concentration can only be reduced to 25–60 mg/L [1,3,5]. Poor settling of the CaF_2 precipitates is a major additional difficulty which resulted in turbidity higher than permissible limits [3]. Moreover, fluoride may redissolve once the effluent is combined with other acidic media [6]. Coagulation with aluminium salts is currently associated as a polishing treatment. Aluminium salts reduce excessive residual fluoride and destabilize colloidal CaF_2 particles. This step is followed by flocculent addition to enhance solid–liquid separation by sedimentation, flotation or filtration [1,5–7]. However, to ensure effectiveness of the process, big quantities of reagents are added. Accordingly, salinity of the treated water increases which reduce water reusability. Furthermore, large amounts of sludge are generated whose subsequent treatment and management would require extremely large facilities [8,9].

Electro-coagulation (EC) has been proposed as an alternative method to classic chemical coagulation (CC) for many wastewater treatments [9–11]. A conventional EC apparatus comprised of two distinct units: EC and separation [11]. In practice, EC followed by sedimentation is the most common option. In addition, the separator for settling may need a filtration step [12,13]. Thus, this process increases the investment, space and time demand for treatment [14]. Owing to the benefits of electro-flotation (EF) over sedimentation [15,16], EC combined to EF (EC–EF) has been suggested as an alternative to EC–sedimentation. The EC–EF process was shown to have two significant advantages, lower water content in the produced sludge and a shorter retention time. Less land, therefore, is needed for the treatment plant [17,18]. A typical EC–EF unit includes an EC cell and an EF chamber [17]. This later includes, most often, DSA anode for O_2 evolution and a stainless steel for H_2 evolution. Such a system had been successfully used by Shen et al. [17] in treating fluoride-containing wastewater. Hu et al. [3] have demonstrated that EC–EF process is efficient to remove the dissolved fluoride ions and CaF_2 particles in the semiconductor wastewater after calcium precipitation. However, these studies presented processes that combine different techniques in a multi-step fashion but not in the same compartment.

Recently, few studies focused on integrated electrochemical processes. Cotillas et al. [19] described a novel integrated electrochemical process for urban wastewater regeneration. In this cell, it is possible to carry out, at the same time, two different electrochemical processes: electro-disinfection and EC which are traditionally carried out separately. The process will reduce investment and operation costs inherent to electrochemical technology. This process integration allows working towards the intensification of water treatment processes [19]. More recently, Khelifa et al. [20] developed a new integrated electro-chlorination–electro-flotation reactor allowing simultaneous removal of EDTA and heavy metals together with clarification in a one-step process. Zhao et al. [21] used an integrated electro-oxidation and EC system to remove As(III) and F- ions from water simultaneously. Bennajah et al. [13] studied an innovative one- compartment system based on aluminium electrodes which ensures EC and EF using an airlift reactor for drinking water. The authors successfully carried out defluoridation. Complete flotation of the sludge was achieved by means of hydrogen bubbles from the cathode [13]. However, this defluoridation study only focuses on drinking water case.

Acid fluoride-containing effluents from CRTSE (Algiers, Algeria) wafer manufacturing facilities are subject of lime precipitation pre-treatment. But these effluents still contain fluoride ions up to 80 mg/L together with a turbidity ranged from 10 to 35 NTU. Our previous studies have demonstrated the efficiency of EC in fluoride removal [4,5,9]. There is a need to develop an integrated electrolytic coagulation and clarification device for turbid-fluoride bearing wastewater in order to satisfy the requirements of the water reuse and reclamation.

Therefore, this paper aimed to propose an integrated electro-coagulation–flotation (ECF) as post-treatment of semiconductor wastewater after calcium precipitation. The effects of the main parameters: electrode nature and arrangement, treatment time, initial pH, current intensity, initial concentration, type and concentration of supporting electrolyte on fluoride and turbidity removal were studied.

2. Experimental

2.1. Experimental set-up

The ECF experiments were performed in a one-compartment electrolytic cell. The cell was designed and constructed as shown in Fig. 1. The electrochemical reactor is made of glass (230 × 195 × 75 mm). Two parallel aluminium (99.5% purity) plates (240 × 55 mm), at a distance of 100 mm, were placed vertically in the middle of the reactor and were used as anode. The effective area of each anode was 75 cm^2. A stainless steel sheet (190 × 70 mm) is placed horizontally beneath anodes and in the bottom of the cell. This configuration has been chosen to provide optimal bubble distribution which enhances flocs collision, attachment and flotation

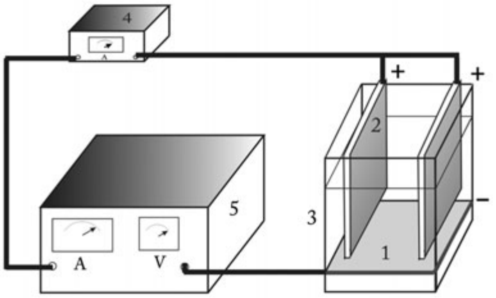

Fig. 1. Schematic diagram of the experimental set-up (1: Stainless steel cathode; 2: Aluminium anode; 3: Electrolytic cell; 4 : Ammeter; 5: DC power supply).

to the surface and to prevent their accumulation in the bottom. It is also able to improve mixing by bubble turbulence. The electrodes were connected to a digital DC power supply (Metrix AX502, 0–2.5 A and 0–30 V). An ammeter (Chauvin-Arnoux C.A 401) was used to monitor the current during ECF process. In all tests, no stirring was applied. The volume of the solution to be treated was 2,500 mL. In order to achieve optimal clarification, experiments were first undertaken to compare the ECF system (cell 1) with other cells. Cell 2 includes two parallel horizontal electrodes. Stainless steel cathode in the bottom and above is placed a perforated aluminium anode in order to allow the gas generated to pass to the reactor liquid and to avoid its accumulation between the electrodes. The anode was perforated with holes of 0.7 cm of diameter, distributed homogenously; the gap between the electrodes was 2 cm. The latter has the same dimensions of stainless steel cathode. Cell 3 is the same as cell 1, but the cathode is made of aluminium material instead of stainless steel.

2.2. Experimental procedure

In order to simulate the semiconductor wastewater after calcium precipitation, desired amounts of HF solutions are first prepared by dilution of 1 N HF stock solution in distilled water and then reacted to lime ($Ca(OH)_2$). After a rapid mixing at 400 rpm of 1 min, pH was adjusted to the desired value and a moderate stirring at 200 rpm takes place for 30 min. Precipitation conditions were predefined in a separate study and maintained constant for all experiments. The resulting solutions are thereby characterized by their fluoride concentration and turbidity due to CaF_2 formation. Solutions are immediately introduced in the ECF reactor for the polishing treatment. ECF was conducted in galvanostatic mode. NaCl was used as supporting electrolyte except when investigating the influence of co-existing anions, where quantities of Na_2SO_4, $NaNO_3$ or NaH_2PO_4 were added to the solutions. All the experiments were conducted at room temperature (20 ± 1˚C). In order to ensure surface reproducibility, prior to each experiment, the aluminium plates were manually polished using abrasive paper, degreased in acetone, rinsed with distilled water, submerged in 2 M NaOH solution for 5 min and rinsed again with distilled water. The total time duration of electrolysis was 120 min. Samples were extracted periodically and then immediately filtered through a 0.2 μm membrane syringe filter in order to measure residual fluoride. While the evolution of turbidity over time was measured on non-filtered samples and without any further settling in order to follow the clarification by flotation over time.

2.3. Analytical methods

A combined selective ion electrode (sension1 from HACH) was used to determine the fluoride concentration according to the ionometric standard method [22]. The TISAB II at pH 5.3 containing CDTA was added to samples in order to maintain constant ionic strength and to prevent the interference from Al^{3+} and Ca^{2+} cations. The pH values were determined by using pH meter (sension1 from HACH). Turbidity in samples was measured as NTU using the turbidimeter **(**HI88703 from HANNA**).**

3. Results and discussion

3.1. Effect of electrode nature and arrangement on turbidity removal

It has been stated that EC reactor design affects operational parameters such as flocs formation, removal yield and flotation–settling characteristics [23,24]. The majority of EC studies were conducted using the traditional vertical parallel plate cell equipped with a mixing system [23]. A downstream unit is often required to separate pollutant and water [25], while, EF was conducted using cells with horizontal electrodes [25]. Besides, some researchers call the EC process the ECF process because they take into consideration the flotation performance of EC [3,26]. But, only about 60% of the total flocs could be floated by hydrogen bubbles [27,28]. In order to obtain optimal use of produced hydrogen for more efficient flotation, two key factors are to be considered. First, the use of a proper material such as stainless steel which provides cathodic production of fine hydrogen bubbles. Secondly, an adequate electrode arrangement includes horizontal position of cathode and vertical position of aluminium sacrificial anodes. Such an integrated design is expected to considerably improve floc–bubble attachment and rising to the surface. In this study, the latter design (cell 1) is compared with currently encountered configurations by changing anode orientation (cell 2) and by changing cathode nature (cell 3). Table 1 clearly indicates that the best clarification is achieved by cell 1 with 85% of turbidity removal which corresponds to a final turbidity of 3.09 NTU, while, with cell 2, only 60% of turbidity removal is obtained which corresponds to a final turbidity of 8.08 NTU and which is higher than standard discharge limit (5 NTU) [29]. With cell 3, no clarification is obtained and the final turbidity is much greater than the initial value. It is well known that the clarification efficiency is strongly dependent on the size of the formed bubbles. An effective EF is obtained by uniform and tiny bubbles. This is because smaller bubbles provide larger surface area for particle attachment. The size of the hydrogen bubbles is affected by cathode surface condition [25]. The polished surface of the stainless steel plate used in cell 1 gives the finest bubbles and results in higher turbidity removal. Whereas, the deterioration of clarification of cell 3 is due to the coarse aluminium anode surface which results in significant increase the size of the hydrogen electrolytic bubbles [30]. Consequently, all subsequent experiments were carried out with cell 1.

3.2. Effect of treatment time

The semiconductor wastewater after calcium precipitation contains soluble fluoride ions and CaF_2 nanoparticles, usually in concentrations much higher than the permissible levels [3]. A post-treatment is then required. In this work, ECF was studied as a polishing treatment.

The ECF main reactions are as follows:

$$\text{Anode:}\quad Al_{(s)} \rightarrow Al^{3+} + 3e^- \tag{2}$$

$$\text{Cathode:}\ 3H_2O + 3e^- \rightarrow (3/2)H_{2(g)} + 3OH^- \tag{3}$$

Depending on pH conditions, various aluminium-based monomeric and polymeric species are formed which finally transform into insoluble amorphous $Al(OH)_{3(s)}$ [31].

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \tag{4}$$

Freshly formed amorphous $Al(OH)_{3(s)}$ flocs have large surface areas, which are beneficial for adsorption of soluble inorganic compounds and trapping of colloidal particles. Finally, these flocs are removed from aqueous medium by hydrogen flotation [31].

Fig. 2 shows the abatement kinetics of both fluoride and turbidity in the same ECF cell. After 60 min of treatment, fluoride concentration was 12.61 mg/L. Less than 60 min are required to bring fluoride concentration down to discharge limit. Fluoride removal is ascribed to interaction with aluminium compounds generated by anode electro-dissolution. Many authors had demonstrated that EC is very effective in defluoridation [4,9,32]. It was reported that EC system performed better than CC system in defluoridation efficiency [4,32]. Additionally, the obtained results show a remarkable turbidity removal. The turbidity dropped at 3.54 NTU after 90 min of treatment. Less than 90 min are necessary to make residual turbidities below discharge standard limit. The clarification of the solution is thus achieved. Consequently, no separation post-treatment such as filtration is needed for the treated solution. Solution turbidity is due to the presence of fine colloidal CaF_2 particles. Coagulants, formed by anode electro-dissolution, destabilize colloids. The formed flocs are then lifted to the surface by hydrogen-rising bubbles which results in solution clarification. The pH rise during ECF treatment was also observed. In fact, the pH jumps from 7 to 9.41 at the end of treatment.

Table 1
Effect of cell design on ECF efficiency; [NaCl], 2 g/L; *I*, 640 mA; *t*, 120 min

	Fluoride concentration (mg/L)		Turbidity (NTU)		pH	
	Initial	Final	Initial	Final	Initial	Final
Cell 1	42	4.61	20.4	3.09	7	9.41
Cell 2	42	6.12	20.3	8.08	7	9.53
Cell 3	42	5.32	21.05	125	7	9.68

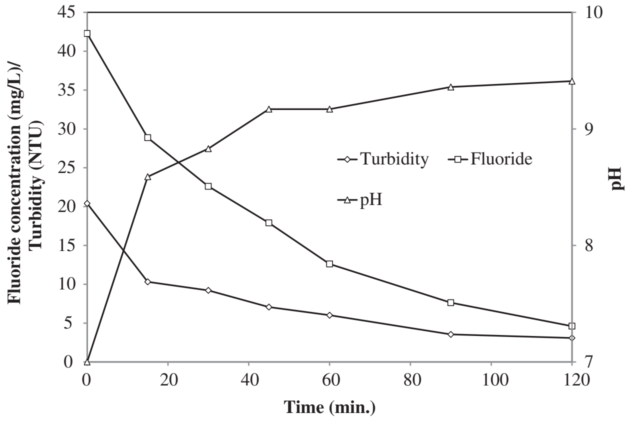

Fig. 2. Effect of time on final fluoride concentration, turbidity and pH; pH_0, 7; [NaCl], 2 g/L; *I*, 640 mA.

3.2. *Effect of current intensity*

Many researchers reported that the current intensity influenced the electro-chemical process efficiency [5,7,10]. In order to assess current effect on the present process, runs were done by applying the following intensities: 320, 480, 640 and 800 mA. Current intensity effect is illustrated in Figs. 3(a), 3(b) and 3(c). Results from Fig. 3(a) indicate that increasing current intensity leads to the decrease in final fluoride concentration. Applying an intensity of 320 mA gives 12.35 mg/L residual fluoride at the end of treatment while 800 mA gives 1.75 mg/L. In addition, the removal was observed to be faster by increasing the current intensity. In all studied cases, less than 90 min treatment is necessary in order to reach the fluoride discharge standard limit. Higher current intensity will generate significant amount of coagulants, which in turn will adsorb the pollutants and enhance the removal efficiency.

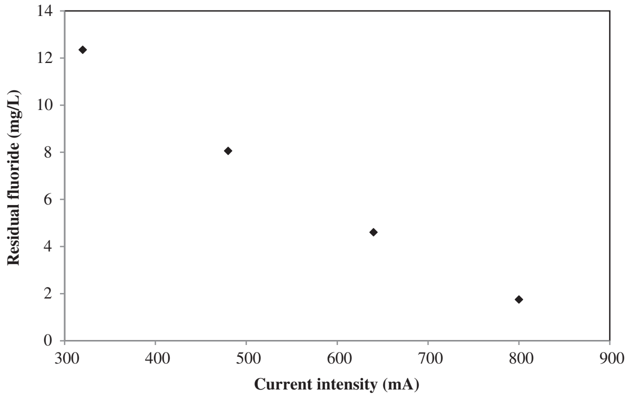

Fig. 3(a). Effect of current intensity on final fluoride concentration; pH_0, 7; [NaCl], 2 g/L; $[F^-]_0$, 42 mg/L; *t*, 120 min.

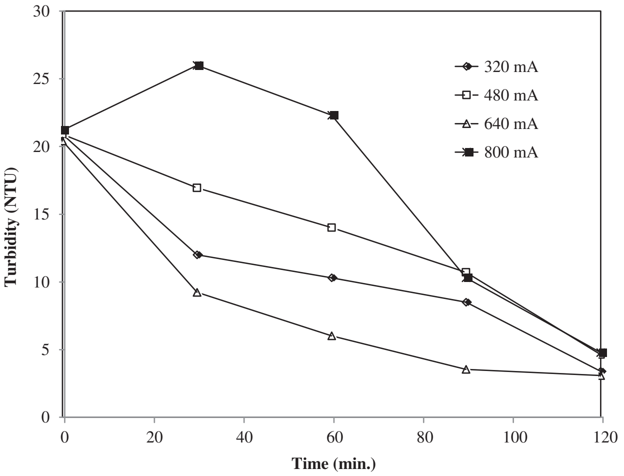

Fig. 3(b). Effect of current intensity on turbidity removal; pH_0, 7; [NaCl], 2 g/L; $[F^-]_0$, 42 mg/L.

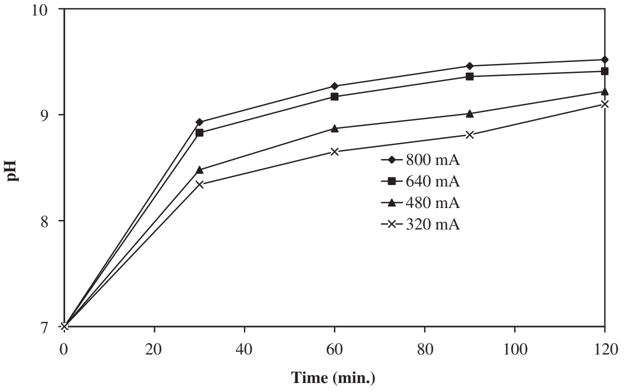

Fig. 3(c). Effect of current intensity on pH evolution; pH_0, 7; [NaCl], 2 g/L; $[F^-]_0$, 42 mg/L.

Contrary to fluoride, there is no clear trend in the variation of turbidity with current. However, it can be observed from Fig. 3(b) that final turbidity remained at values lower than 5 mg/L over the whole studied current range. Results also show that further current increase improves fluoride removal efficiency but results in floc destruction by bubble turbulence at higher flows and hence clarification deterioration. According to Chen [25], at higher current intensities, some hydrogen bubbles may coalesce to form useless large bubbles. This not only decreases the availability of the effective small bubbles, but also increases the possibility of breaking the flocs formed previously, affecting the flotation efficiency. Fig. 3(b) illustrated that for 800 mA current intensity there has been observed an increase in the turbidity in the first moments before the turbidity decreases to lower residual values. This phenomenon may be explained by the additional turbidity to that of CaF_2 due to the higher $Al(OH)_3$ flocs generation at this current. Fig. 3(c) indicated the pH increases by varying current intensity. It may be seen that the higher the current intensity, the faster the pH increase and the higher the final pH value, this means that the cathodic reduction of water molecules (Eq. (3)) is the main reason causing pH rise during ECF treatment.

3.3. Effect of initial pH

In most literatures dealing with electro-chemical wastewater treatment, initial pH is reported as a key factor [13,32]. In this study, the initial pH effect was studied in the range from 3 to 11. The corresponding results are shown in Figs. 4(a), 4(b) and 4(c). From Fig. 4(a), it can be concluded that the initial pH has strong effect on fluoride removal. In fact, the residual fluoride increases when initial pH increases. It is worth to mention that for all studied pH values, the corresponding final fluoride concentrations are below discharge limit. Higher remaining fluoride concentrations are recorded for alkaline pH 9 and pH 11. This is due to the formation of soluble anionic species such as $Al(OH)_4^-$ which are unsuitable for fluoride removal [9]. The best results are recorded for acidic initial pH values with an optimum at pH equal to 3.0. The corresponding residual fluoride concentration is 2.74 mg/L. This finding is in good agreement with those found by previous authors [17,27,33]. One explanation is that given by Shen et al. [17] and Emamjomeh and Sivakumar [33], according to them, fluoride removal can be taken as the ion exchange of F^- with OH^- in $Al(OH)_3$. When OH^- concentration decreases, the ion-exchange equilibrium shifts towards the right side. While for defluoridation of drinking water it is not recommended to work at acidic media because it involves pH adjustment and thus supplementary pre-treatment [14,33]. This may be, at the contrary, an important advantage when treating acidic fluoride-containing wastes because limiting lime addition during neutralization at pH 3 would result at reducing costs with better efficiency. Owing to ECF pH rise, no excess of lime is needed or no excessive pH adjustment for neutralizing. It has generally been considered that, for precipitation, pH does not affect fluoride removal efficiency in the range of $pH > 4$ [34]. In our study, it was found that the fluoride concentration after precipitation is practically identical for pH from 3 to 11, while resulting turbidity (Fig. 4(c)) increases with pH increase, it is weakest at pH 3 (14 NTU).

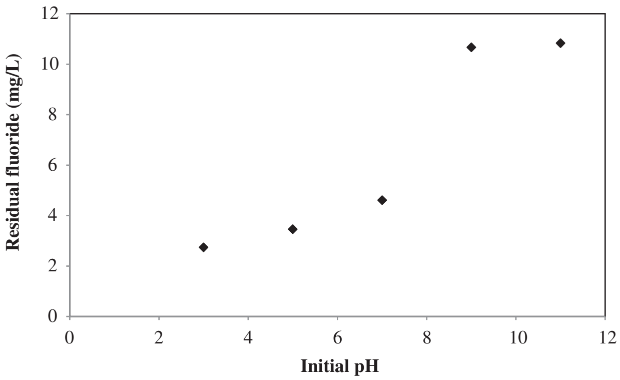

Fig. 4(a). Effect of initial pH on final fluoride concentration; *I*, 640 mA; [NaCl], 2 g/L; $[F^-]_0$, 42 mg/L; *t*, 120 min.

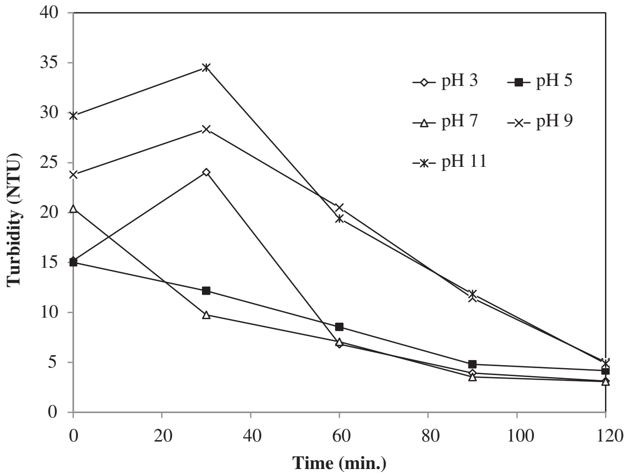

Fig. 4(b). Effect of initial pH on turbidity removal; *I*, 640 mA; [NaCl], 2 g/L; $[F^-]_0$, 42 mg/L.

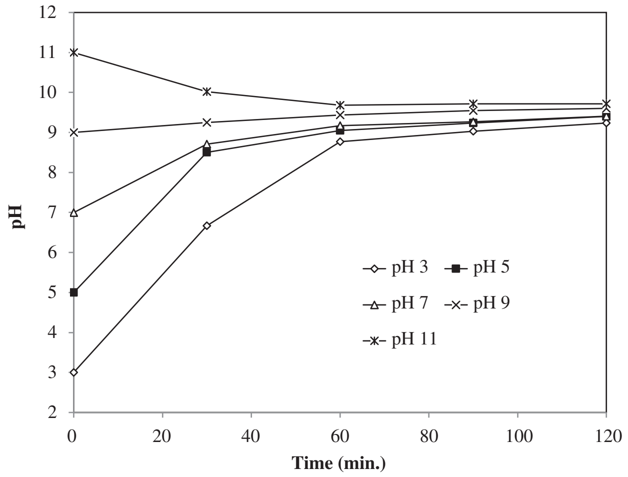

Fig. 4(c). Effect of initial pH on pH evolution; *I*, 640 mA; [NaCl], 2 g/L; $[F^-]_0$, 42 mg/L.

As shown in Fig. 4(b), initial pH effect does not seem to have clear tendency on turbidity removal. However, for alkaline values, the kinetics is slower and initial turbidities are higher as the pH is greater. All pH values lead to the solution clarification with final turbidities which are lower than permissible discharge limits. Fig. 4(c) shows the changes of pH during ECF treatment. It may be observed that pH changes strongly depend on the initial pH values. It may be observed that pH evolution is increasing for solutions of initial pH lower than 9 and is decreasing for alkaline solutions. For acidic and neutral initial pH conditions, the increase in pH can be explained by the production of OH^- ions from the reduction of H_2O on the surface of the cathode (Eq. (3)) [35]. while, for solutions with initial pH higher than 9, the decrease in pH could be attributed to the consumption of higher amounts of OH^- ions to form anionic hydroxo–aluminum species such as $Al(OH)_4^-$ and $Al(OH)_5^{2-}$ [35]. At the end of electrolysis, the majority of aqueous solutions stabilize at a pH value of about 9.5. This stabilization can be explained by a buffering effect of hydroxo–aluminum species [35].

3.4. Effect of anion nature

Mixed acids are commonly used in the semiconductor industry for wafer etching and cleaning. Consequently, sulphate, nitrate, chloride and phosphate anions may be found in fluoride-containing wastewater [36]. These anions may potentially affect the ECF removal process. In order to quantify their effect, four types of salts with the same cation Na^+: NaCl, $NaNO_3$, Na_2SO_4 and NaH_2PO_4 were examined. The experiments were carried out with the same molar concentration (0.05 M). Preliminary tests were conducted for each anion, the ECF process stopped in a few minutes because of the voltage increase up to the DC power supply limit (30 V). Small amounts of NaCl (29.25 mg/L) were then added to overcome the passivation of anodes. A similar procedure was adopted in conventional EC process. Mouedhen et al. [37] indicated that a threshold Cl^- concentration of 60 ppm was required to breakdown the anodic passive film of an aluminium electrode. Yang and Dluhy [38] found that a small quantity of 50 ppm NaCl is enough to induce aluminium coagulant production. The required quantity of NaCl is evidently dependant on reactor design and solution characteristics. It can be observed from Fig. 5(a), that the residual fluoride concentration is tightly linked to the anion type. It is clear that the fluoride removal is reduced when anion other than chloride is used. The fluoride values are 4.39, 7.16, 12.86 and 20.8 mg/L for Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-},

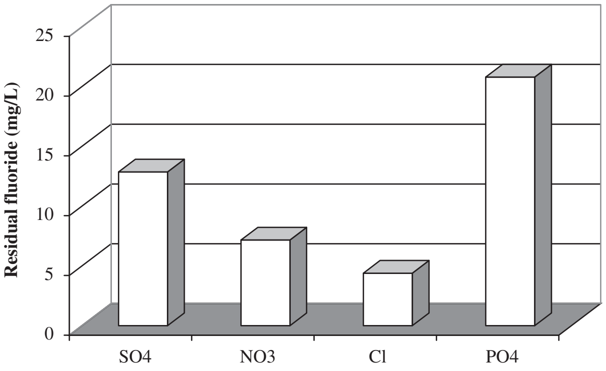

Fig. 5(a). Effect of anion nature on final fluoride concentration, $[F^-]_0$, 42 mg/L; I, 640 mA; [anion], 0.05 M; pH_0, 7, [NaCl], 29 mg/L; t, 120 min.

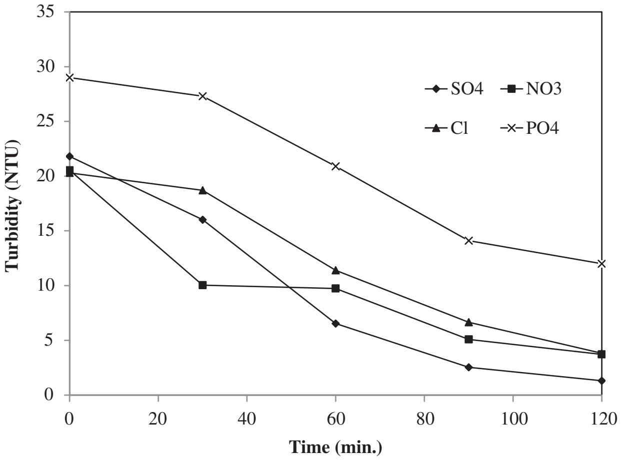

Fig. 5(b). Effect of anion nature on turbidity removal; $[F^-]_0$, 42 mg/L, I, 640 mA; [anion], 0.05 M; pH_0, 7, [NaCl], 29 mg/L.

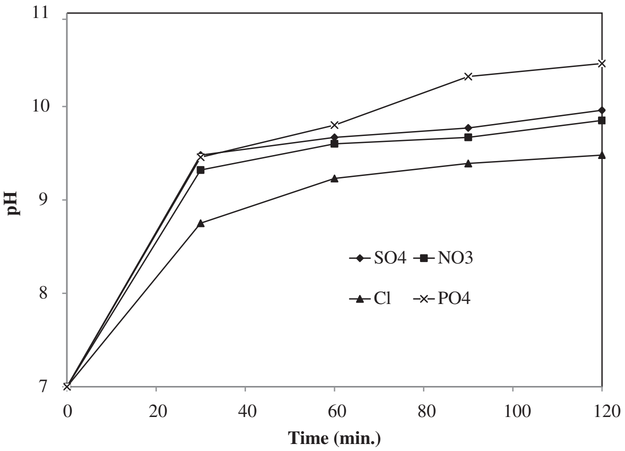

Fig. 5(c). Effect of anion nature on pH evolution; $[F^-]_0$, 42 mg/L, I, 640 mA; [anion], 0.05 M; pH_0, 7, [NaCl], 29 mg/L.

respectively. Presence of nitrate gives less efficiency than chloride, whereas, presence of sulphate and phosphate significantly inhibits fluoride removal. The same order of anion efficiency was observed in previous works studying co-anions effect on defluoridation by conventional EC [3,17]. Chloride ion enhances aluminium pitting corrosion which results in more produced coagulants [32]. The negative effects of NO_3^-, SO_4^{2-} and PO_4^{3-} anions could be attributed to the passivation of electrodes [17]. In addition, and knowing that PO_4^{3-} has a strong affinity to $Al(OH)_3$ [11], the excessive decrease of fluoride removal in presence of PO_4^{3-} is ascribed to the competitive adsorption between this anion and F^- [17]. From Fig. 5(b), it can also be seen that for all salt types, final turbidities converge to discharge standard or lower except for PO_4^{3-} where final turbidity is as high as 12 NTU. Hu et al. [3] found that PO_4^{3-} had an adverse impact on both fluoride and CaF_2 removal by EC process. Additionally, Fig. 5(c) showed pH change as function of anion nature. Higher final pH values are observed for NO_3^-, SO_4^{2-} and PO_4^{3-}. This excessive increase may be due to the cathodic reduction reaction of nitrate ions as in Eq. (5):

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2\,OH^- \tag{5}$$

While for sulphate and phosphate, this pH rise is of chemical origin and is most probably due to the ion exchange between these anions and $Al(OH)_3$ which results in more hydroxyl liberation [40].

3.5. Effect of supporting electrolyte concentration

It has been demonstrated that the types and concentrations of co-existing anions play important roles in EC defluoridation system [3,17,41]. Chloride ions are most commonly used in EC process in order to improve the treated solution conductivity and to depassivate anodes. The effect of chloride anion concentration on ECF performance was investigated using different molar concentrations of NaCl. It may be noted from Fig. 6(a) that the chloride ion concentration has a slight effect on fluoride removal in the studied range, in spite of wide chloride concentration change. The final fluoride concentrations were 5.31, 5.03, 4.39 and 5.79 mg/L for 0.005, 0.01, 0.05 and 0.1 M chloride solutions, respectively. The best result being for the value of 0.05 M. A similar trend was found by many works dealing with conventional EC using aluminium electrodes. Bensadok et al. [42] observed that when NaCl concentration increased to an optimum value, the pollutants removal efficiency increased. However, an additional NaCl

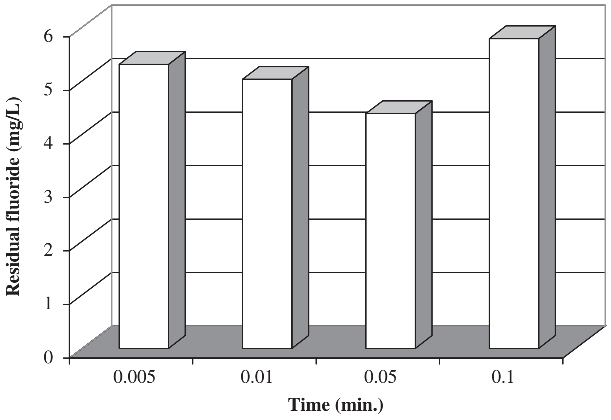

Fig. 6(a). Effect of NaCl molar concentration on final fluoride concentration, *I*, 640 mA; pH_0, 7; $[F^-]_0$, 42 mg/L; *t*, 120 min.

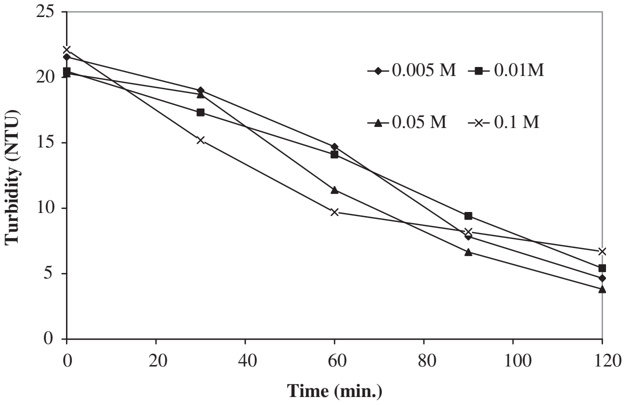

Fig. 6(b). Effect of NaCl molar concentration on turbidity removal; I,640 mA; pH_0, 7.

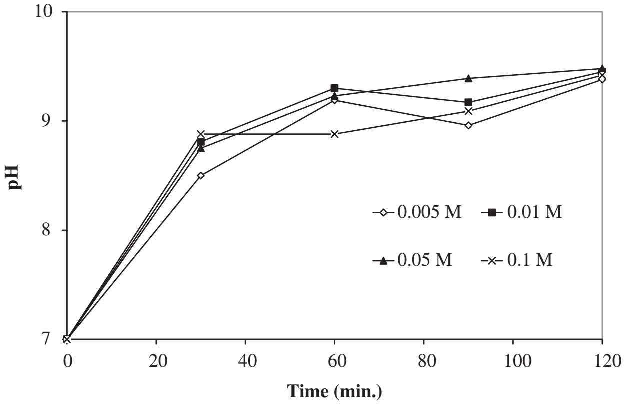

Fig. 6(c). Effect of NaCl molar concentration on pH evolution; *I*, 640 mA; pH_0, 7.

increase led to a decrease in the pollutants removal efficiency decrease. Fig. 6(b) illustrates variation of turbidity as function of time in the presence of various NaCl molar concentrations. The different salt levels did not seem to exert any effect on turbidity variation. But for all the values, low residual turbidities were obtained. In Fig. 6(c), the pH is plotted against time in the presence of various NaCl concentrations. No influence was observed on pH evolution and final pH values with the considered NaCl concentrations.

3.6. Effect of initial concentration

Semiconductor industry generates wastewaters with different levels of contamination, depending on the process employed for the wafer fabrication. Additionally, wastewater quality may fluctuate continuously. Experiments were conducted by changing initial pollutant concentration and keeping all other experimental conditions similar. Fig. 7(a) showed that decreasing fluoride initial concentration results in lower final fluoride concentrations. When fluoride initial concentrations are 55.06, 46.79, 42.29 and 25.72 mg/L, final fluoride concentrations are 11.6, 6.84, 4.61 and 2.32 mg/L, respectively. However, all final values remained below fluoride standard limit. Runs took place under the same intensity, and thus the same coagulant amount is expected. The drop in fluoride removal is due to the insufficient quantity of aluminium hydroxide necessary to the coagulation of the pollutant excess at higher concentration. Fig. 7(b) depicts the depletion of the turbidity as a function of time. It was found that the weaker is the initial turbidity the greater is the abatement. Initial turbidities 65.5, 39, 30.1, 20.4 and 13.4 NTU gave, respectively, 25.6, 6.7, 5.15, 3.09 and 2.52 NTU. It should be noted that for initial turbidities higher than 30.1 NTU, the final turbidities are beyond the standard limit and the treated solution is less and less clearer. The corresponding kinetics is also slower. This means that the ECF is suitable for dilute solutions. ECF being a finishing treatment, its performance drops for loaded solutions. Fig. 7(c) showed pH variation vs. time at different initial fluoride concentrations. It is clear that no effect was observed in this initial conditions range.

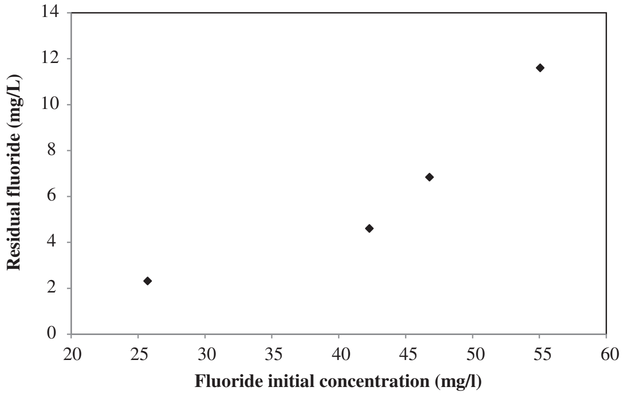

Fig. 7(a). Effect of initial concentration on final fluoride concentration, I, 640 mA; [NaCl], 2 g/L; pH_0, 7; t, 120 min.

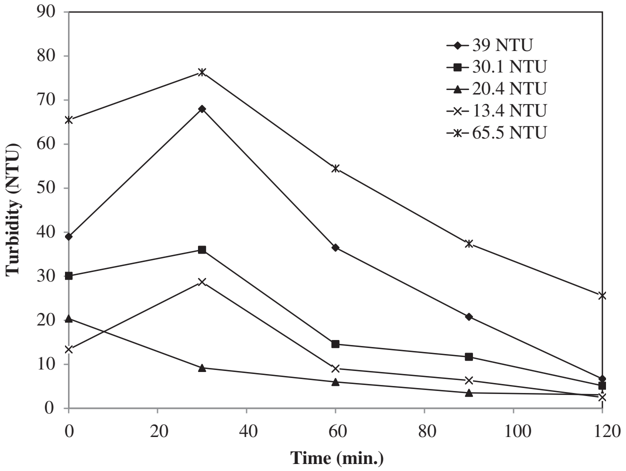

Fig. 7(b). Effect of initial concentration on turbidity removal; I, 640 mA; [NaCl], 2 g/L; pH_0, 7.

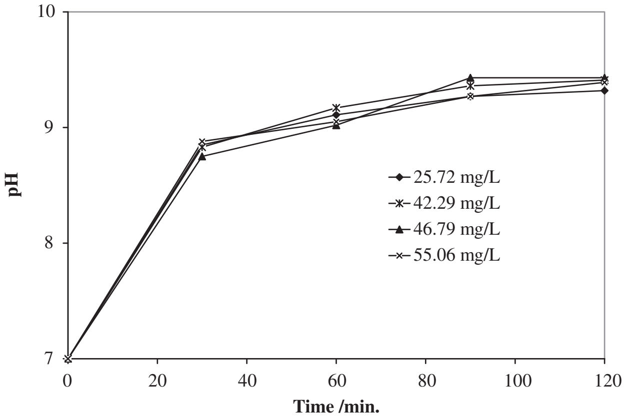

Fig. 7(c). Effect of initial concentration on pH evolution, I, 640 mA; [NaCl], 2 g/L; pH_0, 7.

4. Conclusion

This paper demonstrates that ECF may be an alternative for the conventional finishing treatments for semiconductor effluents after lime precipitation. An adequate electrode arrangement enables a one-step process combining EC and EF. The simultaneous reduction of fluorides and turbidity is achieved as this system allows harnessing cathode hydrogen bubbles. The process is carried out without mechanical agitation, without the need for collectors and can be achieved without air injection. In addition, no subsequent settling or filtration is needed to reach the required environmental standards.

From the study of parameters, the following conclusions can be drawn:

- Insufficient or deteriorated clarification was obtained with configurations using horizontal anode or aluminium cathode, respectively.
- Increasing current intensity results in increasing fluoride elimination rate and decreasing residual fluoride concentration but no clear effect of current intensity was observed on turbidity behaviour. Furthermore, increasing current intensity results in increasing pH rise rate.
- Defluoridation is strongly pH dependant. Increasing pH from 3 to 11 leads to the increasing of residual fluoride concentration. Low initial pH value was observed to be beneficial to fluoride removal. Conclusions obtained from this result will be useful from the engineering point of view as working at pH 3 allows optimal fluoride and turbidity removal with less lime adding. No clear tendency is observed on turbidity with the different initial pH values. In addition, pH evolution is increasing for solutions of initial pH lower than 9 and is decreasing for alkaline solutions.
- Optimum fluoride removal was obtained with chloride. Nitrate was less efficient, while sulphate and phosphate are detrimental to fluoride removal. Fluoride removal is accordingly in the following order: $PO_4^{3-} < SO_4^{2-} < NO_3^- < Cl^-$. In addition, except for phosphate all these anions gave lower final turbidity values. Additionally, final pH values are accordingly in the following order: $Cl^- < NO_3^- < SO_4^{2-} < PO_4^{3-}$.
- Chloride molar amount has a slight effect on defluoridation. However, an optimum is recorded at 0.05 M. Besides, turbidity variation seemed to be unaffected by chloride concentration. Concerning the effect of the concentration of salt on pH evolution, there was no marked tendency.
- The lower is the fluoride concentration and turbidity the better is their removal efficiencies. There was no marked tendency for the effect of the initial concentration on pH evolution.

The laboratory scale study yields promising results; ongoing research is undertaken on further in-depth development study and optimization of parameters for a more reliable and cost-effective operation.

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Abbreviations

ECF	—	electro-coagulation–flotation
EC-EF	—	electro-coagulation–electro-flotation
HF	—	hydrofluoric acid
DC	—	direct current
EDTA	—	ethylenediaminetetraacetic acid
DSA	—	dimensionally stable anode
R (%)	—	removal efficiency
TISAB	—	total ionic strength adjustment buffer
CDTA	—	cyclohexylenediaminetetraacetic acid
NTU	—	nephelometric turbidity unit
CC	—	chemical coagulation
rpm	—	revolutions per minute
SS	—	stainless steel

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